

CO₂ Capture by Aqueous Absorption Summary of First Quarterly Progress Reports 2011

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Introduction

This research program is focused on the technical obstacles to the deployment of CO₂ capture and sequestration from flue gas by alkanolamine absorption/stripping and on integrating the design of the capture process with the aquifer storage/enhanced oil recovery process. The objective is to develop and demonstrate evolutionary improvements to monoethanolamine (MEA) absorption/stripping for CO₂ capture from coal-fired flue gas. The Luminant Carbon Management Program and the Industrial Associates Program for CO₂ Capture by Aqueous Absorption support 17 graduate students. These students have prepared detailed quarterly progress reports for the period January 1, 2011 to March 31, 2011. The Ph.D. dissertation by Stephanie Freeman on piperazine degradation is attached.

Conclusions

Thermodynamics and Rates

Quantitative ¹H and ¹³C NMR spectra for 4 m 2MPZ/4 m PZ at CO₂ loadings of 0 to 0.44 mol/mol alkalinity shows that PZ monocarbamate and unhindered 2MPZ monocarbamate are the main reaction products. The former accounts for more than 50% of CO₂ in the solution, which is roughly 20% to 50% more than total unhindered 2MPZ carbamate. The amount of PZ dicarbamate and hindered 2MPZ carbamate increases with loading and reaches 11% and 7% of the total carbamate at loading of 0.3 mol/mol alkalinity.

Sarcosine is less soluble in its sodium salt (4.5 m) form than its potassium salt form (> 6 m).

4.5 m SarNa has the same CO₂ solubility as SarK solvents. The capacity of 4.5 m SarNa is less than 6 m SarK, and is approximately 30–40% less than 7 m MEA. 4.5 m SarNa has low heat of absorption, about 40% less than 7 m MEA, but good absorption rates, about the same as 7 m MEA. The absorption rate of 7 m MDEA/2 m PZ at 30 °C is the same as its rate at 40 °C and 60 °C. The wetted wall column can operate with stable conditions at 30 °C with the current set up.

The data suggest the following for a blend of 6 m PZ/2 m Amine X:

- A lean solubility limit between 0.3–0.35, with no real rich solubility limit;
- A working capacity of about 0.64 mol CO₂/kg solvent (compared to 0.76 mol CO₂/kg solvent for 8 m PZ);

- Enthalpy of absorption equal to about -74 to -75 kJ per mol CO₂ absorbed (this is compared to -65 kJ .per mol CO₂ absorbed for 8 m PZ);
- A CO₂ absorption rate between 50 and 75% of that of 8 m PZ.

CO₂ partial pressure and heat of absorption in 0.9–13 m PZ can be expressed as follows:

$$\ln P_{CO_2} = 35.5 + \frac{-11067}{T} - 21.5 \cdot \alpha^2 + 4710 \cdot \frac{\alpha}{T} + 11419 \frac{\alpha^2}{T}$$

$$\Delta H_{abs} = -R(-11067 + 4710\alpha + 11419\alpha^2) \text{ (J/mol CO}_2\text{)}$$

CO₂ partial pressure in 8 m 2MPZ and heat of absorption can be expressed as follows:

$$\ln P_{CO_2} = 40.1 + \frac{-12513}{T} - 22.1 \cdot \alpha^2 + 14099 \cdot \frac{\alpha}{T}$$

$$\Delta H_{abs} = -R(-12513 + 14099\alpha) \text{ (J/mol CO}_2\text{)}$$

Fogging formed in the outlet vapor steam of 150 ° C 7.3–7.7 bar CO₂ loaded 8 m PZ.

The partition coefficient for amines infinitely diluted in water (at 25 °C) has been adequately predicted using a molecular group contribution scheme established by Hine and Mookerjee with the addition of 3 new parameters used to account for the cyclic structures of PZ and its derivatives. The percent errors between measured and predicted values are less than 3%.

At 40–120 °C, C_p of the unloaded 7 m MDEA/2 m PZ blend ranges from ~3.71–4.11 J/g_{solvent}*K. Over a range of very lean to very rich loading (~0.04–0.27 mol CO₂/mol alkalinity), C_p is ~3.29 – 4.10 J/g_{solvent}*K.

At 40 – 120 °C, C_p of the unloaded 5 m MDEA/5 m PZ blend ranges from ~3.49-3.93 J/g_{solvent}*K. At any given temperature, C_p of the 5/5 blend is less than that of the 7/2 blend due to a smaller contribution of MDEA enthalpy to the total heat of solution. Over a range of lean to rich loading (~0.186 – 0.315 mol CO₂/mol alkalinity), C_p is ~3.22 – 3.88 J/g_{solvent}*K.

Modeling

The discrepancy between Aspen Plus® and Gibbs-Helmholtz predictions for the heat of absorption has been minimized through the use of thermodynamically consistent methodology. The greatest deviation for 8 m PZ occurred at higher temperatures (>100 °C) and loadings, though it was never greater than 5%.

The kinetics of 8 m PZ, 7 m MDEA/2 m PZ, and 5 m MDEA/5 m PZ were fit over operationally significant temperature and loading ranges by adjusting rate constants, loadings, and binary diffusivities. Between 40 °C and 100 °C the average error in predicted CO₂ absorption rates was 6.7%.

The sensitivity of the Fawkes model to the diffusivity of reactants and products was unexpectedly high. The hybrid sensitivity to D_{CO2} and D_{OTHER} may be a consequence of the numerical method used to determine concentration profiles in the liquid film.

Rich solution flow rate was found to be the best manipulated variable to respond to absorber foaming, as it can decrease the magnitude of overshoot and keep the pressure close to the set point.

The gas film coefficient for 1-inch plastic Pall rings is greater than that for other related packings and varies with gas rate^{0.93}.

Solvent Management

7 m MDEA/2 m PZ oxidizes to produce diethanolamine (DEA) and methylaminoethanol (MAE). As MDEA continues to oxidize, these secondary amines result in the production of bicine and hydroxyethylsarcosine (HEA), respectively.

When 6 m MDEA/1 m MAE is oxidized in the cyclic system, the DEA and bicine production were suppressed.

HES was synthesized and identified as a single, standalone peak using the HPLC amino acid method. The concentration of HES at the end of experiment C-21, where 7 m MDEA/2 m PZ was cycled from 55 to 120 °C, was approximately 192 mM, which represented approximately 10.5% of lost carbon as MDEA and PZ loss.

Oxidation of 7 m DEA at 55 °C produces MEA with a DEA loss rate of 18.2 mM/hr. Glycolamide formed rapidly, but behaved as a reaction intermediate, decreasing in concentration after approximately 150 hours.

Oxidation of 7 m MAE at 55 °C produced a rapid loss in MAE, accompanied by the production of MEA, HES, and total formate.

In the oxidation of MAE and DEA at 55 °C, total formate was ~10X free formate. In cycling experiments with 7 m MDEA and 7 m MDEA/2 m PZ, the ratio of total formate to free formate was typically about 2. 7 m MDEA/2 m PZ did not degrade at 120 to 150 °C in unloaded solutions. The degradation rate appears to be proportional to CO₂ loading from 0.1 to 0.25 mol CO₂/mol alkalinity.

Thermal degradation of 7 m MDEA/2 m PZ led to the formation of PZ derivatives including 1-methylPZ, 1,4-dimethylPZ, aminoethylPZ, and n-formyl-PZ.

An 8 m PZ, 0.1 mol Inh A per kg H₂O solution formed two liquid phases for $0 \leq \text{loading} \leq 0.375$ by addition of anhydrous K₂CO₃. For a total solution loading of approximately 0.375, K⁺ and CO₂ are 50 and 60 times more concentrated in the bottom, aqueous phase, respectively. PZ was 335 times more concentrated in the top, organic phase. Measurable Inh A was 2 times more concentrated in the top, organic phase.

Adding anhydrous KOH to an 8 m PZ, 0.1 mol Inh A per kg H₂O, 0.3 mole CO₂ per mole alkalinity solution precipitated KHCO₃, preventing liquid-liquid separation.

The pKa of the free amine functionality group for FPZ (N-formyl piperazine) was measured as 7.807. At high pH conditions in a reclaimer, FPZ will exist primarily as the molecular species, increasing its volatility.

A 20 m PZ solution initially loaded to 0.1 moles CO₂ per mole alkalinity was thermally degraded for a period of 10 weeks at 175 °C. The average loss rate of total alkalinity, PZ, and CO₂ was 0.185, 0.212, and 0.093 mol/kg-wk, respectively. The ratio of total alkalinity and PZ loss to CO₂ loss was 1.990 and 2.280, respectively. FPZ was the dominant degradation product followed by formate, ammonium, and EDA. Glycolate and oxalate were determined to be insignificant carboxylate degradation products. Nitrite, nitrate, HEP, and DMPZ were found in negligible concentrations. Dissolved metals, particularly Fe and Ni, increased with thermal degradation time. Cr was found in negligible amounts.

Solids precipitated at 0 °C from 4 m 2MPZ/4 m PZ at CO₂ loading less than 0.15 mol/mol alkalinity and from 3.75 m 1MPZ/3.75 m PZ/0.5 m 1,4-dimethyl-PZ at loading less than 0.23. No solids precipitated from these blends at loading up to 0.43 and 0.47, respectively. Solids precipitated at 0 °C from 8 m 2MPZ at 0.47 mol CO₂/mol alkalinity.

1. Speciation of 2MPZ - PZ - CO₂ – H₂O

p. 15

by Xi Chen

Quantitative ¹H and ¹³C NMR studies were performed on 4 m 2MPZ/4 m PZ to acquire speciation and validate the thermodynamic model developed in the previous quarter. The CO₂ loading (α) of the NMR samples ranges from 0 to 0.44 mol CO₂/mol alkalinity. PZ carbamate, 2MPZ carbamate and their protonated forms are found to be the major reaction products. The number of PZ carbamate species is approximately 1.2 ~ 1.5 times that of 2MPZ carbamate species within the loading range studied, which indicates that CO₂ prefers to react with PZ than with 2MPZ. A considerable amount of PZ dicarbamate and (protonated) hindered 2MPZ carbamate was also produced. At loading of 0.3, these species account for ~11% and 7% of total CO₂ in the solution, respectively. Due to peak overlap at rich loading, it is hard to get separate peak areas and quantify each species. The current thermo model for 2MPZ/PZ has to be modified to match the speciation data.

2. CO₂ Rates with Amino Acids

p. 30

by Le Li

The CO₂ absorption performance for 4.5 m SarNa and a blend of 2 m amine X/6 m PZ was tested using the wetted wall column. 4.5 m SarNa is the first sodium-neutralized amino acid solvent tested in the group and was chosen due to the attractive results of 6 m SarK. The sodium-based sarcosine solvent is less soluble than the potassium form. The capacity of 4.5 m SarNa is less than 6 m SarK due to the lower solvent concentration. The CO₂ solubility of sarcosine does not change with the choice of neutralizing base, and is also independent of solvent concentration. The absorption rate of 4.5 m SarNa is lower than 6 m SarK at high loading, but is competitive with 7 m MEA and faster than other amino acid solvents. The heat of absorption for 4.5 m SarNa is much lower than 7 m MEA by approximately 40%. The blend aimed at combining the expected high heat of absorption and thermal stability of amine X with the fast rate and high capacity of PZ. However, measured rate and CO₂ solubility results show this blend to have performance similar to 7 m MEA and 8 m PZ. The absorption rate and capacity of 2 m amine X/6 m PZ were much lower than 8 m PZ, while the heat of absorption of the blend is higher than 8 m PZ. The wetted wall column was used to obtain rate and P_{CO₂*} measurements at 30 °C, beyond the temperature range of previous experiments. The absorption rates of 7 m MDEA/2 m PZ were similar to its rates at 40 °C and 60 °C. The apparatus is stable at 30 °C.

3. Piperazine/Amine X for use in CO₂ Capture

p. 49

by Omkar Namjoshi

A blend of proprietary amine X and PZ was evaluated as a potential CO₂ capture solvent. A total amine strength of 8 m was used (6 m PZ and 2 m amine X) and compared to the performance of 8 m PZ. In this quarter, the solubility window, CO₂ working capacity, heats of absorption, and rates of absorption were evaluated. The wetted wall column and the total pressure apparatus were used to acquire these data.

The data suggest that the lower solubility limit is somewhere between a loading of 0.3 and 0.35 mol CO₂/mol alkalinity at room temperature. There is no upper solubility limit. In addition, the data suggest that the working capacity of the solvent is about 85% that of 8 m PZ, with an operating lean and rich loading of about 0.35 and 0.42, respectively. Amine rates of absorption of the blend are between 50–75% that of 8 m PZ, and the heat of absorption is about 14% greater than that of 8 m PZ.

Goals for the next quarter include evaluating thermal and oxidative degradation of the amine blend as well as evaluating the amine volatility.

4. CO₂ and Amine Volatility at High Temperature

p. 57

by Qing Xu

In this quarter the total pressure screening at 100–160 °C has been continued with 7 m/2 m MDEA/PZ, 5 m/5 m MDEA/PZ, 11 m MEA and 10 m PZ. CO₂ partial pressure was derived from the total pressure data. At 100 °C, CO₂ partial pressure is 35 and 185 kPa for 0.135 and 0.234 loading in 7 m/2 m MDEA/PZ, 40 and 109 kPa for 0.222 and 0.277 loading in 5 m/5 m MDEA/PZ. At 160 °C, CO₂ partial pressure is 769 and 2020 kPa for 0.113 and 0.179 loading in 7 m/2 m MDEA/PZ, 1122 and 1746 kPa for 0.198 and 0.241 loading in 5 m/5 m MDEA/PZ. Based on the data at 40–160 °C, empirical models of CO₂ partial pressure were developed or updated; the heat of absorption of CO₂ is given by the derivative of that expression. In the following equations P_{CO₂} is in Pa, T is in K and α is the CO₂ loading.

$$7 \text{ m/2 m MDEA/PZ: } \ln P_{\text{CO}_2} = (31.2 \pm 0.2) + \frac{-8671 \pm 61}{T} + (22.4 \pm 1.2) \cdot \alpha + (-17.0 \pm 3.6) \cdot \alpha^2$$

$$5 \text{ m/ 5 m MDEA/PZ: } \ln P_{\text{CO}_2} = (35.8 \pm 0.3) + \frac{-11063 \pm 258}{T} + (11098 \pm 1148) \cdot \frac{\alpha}{T} + (-26.4 \pm 6.4) \cdot \alpha^2$$

$$\text{MEA: } \ln P_{\text{CO}_2} = (38.9 \pm 0.6) + \frac{-12030 \pm 184}{T} + (-16.5 \pm 3.4) \cdot \alpha^2 + (1086 \pm 414) \cdot \frac{\alpha}{T} + (12030 \pm 1396) \cdot \frac{\alpha^2}{T}$$

$$\text{PZ: } \ln P_{\text{CO}_2} = (35.5 \pm 0.3) + \frac{-11082 \pm 125}{T} + (-22.5 \pm 3.1) \cdot \alpha^2 + (4713 \pm 411) \cdot \frac{\alpha}{T} + (11722 \pm 1345) \cdot \frac{\alpha^2}{T}$$

Among the nine screened solvents, at the mid-loading which corresponds to 1.5 kPa P_{CO₂} at 40 °C, the ΔH_{abs} are in the following sequence: DGA[®] > MEA ≈ 7/2 MDEA/PZ > PZ/1MPZ/1,4-DMPZ > 1MPZ ≈ 5/5 MDEA/PZ > PZ ≈ 2MPZ ≈ PZ/2MPZ. At the mid-loading, the ΔH_{abs} is 72 and 69 kJ/mol CO₂ for 7 m/2 m MDEA/PZ and 5 m/5 m MDEA/PZ, respectively.

In this period the oil leaking problem from the last quarter with the high temperature VLE apparatus has been solved by adding filters in the vapor sampling line. A cooling pack was used to avoid flashing of the liquid sample.

The high temperature VLE apparatus was tested by MEA-H₂O as a benchmark. The data from this work are comparable to literature data.

The Aspen Plus[®] Hilliard model for MEA over-predicts the high temperature data and under-predicts 40 °C data. Aspen Plus[®] PZ Fawkes Model fairly predicts the data at 40, 60, 120, and 150 °C.

In this period total pressure was measured with 10 m PZ and 8 m 2MPZ at 100–160 ° C in an autoclave. CO₂ partial pressure was derived from the total pressure data and semi-empirical models were correlated. According to the Gibbs-Helmholtz equation, CO₂ heat of absorption was derived from CO₂ partial pressure models. The updated models are as follows:

0.9–13 m PZ:

$$\ln P_{CO_2} = 35.5 + \frac{-11067}{T} - 21.5 \cdot \alpha^2 + 4710 \cdot \frac{\alpha}{T} + 11419 \cdot \frac{\alpha^2}{T}$$

$$\Delta H_{abs} = -R(-11067 + 4710\alpha + 11419\alpha^2) \text{ (J/mol CO}_2\text{)}$$

8 m 2MPZ:

$$\ln P_{CO_2} = 40.1 + \frac{-12513}{T} - 22.1 \cdot \alpha^2 + 14099 \cdot \frac{\alpha}{T}$$

$$\Delta H_{abs} = -R(-12513 + 14099\alpha) \text{ (J/mol CO}_2\text{)}$$

Pilot plant work by Eric Chen showed that fogging might occur in the condenser of the 2-stage flash and cause solid formation and clogging in the pipe. Thus an apparatus has been set up at bench scale to test fogging. One experiment with 8 m PZ was conducted and fogging was observed at 150 ° C, 7.3–7.7 bar. The condensate accumulated from 7.3–12.3 bar contains 2.84 wt % PZ and 0.92 wt % CO₂. In future, more experiments will be done at various temperature and pressure levels in order to find the boundary condition of fogging formation.

In the next quarter the electrolyte-NRTL thermo model of CO₂-MEA-H₂O will be improved with more experimental data and fewer parameters.

5. Amine Volatility and Heat Capacity

p. 67

by Thu Nguyen

The partition coefficient, or the ratio of the amine concentration in water near infinite dilution to its concentration in the vapor, of 21 amines (12 amines from this work and 9 alkylamines) was successfully modeled by using a group contribution approach by Hine and Mookerjee. The residual errors between measured and predicted values were less than 5%. The empirical expression used to predict the amine partition coefficient at infinite dilution in water at 25 °C is: $\log K_{\text{amine}, 25^\circ\text{C}} = 0.389 + 3.08 \cdot \text{OH}(\text{C}) - 0.124 \cdot \text{CH}_2(\text{C})(\text{N}) + 1.79 \cdot \text{N}(\text{C}_3) - 0.34 \cdot \text{CH}_3(\text{X}) + 1.37 \cdot \text{C}_{\text{cy}}\text{H}_2(\text{C}_{\text{cy}})(\text{N}_{\text{cy}}) + 0.58 \cdot \text{N}_{\text{cy}}\text{H}(\text{C}_{\text{cy}})_2 + 0.14 \cdot \text{CH}_2(\text{C})(\text{O}) + 3.45 \cdot \text{NH}_2(\text{C}) + 1.39 \cdot \text{C}_{\text{cy}}\text{H}(\text{N}_{\text{cy}})(\text{C}_{\text{cy}})(\text{CH}_3) + 3.45 \cdot \text{NH}(\text{C})_2 - 0.103 \cdot \text{CH}_2(\text{C})_2 - 0.007 \cdot \text{CH}(\text{C})_2(\text{N})$. The subscript cy designates a cyclic structure.

The experimental heat capacity method was validated by benchmarking H₂O and Al₂O₃ C_p measurements to literature values. It was determined that there is a ±10% uncertainty in the data which is well within the margin of error expected for this methodology. C_p for the 7 m MDEA/2 m PZ solution ranges from ~3.06–3.95 J/g*K over the loading range 0.04–0.27 mol CO₂/mol total alkalinity for 40–120 °C. The blend C_p decreases as loading increases as CO₂ appears to have negligible heat capacity. The C_p for the 5 m MDEA/5 m PZ blend ranges from ~2.92–3.56 J/g*K over the loading range 0.19–0.31 mol CO₂/mol total alkalinity for 40–120 °C. The unloaded C_p for the 5/5 blend is less than that of the 7/2 blend at any given temperature because the enthalpy contribution of MDEA to the total enthalpy is less as the MDEA concentration in the 5/5 is less than in the 7/2. MDEA has the greatest C_p of all the components present in the blend.

6. Modeling MDEA/PZ Thermodynamics, Hydraulics, and Kinetics

p. 80

by Peter Frailie

The goal of this study is to evaluate the performance of an absorber/stripper operation that utilizes MDEA/PZ. Before analyzing unit operations and process configurations, thermodynamic, hydraulic, and kinetic properties for the blended amine must be satisfactorily regressed in Aspen Plus[®]. Thermodynamic, hydraulic, and kinetic data have been regressed for 8 m PZ, 7 m MDEA/2 m PZ, and 5 m MDEA/5 m PZ. Heat of absorption predictions have been calculated and compared using Aspen Plus[®] calorimetry and the Gibbs-Helmholtz equation. CO₂ absorption rate data for all solvents were fit using the same set of reactions, rate constants, and binary diffusivities. The CO₂ absorption rate was fit with an average deviation of 6.7% over operational loading and temperature ranges for all solvents. The goal for the next quarter is to begin optimizing an absorption/stripping/compression operation using 7 m MDEA/2 m PZ and 5 m MDEA/5 m PZ.

7. Modeling Stripper Performance for CO₂ Capture by Amines

p. 88

by David Van Wagener

This quarter focused on two tasks: reconciliation of two previous pilot plant campaigns with concentrated PZ, and development of a stripper configuration to be used with geothermal heating. The initial run of the 2008 pilot plant campaign was first studied using a manual, step-by-step variation of data values. The lean loading, rich loading, and heat loss were sequentially manipulated in that order to match the change in loading and overhead condensate rate measured at the pilot plant. This method was found to be insufficient because the overhead CO₂ rate could not be matched with a fixed change in loading. Instead, the first run from each of the 2008 and 2010 pilot plant campaigns were reconciled using the Data Fit package in Aspen Plus[®] and their data values were mostly matched within 2.7% and 2.2%, respectively. The other runs could not be fit to the desired accuracy, so the fitting method will be altered in the future. Next, a flowsheet was designed that is expected to use geothermal heat efficiently. Brine from a geothermal source delivers heat at variable temperature, unlike steam from the power plant, so the flowsheet must be designed with more complex heat exchange to maximize its reversibility. The proposed flowsheet resulted in very small temperature approaches for most exchangers due to highly imbalanced heat capacity of the exchanging streams. This flowsheet will be optimized and combined with results from a model for geothermal heating.

8. CO₂ Absorption Modeling Using Aqueous Amines

p. 107

by Jorge M. Plaza

The discrepancies between the laminar jet and the wetted wall column model for MEA were assessed. Previous results showed large differences between the extracted kinetics from both models. Analysis showed issues with diffusivities of CO₂ and amine species, and activity coefficients of CO₂ and MEA. The diffusion coefficient was modified by user FORTRAN subroutines to match diffusion behavior reported by Aboudheir (2002). The activity coefficient of CO₂ was initially corrected with the correlations used by Dugas (2009). However, the MEA activity coefficient values and behavior largely deviated from the data reported by Dugas. It is not possible to correct the MEA activity coefficient without re-regressing the thermodynamic framework. Initially, the CO₂ activity coefficient was adjusted in an attempt to compensate the

issues related to the MEA activity coefficient. This adjustment affected the fit for the equilibrium pressure of CO₂ vs. loading. The solution of this issue requires re-regression of the CO₂-MEA-H₂O parameters.

Samples from the September 2010 PZ campaign have been analyzed for loading and compared to the values obtained at the pilot plant. Results show a consistently higher measurement for the midpoint and rich data for the titrations at the pilot plant.

9. Measurement of Packing Effective Area and Mass Transfer Coefficients

p. 113

by Chao Wang

(supported by the Carbon Management Project of the Process Science and Technology Center)

Packing is widely used in distillation, stripping, and scrubbing processes because of its relatively low pressure drop, good mass transfer efficiency, and ease of installation. Packing is being investigated for post-combustion carbon capture for these reasons. Research continues to focus on development of high performance packing, especially on minimizing pressure drop, maximizing mass transfer efficiency, and minimizing costs. The design of packed absorbers for carbon dioxide capture will require the reliable measurement and accurate prediction of the effective area a_e , gas and liquid film mass transfer coefficient k_G and k_L . My research is focused on the measurement of these important fundamental parameters for packings and construction of a mechanistic design model.

In this quarter, new gas film mass transfer coefficient measurements have been completed for 1-inch plastic pall rings. A second low range SO₂ analyzer has been installed to allow measurements of ppb level SO₂ concentrations. Therefore, a 10 ft bed of packing can be used which helps to minimize any end effects and provides a deeper bed for formation of natural flow distribution within the packing. The kg measurements show performance and dependence similar to that observed with previous packings such as no dependence on liquid rate and a dependence on gas rate to 0.93 power.

The Rocha-Bravo-Fair (RBF) mass transfer model (1996) has been evaluated in this quarter. The RBF model is based on distillation systems with organic solutions and very low surface tensions. As a result, the RBF mass transfer model depends on its corresponding area model. Thus one would expect trouble with the mass transfer coefficient prediction when used with the Tsai area model. It makes more sense to use RBF $k_{G/L}$ model multiplied by RBF area model to predict $k_{G/L}a$ data instead of using RBF $k_{G/L}$ model alone. In this quarter, both RBF $k_{G/L}$ -RBF area model and RBF $k_{G/L}$ -Tsai area model are used to predict experimental ka numbers. Results show that RBF $k_{G/L}$ -RBF area model is much closer to the experimental data, which means we should use RBF k model and RBF area model together to predict ka numbers in the future.

Another dimensionless k_L model is proposed in this quarterly report. This model is based on Brunazzi (1997). Results show that this k_L model fits well with our experimental data; the average deviation is 24%.

10. Pilot Plant Testing of Advanced Process Concepts using Concentrated Piperazine

by Dr. Eric Chen

Supported by the CO₂ Capture Pilot Plant Project of the Process Science and Technology Center

and by NRG Energy Contract with DOE

In this reporting period, the first campaign with the high-temperature two-stage flash regeneration process with 8 m PZ and absorber intercooling was completed in early January 2011 at the UT SRP pilot plant facility. A number of issues were identified during the operation of the flash skid. Modifications to the skid and SRP pilot plant are currently in progress. A new high pressure Alfa Laval TL6 multi-pass cross-exchanger was ordered to replace the existing single pass cross-exchanger on the skid. The gas-liquid separators have been re-rated to 281 and 225 psia at 400 °F. Additional static and differential pressure measurements will be installed on the cross-exchanger, two steam heaters, pump suction and discharge, and skid lean outlet to provide better process control and minimize process upsets resulting from flashing. A skid liquid return pump will be installed downstream from the low pressure separator to facilitate cold plant startups. Sight glasses will be installed at two locations in the SRP pilot plant, one downstream from the condenser gas line and another in the CO₂ gas recycle line to verify the existence of piperazine fogging. The two online viscometers will be relocated from the skid to the inlet and outlet piping of the SRP absorber feedtank and should provide viscosity and density measurements that will not be affected by flashing. Finally, a wash nozzle will be installed upstream from the flow straightener and a weekly cleaning will be performed each Friday immediately after plant shutdown for the weekend.

More detailed reporting of this activity is limited to sponsors of the CO₂ Capture Pilot Plant Project and does not appear in this report to Luminant sponsors.

11. Effects of Solvent Storage on MEA Plant Performance ***p. 120***

by Sepideh Ziaii

Co-supervised by Professor Thomas Edgar

This work presents results on dynamic effects of absorber foaming on MEA absorption/stripping, explores possible control strategies, and identifies effective strategies for safe and stable plant operation.

To simulate foaming on the absorber packing bed, the liquid hold-up time in the absorber packing was increased with a +10% step change in a linear factor affecting the liquid hold-up equation used in the model.

Open loop analysis indicated a sharp overshoot in the stripper pressure, which mainly resulted from the initial rise and drop in the rich loading. This dynamic behavior necessitates pressure control on the stripper to protect the stripper column and multi-stage compressor. Controlling stripper pressure by either steam valve or pressure valve is not an effective strategy especially if these valves are wide open normally and become saturated during abnormal conditions.

Rich solution flow rate was found to be the best manipulated variable to respond to absorber foaming, as it can decrease the magnitude of overshoot and keep the pressure close to the set point. This variable dampens the influence of the rich loading on the stripper pressure by decreasing the CO₂ desorption.

According to the dynamic results, level ratio control on the lean and rich tank by lean solution flow rate is necessary to keep the liquid levels in balance and prevent the pumps from running dry. If this control loop acts with a delay time equal to the liquid hold-up time in the equipment

between tanks (reboiler and stripper), it gives the best dynamic response for stripper pressure and other process variables.

12. Modeling CO₂ Recovery for Optimal Dynamic Operations *p. 131*

by Dr. Ricardo Dunia

This report presents the use of the Subspace Identification Method with Principal Component Analysis (SIMPCA), a subspace system identification technique used to develop a dynamic empirical model for a Linear Quadratic Gaussian (LQG) controller with integral action. Such a controller is made to attain optimal operating conditions for a CO₂ capture pilot plant. Reference signals are used in conjunction with the controller integral action to bring some process outputs towards their set-points.

13. Electric Grid-Level Implications of Flexible CO₂ Capture Operation *p. 135*

by Stuart Cohen

Supported by the EPA STAR Fellowship Program

Flexible post-combustion absorption/stripping that vents carbon dioxide (CO₂) or stores rich solvent at partial or zero load was investigated using a previously developed model that maximizes annual profits for a coal-fired facility using 7 m monoethanolamine (MEA) for CO₂ capture. The model uses electricity prices as input and chooses base plant and CO₂ capture operating points in each 15-minute interval, subject to constraints on base plant and CO₂ capture system operation. In this quarter, the model was used to compare operating profits, net present value, and CO₂ emissions of a facility with and without flexible and inflexible CO₂ capture for three disparate 20-year CO₂ price paths.

Major conclusions were:

- Flexible CO₂ capture in response to volatile electricity prices is most valuable if future CO₂ prices hover near a range of \$40–50/tCO₂.
- Sustained CO₂ prices above \$100/tCO₂ are required to make CO₂ capture retrofit preferable to continued operation of a facility without CO₂ capture, but the benefit of flexibility could be limited in this CO₂ price regime.
- Flexible and inflexible CO₂ capture reduces CO₂ emissions substantially over a broad range of CO₂ price scenarios.

14. MDEA/PZ Degradation in Cycled Solvents *p. 150*

by Fred Cloosmann

(supported by the Luminant Carbon Management Project and the Process Science & Technology Center)

When cycled and oxidatively degraded using the low-gas method, 7 m MDEA in the blend oxidatively degraded to DEA, which then oxidized to bicine. We demonstrated that when methylaminoethanol (MAE) was formed in these same experiments with 7 m MDEA and the blend, the MAE subsequently oxidized to hydroxyethylsarcosine (HES). In low gas experiments with both solvents at 55 °C, loss rates of DEA and MAE were ~ 18–20 mM/hr.

When 6 m MDEA/1 m MAE was cycled from 55 to 120 °C, the production of DEA was either suppressed or masked, and bicine production was suppressed. Indicators of amine degradation including formate, total formate, primary/secondary amine production, and parent amine (MDEA) and alkalinity loss were also suppressed, indicating that either a competition for oxygen to oxidize MAE to HES or a general suppression of overall oxidation is occurring.

HES was synthesized and identified as a single, stand alone peak using the HPLC amino acid method. The concentration of HES at the end of experiment C-21, which cycled 7 m MDEA/2 m PZ from 55 to 120 °C, was approximately 192 mM, which represented approximately 10.5% of lost carbon as MDEA and PZ loss.

When the oxidative degradation effects in 7 m DEA in low gas experiment OD-6 were isolated, it was determined that the major amine degradation product was MEA, which was rapidly formed in correlation with rapid initial loss of DEA (18.2 mM/hr). Total formate was approximately 10X formate alone, and glycolamide formed rapidly, but behaved as a reaction intermediate, decreasing in concentration after approximately 150 hours. In low gas experiment OD-7, 7 m MAE was degraded at 55 °C, and measured a rapid loss in MAE concentration accompanied by the production of MEA, HES, and total formate. MEA and HES both reached a steady state concentration after approximately 150 hours. As observed in OD-6, total formate was ~10X formate concentration.

Oxidative degradation mechanisms have been postulated for the degradation of MDEA and the generation of DEA, MAE, bicine, and HES in 7 m MDEA and 7 m MDEA/2 m PZ. In each case, the pathway relies on the presence of free radicals to initiate an e^- abstraction from an α -carbon on the amine, a subsequent H^+ abstraction, and the formation of a hydroperoxide compound which will decompose to an amine/amino acid and an aldehyde.

7 m MDEA/2 m PZ did not thermally degrade over the range of 120 to 150 °C in unloaded solutions. However, lean ($\alpha = 0.1$) and rich ($\alpha = 0.25$) solutions of the solvent readily degraded both components over the temperature range of 120 to 150 °C. At 135 and 150 °C, the fraction PZ remaining was essentially zero within 50 and 15 days, respectively. Thermal degradation led to the formation of PZ derivatives including MPZ, DMPZ, AEP, and NPZ. When their concentrations are compared to those of PZ loss, only ~50% of the PZ functional group can be accounted for. DMAE did not behave as a reaction intermediate.

15. Thermal Degradation and Oxidation of Aqueous Piperazine for Carbon Dioxide Capture

p.

by Stephanie Freeman

This is the abstract of the dissertation prepared by Freeman and attached in its final version.

Absorption-stripping with aqueous, concentrated piperazine (PZ) is a viable retrofit technology for post-combustion CO₂ capture from coal-fired power plants. The rate of thermal degradation and oxidation of PZ was investigated over a range of temperature, CO₂ loading, and PZ concentration. At 135 to 175 °C, degradation is first order in PZ with an activation energy of 183.5 kJ/mole. At 150 °C, the first order rate constant, k_1 , for thermal degradation of 8 m PZ with 0.3 mol CO₂/mol alkalinity is $6.12 \times 10^{-9} \text{ s}^{-1}$. After 20 weeks of degradation at 165 °C, 74% and 63%, respectively, of the nitrogen and carbon lost in the form of PZ and CO₂ was recovered in quantifiable degradation products. N-formylpiperazine, ammonium, and N-(2-aminoethyl) piperazine account for 57% and 45% of nitrogen and carbon lost, respectively. Thermal

degradation of PZ likely proceeds through S_N2 substitution reactions. In the suspected first step of the mechanism, 1-[2-[(2-aminoethyl) amino]ethyl] PZ is formed from a ring opening S_N2 reaction of PZ with H^+PZ . Formate was found to be generated during thermal degradation from CO_2 or CO_2 -containing molecules.

An analysis of k_1 values was applied to a variety of amines screened for thermal stability in order to predict a maximum recommended stripper temperature. Morpholine, piperidine, PZ, and PZ derivatives were found to be the most stable with an allowable stripper temperature above 160 °C. Long-chain alkyl amines or alkanolamines such as N-(2-hydroxyethyl)ethylenediamine and diethanolamine were found to be the most unstable with an allowable stripper temperature below 120 °C.

Iron (Fe^{2+}) and stainless steel metals (Fe^{2+} , Ni^{2+} , and Cr^{3+}) were found to be only weak catalysts for oxidation of PZ, while oxidation was rapidly catalyzed by copper (Cu^{2+}). In a system with Fe^{2+} or SSM, 5 kPa O_2 in the inlet flue gas, a 55 °C absorber, and one-third residence time with O_2 , the maximum loss rate of PZ is expected to be 0.23 mol PZ/kg solvent in one year of operation. Under the same conditions but with Cu^{2+} present, the loss rate of PZ is predicted to be 1.23 mole PZ/kg solvent in one year of operation. Inhibitor A was found to be effective at decreasing PZ loss catalyzed by Cu^{2+} . Ethylenediamine, carboxylate ions, and amides were the only identified oxidation products. Total organic carbon analysis and overall mass balances indicate a large concentration of unidentified oxidation products.

16. Oxidative Degradation of Monoethanolamine

p. 170

by Alex Voice

Analysis and oxidation of a field sample of 9 m MEA was carried out using 98 kPa O_2 /2 kPa CO_2 at 55 °C for 17 days. The results were analyzed by anion chromatography, cation chromatography, total alkalinity titration, total nitrogen, total organic carbon, total inorganic carbon, HPLC with electrochemical detection, HPLC with UV and ELSD detection, GC-MS, and high resolution mass spectrometry.

The initial MEA loss rate was 18.4 mmol/kg/hr (for the first 24 hours). After that, the rate decreased substantially. The average rate was 7.4 mmol/kg/hr over the entire experiment (~400 hours).

The nitrogen mass balance was closed by 80–101% for the final samples (after >5 days of oxidation). 1-(2-hydroxyethyl)-imidazole was the largest degradation product. Amides and volatile ammonia accounted for most of the remaining nitrogen-containing products. Several novel products have also been suggested based on masses observed using high-resolution mass spectrometry.

HEI was synthesized from equimolar quantities of glyoxal, formaldehyde, and ammonia added to loaded, aqueous, MEA solution. The yield was close to 100% with excess glyoxal or formaldehyde, but only 80% with excess ammonia. HEI is somewhat thermally stable and is not produced during thermal degradation (high temperature, oxygen-free environment).

Some novel degradation products have been proposed based on formulas observed on high-resolution mass spectrometry. Many products (both old and new) were detected on GC-MS and LC-MS.

Qualitatively, the lab-scale oxidation experiment was observed to result in significantly more oxidation than occurs in a real system.

17. Nitrosamine Formation in CO₂ Capture by Piperazine **p. 200**

by Mandana Ashouripashaki

Secondary amines may react with nitrite to produce carcinogenic products called nitrosamines. They were first described in the chemical literature over 150 years ago, but since the discovery of their carcinogenic properties in 1956 by Barnes and Magee, there has been an explosion of interest in their chemistry and particularly in methods of destroying them. Piperazine (PZ) is an amine of interest in our study and nitrosation products of PZ are N-nitrosopiperazine (MNPZ) and N-N, dinitrosopiperazine (DNPZ).

Four experiments were performed this quarter to measure the reaction of nitrite with 8 m loaded PZ at 60 °C with 0.4 mM Fe^{+2} /0.1 mM Cr^{+2} /0.05 mM N^{1+2} . The experiments included exposure to no gas with added nitrite, to air/CO₂ with added nitrite, or to air/CO₂/NO₂.

The reaction rate of nitrite with 8 m loaded PZ is not changed by contacting the solution with oxygen. Nitrite accumulates when the solution is contacted with gas containing oxygen and NO₂.

We continued to develop a method for detecting and measuring dinitrosopiperazine (DNPZ) and mononitrosopiperazine (MNPZ) using liquid chromatography followed by mass spectrometry (LC-MS) or a UV detector.

18. Reclaiming for Amine-Based CO₂ Capture **p. 217**

by Steven Fulk

In this quarter, liquid-liquid equilibrium experiments were investigated as a means of recycling oxidation inhibitors. Phase separation experiments consisted of heating solution to 60 °C in an agitated isothermal glass-jacketed beaker followed by additions of anhydrous K₂CO₃ to unloaded solutions and KOH to loaded solutions. Additions of K₂CO₃ to an 8 m PZ solution containing Inhibitor A led to formation of two liquid phases below a total solution loading of 0.365 moles CO₂/mole alkalinity. For a total solution loading of 0.365, K⁺ and CO₂ were 50 and 60 times more concentrated in the bottom phase, respectively. PZ and Inh A were 335 and 1.92 times more concentrated in the top phase, respectively. Adding anhydrous KOH to an 8 m PZ, 0.30 loaded solution containing Inh A precipitated instead of liquid-liquid separating.

The pK_a of the free amine functionality group of FPZ was measured by titration with 0.01 M HCl. The pK_a of FPZ was measured at 7.807.

A 20 m PZ, 0.1 loaded solution was thermally degraded in 316 SS cylinders with Swagelok[®] endcaps in a forced convection oven at 175 °C for a period of ten weeks to simulate degradation in a thermal reclaimer. Samples were transferred each week to a glass vial with a nitrogen-sparged headspace. The average loss of total alkalinity, PZ, and CO₂ was 0.185, 0.212, and 0.093 moles/kg, respectively. The ratio of total alkalinity and PZ loss to CO₂ loss was 1.990 and 2.280, respectively. FPZ was the dominant degradation product followed by formate, NH₄⁺, and EDA. Fe and Ni increased to 450 ppm over a period of 10 weeks. Glycolate, oxalate, nitrite, nitrate, HEP, DMPZ, and Cr were found in negligible amounts.

A two-stage integrated thermal reclaimer was simulated in Aspen Plus[®] using the Fawkes thermodynamic framework with MDEA as a surrogate for a collection of contaminants for

thermodynamic modeling purposes. 1×10^{-4} – 1×10^{-3} percent of the lean stream flow rate removed contaminants produced at a rate of 1×10^{-5} moles per mole CO_2 captured. The make-up and disposal costs varied between \$0.3–\$1.5/MT CO_2 captured for varying reclaimer pressure while the energy cost was determined to be independent of reclaimer design.

Goals for next quarter include continued phase characterization experiments for contaminant and inhibitor separation using liquid-liquid separation. Thermal degradation experiments for solutions containing KOH, KHCO_3 , and K_2CO_3 , to mimic neutralized reclaiming solutions, will be analyzed.

19. Amine Reclaiming by Solids Precipitation

p. 240

by Humera Abdul Rafique

8 m PZ (40%) exists in liquid form between loadings of 0.32 and 0.43 mol CO_2 /mol alkalinity. The solid phase at the lean end is $\text{PZ} \cdot 6\text{H}_2\text{O}$ and that at the rich end is $\text{H}^+\text{PZCOO}^-\cdot\text{H}_2\text{O}$. To expand the solubility envelope, solid solubility experiments were carried out for the following blends: 3.75 m PZ/3.75 m 1MPZ/0.5 m 1,4DMPZ; 4 m PZ/4 m 2MPZ; 6 m PZ/2 m 2MPZ. To better understand the properties of the 2MPZ loaded blend, solid solubility for 8 m 2MPZ was also studied. Because of the lower concentration of PZ in the blends, the $\text{PZ} \cdot 6\text{H}_2\text{O}$ precipitated at lower loadings (0.23 and 0.15 mol CO_2 /mol alkalinity for 3.75 m PZ/3.75 m 1MPZ/0.5 m 1,4DMPZ and 4 m PZ/4 m 2MPZ, respectively). A maximum loading of 0.23 and 0.15 mol CO_2 /mol alkalinity was obtained for the 3.75/3.75/0.5 and 4/4, respectively. No solid precipitation was observed as with 8 m PZ. 8 m 2MPZ precipitated $\text{H}^+\text{2MPZCOO}^-\cdot\text{H}_2\text{O}$ at a loading of 0.47 mol CO_2 /mol alkalinity.

The electrolyte-NRTL model in Aspen Plus[®] can be used for data regression of the sulfate solubility experimental analysis to model a sulfate reclaiming system. The model uses an energy parameter, τ , and a non-randomness factor, α , to calculate the activity coefficient of the ionic species specified in the model. This in turn enables us to calculate the solubility product of the salt in PZ over a wide range of temperatures and amine concentrations.

Attachments:

Oxidation of MEA and other Amine-based Solvents used for Post-Combustion CO_2 Capture

Research proposal by Alexander K. Voice

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Oxidation of MEA and other Amine-based Solvents used for Post-Combustion CO_2 Capture

Powerpoint presentation by Alexander K. Voice

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Thermal Degradation and Oxidation of Aqueous Piperazine for Carbon Dioxide Capture

Ph.D. Dissertation by Stephanie Anne Freeman

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Speciation of 2-Methylpiperazine - Piperazine - Carbon Dioxide - Water

Quarterly Report for January 1– March 31, 2011

by Xi Chen

Supported by the Luminant Carbon Management Program

Department of Chemical Engineering

The University of Texas at Austin

April 1, 2011

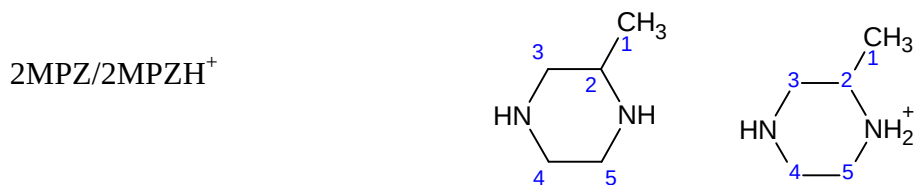
Abstract

Quantitative ^1H and ^{13}C NMR studies were performed on 4 m 2-methylpiperazine (2MPZ)/4 m piperazine (PZ) to acquire speciation and validate the thermodynamic model developed in the previous quarter. The CO_2 loading (α) of the NMR samples ranges from 0 to 0.44 mol CO_2 /mol alkalinity. PZ carbamate, 2MPZ carbamate and their protonated forms are found to be the major reaction products. The amount of PZ carbamate species are approximately 1.2 ~ 1.5 times that of 2MPZ carbamate species within the loading range studied, which indicates that CO_2 prefers to react with PZ than with 2MPZ. A considerable amount of PZ dicarbamate and (protonated) hindered 2MPZ carbamate was also produced. At loading of 0.3, these account for ~11% and 7% of total CO_2 in the solution, respectively. Due to peak overlap at rich loading, it is hard to get separate peak area and quantify each species. The current thermo model for 2MPZ/PZ has to be modified to match the speciation data.

Introduction

A thermodynamic model was created in a previous study to model the VLE and speciation of 2MPZ-PZ- H_2O - CO_2 . To validate the speciation prediction from this model, experimental data must be obtained.

The same convention of atom numbering for 2MPZ was kept in this report. It is shown along with numbering for PZ molecule in Figure 1. The protons and carbons on the same functional group share the same number.



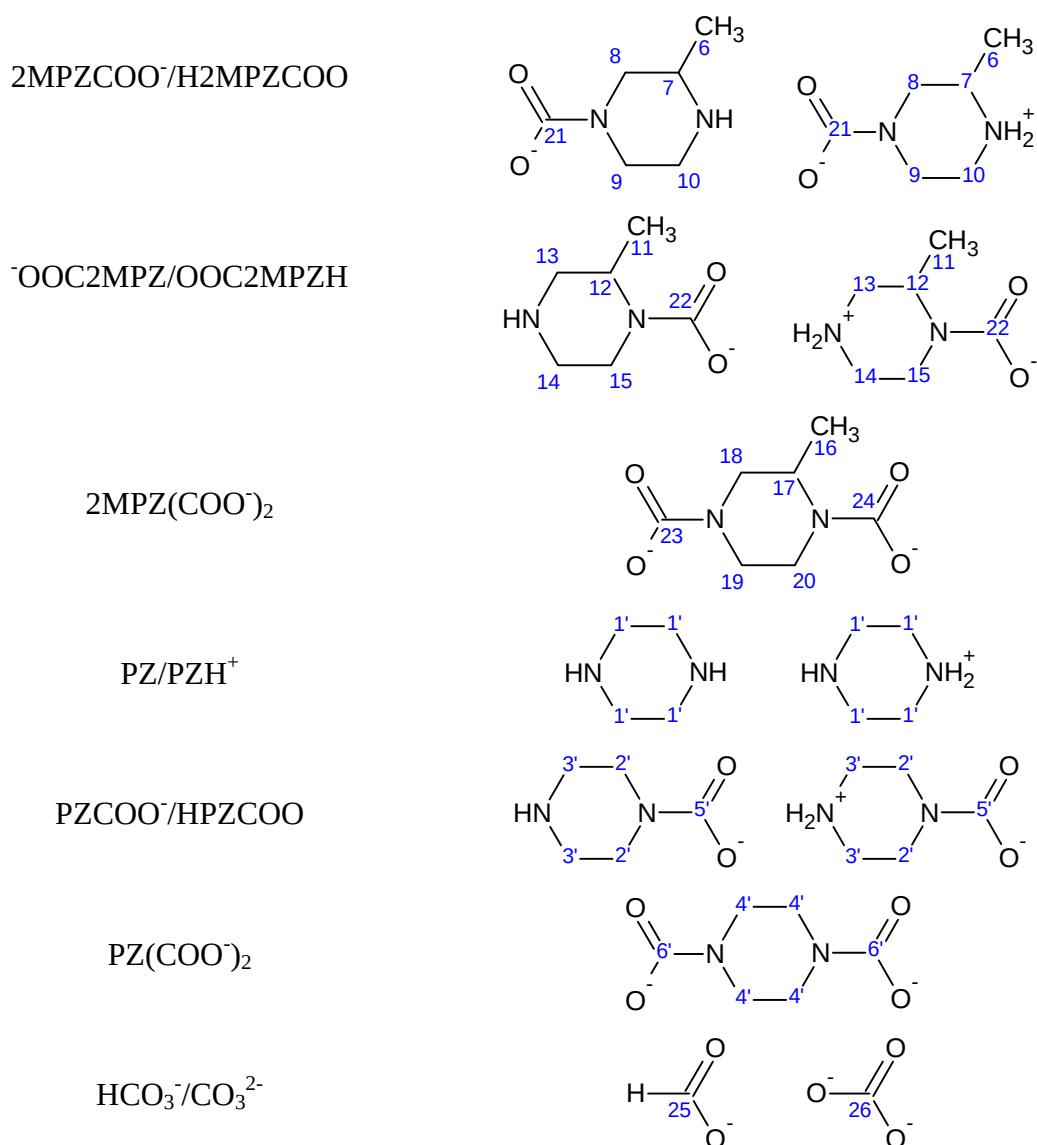


Figure 1: Number labeling of different molecules in 2MPZ-PZ-CO₂-H₂O

Experimental Methods

The same experimental procedure and methods as mentioned in the first and second quarterly reports of 2010 were followed to prepare the NMR samples and analyze the spectra. Since the natural abundance of ¹³C is 1.1%, a factor of 1.1% is used when transforming the area of the peaks from carbonyl group containing nearly 100% ¹³C.

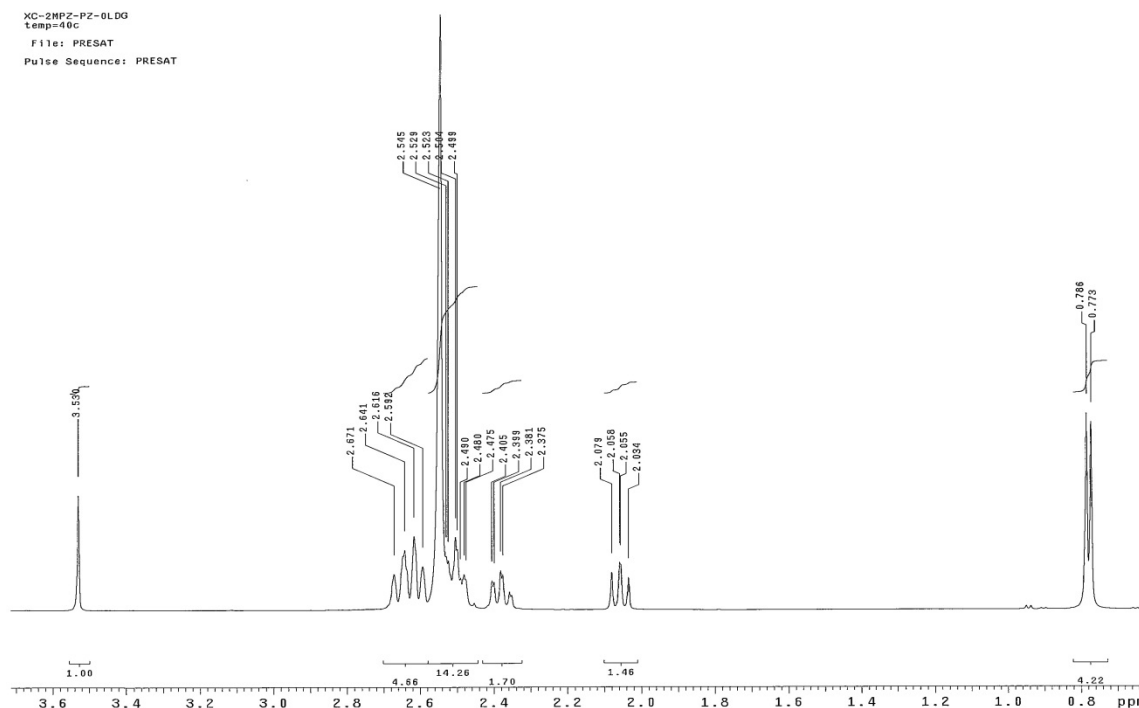
Results and Discussion

The apparent liquid composition of the NMR samples, determined gravimetrically, is shown in Table 1.

Table 1: The liquid composition of the NMR samples in mass (gram)

Component	Sample #				
	1	2	3	4	5
2-MPZ	0.2106	0.2091	0.2084	0.2039	0.2025
PZ	0.1811	0.1798	0.1792	0.1753	0.1742
H ₂ O	0.5260	0.5224	0.5205	0.5093	0.5060
C ¹³ O ₂	0.0000	0.0537	0.0819	0.1100	0.1603
D ₂ O	0.1128	0.1134	0.1132	0.1125	0.1124
Dioxane	0.0163	0.0163	0.0164	0.0161	0.0162
Total	1.0467	1.0948	1.1196	1.1271	1.1715
α (mol/mol alka.)	0.000	0.143	0.219	0.300	0.440

The ¹H, ¹³C, and C-H correlation spectra for zero CO₂ loading are shown in Figure 2, Figure 3, Figure 4, respectively. The peak positions and area agree well with the previous spectra obtained separately for 8 m 2MPZ and 8 m PZ. The highest peak seen in the spectra corresponds to the H1' and C1' on PZ molecule. Unfortunately, the peaks from PZ overlap those from 2MPZ in the chemical shift (δ) range of 2.4–2.8 ppm, adding difficulties of quantification.

**Figure 2: ¹H NMR spectrum for 4 m 2MPZ/4 m PZ at $\alpha = 0$ and 40 °C**

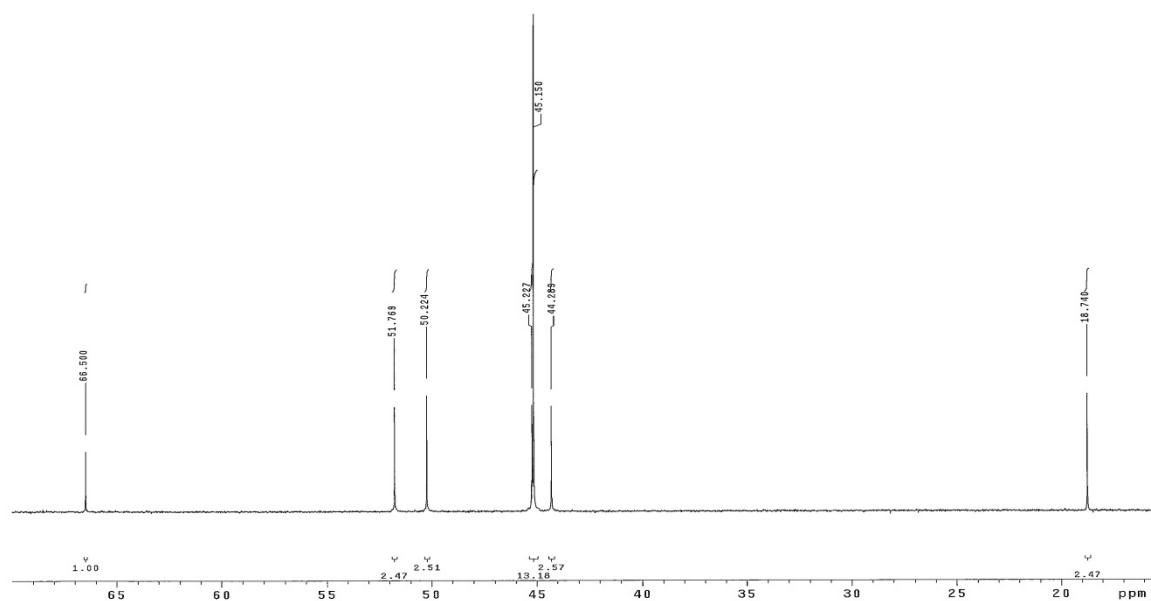


Figure 3: ¹³C NMR spectrum for 4 m 2MPZ/4 m PZ at $\alpha = 0$ and 40 °C

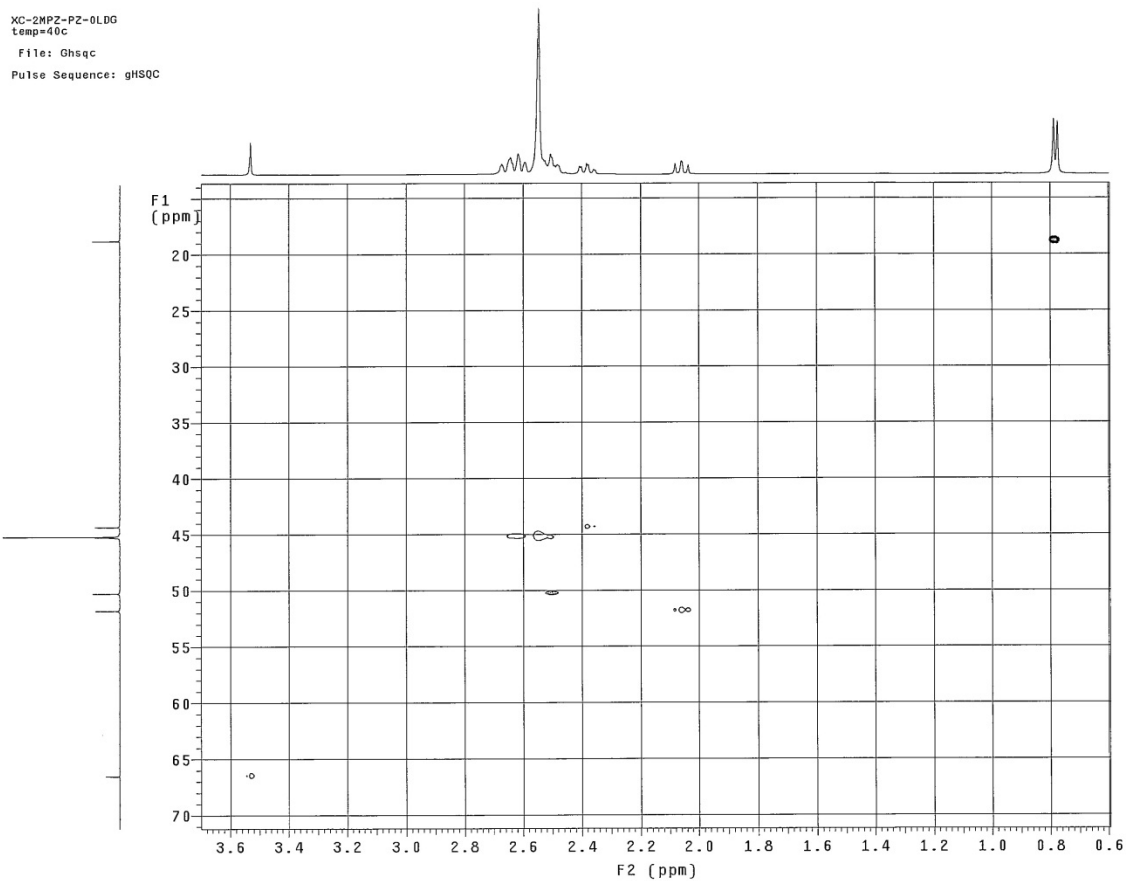


Figure 4: ¹³C-¹H 2D correlation for 4 m 2MPZ/4 m PZ at $\alpha = 0$ and 40 °C

The ^{13}C spectra in downfield and in upfield for $\alpha = 0$ to 0.440 are shown in Figure 9 and Figure 6, respectively. Enlarged spectra with peak position and integral ratio for each loading can be found in the Appendix. Based on peak positions and relative peak areas, the peaks in downfield are assigned to different carbamate species, as indicated by the labels. At high loading of 0.3 and 0.44, the peaks for PZ carbamate and 2MPZ carbamate overlap each other to a great extent. Therefore it is not possible to obtain peak area for each of them.

The integral ratio of peaks is referred to the peak area of dioxane and proportional to the actual concentration. Consequently, given the concentration of dioxane, other species in the solution can be quantified. The peak position and concentration of different species are summarized in Table 2. The chemical shift of monocarbamate decreases with CO_2 loading because the decrease in pH changes the ratio of protonated and unprotonated species. However, the chemical shift of dicarbamate was found to be relatively stable since it is not possible to protonate a dicarbamate species. The δ values for PZ dicarbamate and 2MPZ dicarbamate in the blend was actually very close to those found for straight PZ and 2MPZ solutions.

Table 2: Chemical shift and concentration of different carbamate species based on integral ratio

Chemical Shift δ (ppm)					
α (mol CO_2 /mol alka.)	$[\text{2MPZCOO}^-]/[\text{H2MPZCOO}]$	$[\text{OOC2MPZ}]/[\text{OOC2MPZH}]$	$[\text{2MPZ(COO}^-)_2]$	$[\text{PZCOO}^-]/[\text{HPZCOO}]$	$[\text{PZ(COO}^-)_2]$
0.000	n/a	n/a	n/a	n/a	n/a
0.143	162.524	163.199	163.159	162.659	162.790
0.219	162.419	n/a	163.160	162.530	162.786
0.300	162.324	162.016	163.153	162.233	162.780
0.440	n/a	160.602	n/a	161.872	162.673
Concentration (molality)					
α (mol CO_2 /mol alka.)	$[\text{2MPZCOO}^-]/[\text{H2MPZCOO}]$	$[\text{OC2MPZ}]/[\text{OOC2MPZH}]$	$[\text{2MPZ(COO}^-)_2]$	$[\text{PZCOO}^-]/[\text{HPZCOO}]$	$[\text{PZ(COO}^-)_2]$
0.000	0.0000	0.0000	0.0000	0.0000	0.0000
0.143	0.9093	0.1086	0.0000	1.4014	0.1278
0.219	1.7259	n/a	0.0348	2.2651	0.5297
0.300	n/a	0.5015	0.0917	n/a	0.8110
0.440	n/a	1.7180	n/a	n/a	n/a

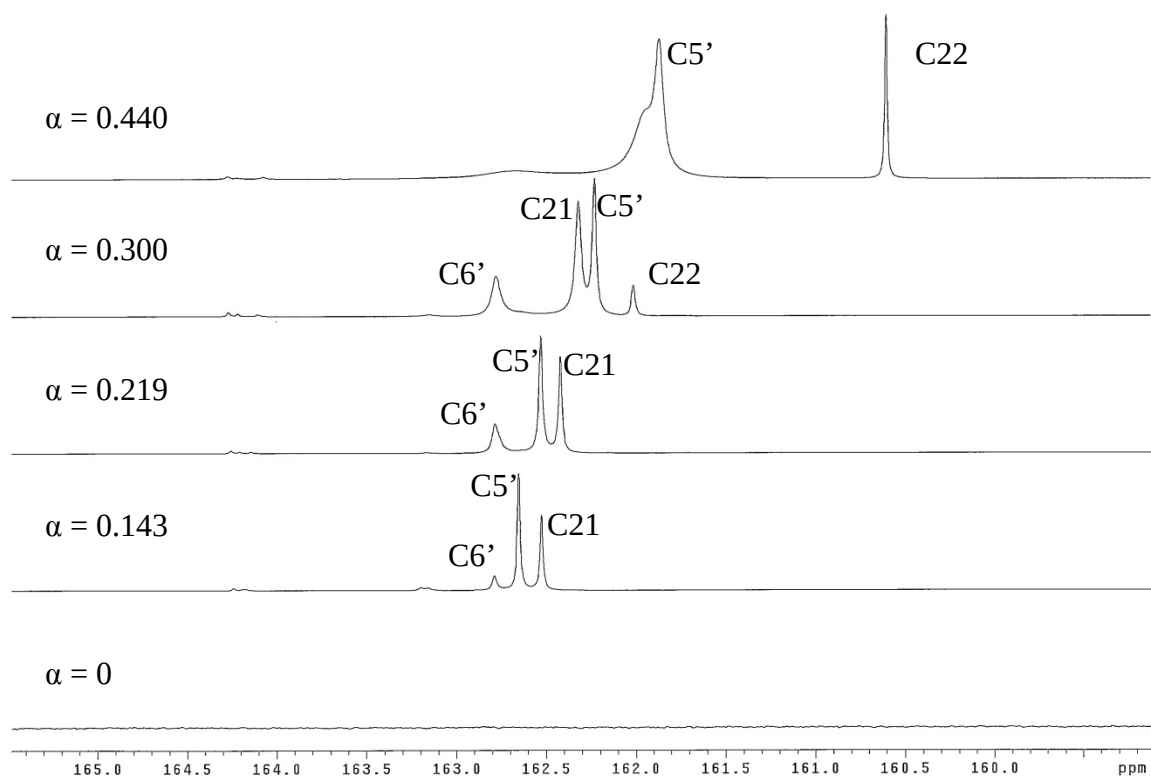


Figure 5: ^{13}C NMR Spectra (downfield) for 4 m 2MPZ/4 m PZ at 40 °C

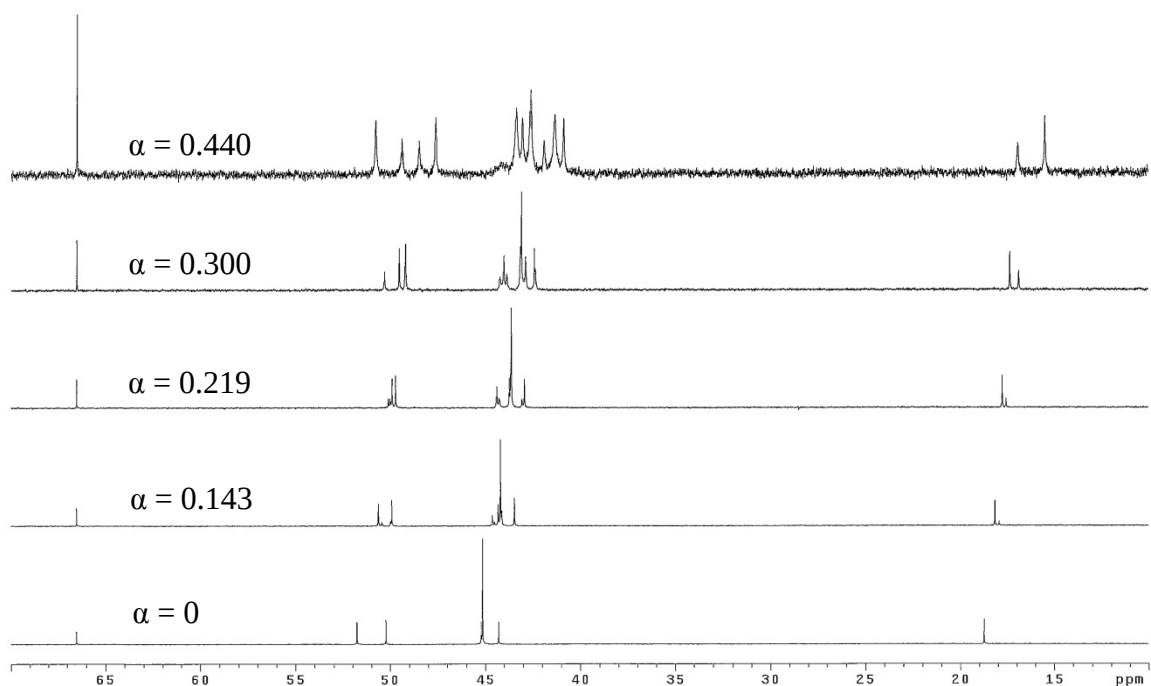


Figure 6: ^{13}C NMR Spectra (upfield) for 4 m 2MPZ/4 m PZ at 40 °C

The peak for bicarbonate or carbonate was not found on all the spectra. It is possible that they are buried underneath other large peaks. As a consequence, the concentration given in Table 2

could be the sum of two or more species. However, the unseen peaks probably exist in a very small amount and should not significantly affect the quantification of the observed species.

In principle, ^{13}C NMR spectra in upfield can be also used for quantification. However, it was found that the results of quantification from peaks in upfield are consistently less than those from the downfield peaks. Carbonyl peaks in downfield with enriched $^{13}\text{CO}_2$ are more sensitive than upfield peaks with natural carbon. Therefore only carbonyl peaks are used for quantification in this study.

The ^1H spectrum for $\alpha = 0.143$ (Figure 7) shows that the introduction of carbamate species greatly complicates the interpretation as well as the quantification of peaks. As CO_2 loading increases, the peaks overlap even more. This limits the usefulness of the ^1H spectrum in quantification.

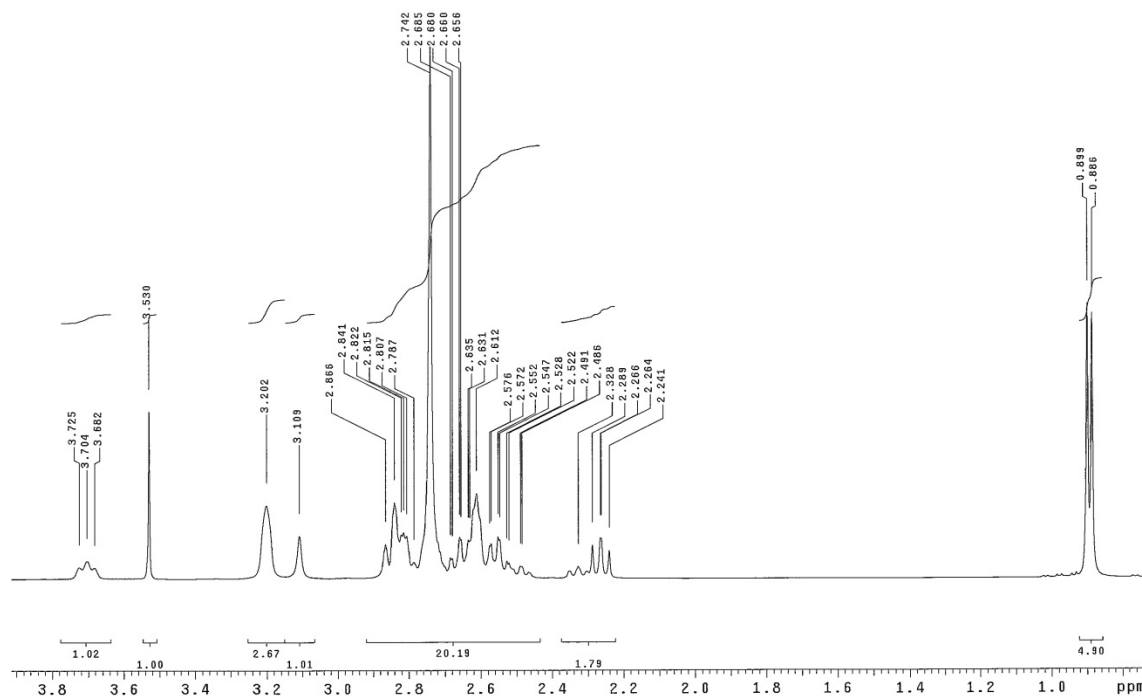


Figure 7: ^1H NMR spectrum for 4 m 2MPZ/4 m PZ at $\alpha = 0.143$ and $40\text{ }^\circ\text{C}$

Comparison of NMR data and model prediction

NMR data shows that $\text{PZCOO}^-/\text{HPZCOO}^-$ exists in a greater amount than $2\text{MPZCOO}^-/\text{H}2\text{MPZCOO}^-$ starting at lean loading. There is also a substantial amount of $\text{PZ}(\text{COO}^-)_2$. This indicates that the amino groups on PZ have a greater tendency to react with CO_2 than the unhindered amino group on 2MPZ. This conclusion is the opposite of the model prediction shown on the last quarterly report (Figure 8). The model predicts that the majority of CO_2 reacts with 2MPZ and forms 2MPZCOO^- at lean loading range. The large discrepancy between the data and the model for 2MPZ/PZ is due to the independent regression of 2MPZ and PZ data. Parameters for the PZ and 2MPZ models have to be reviewed and adjusted to fit the NMR data. Additional parameters may need to be included to account for VLE and speciation data.

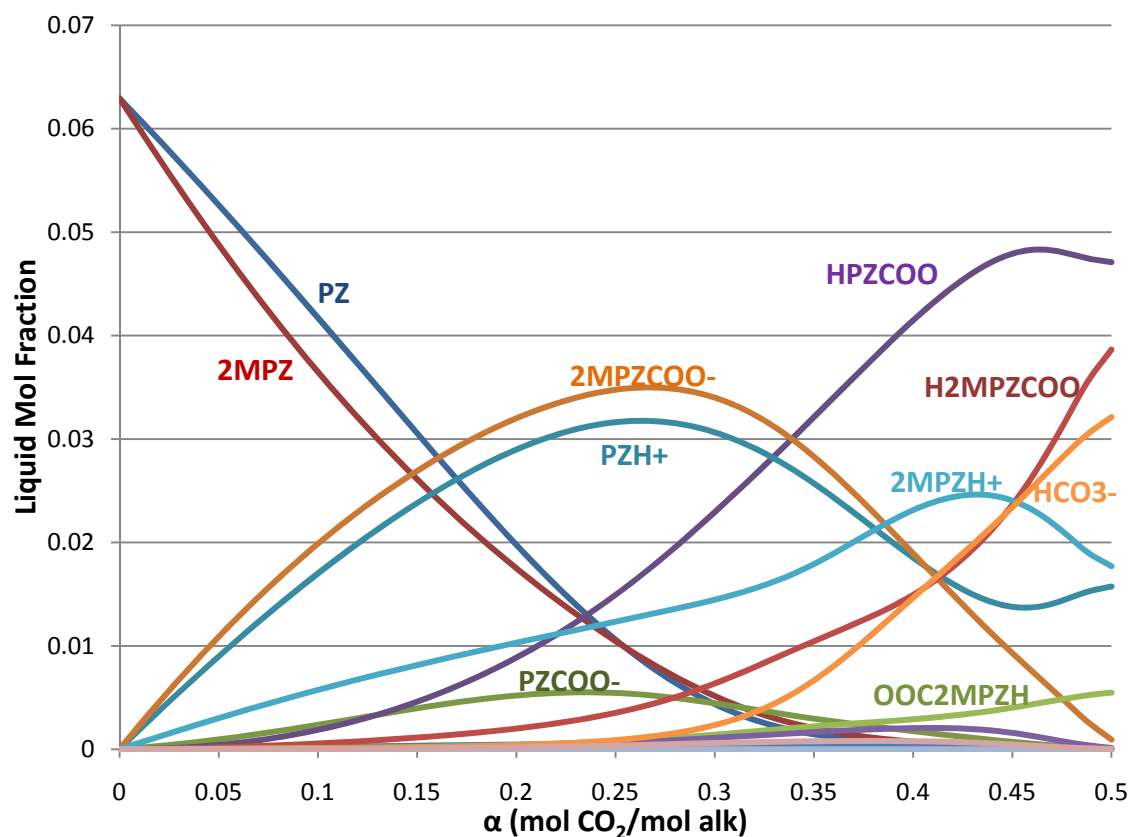


Figure 8: Speciation prediction for 4/4 m 2MPZ/PZ at 40 °C

Conclusions

Quantitative ¹H and ¹³C NMR spectra for 4 m 2MPZ/4 m PZ at CO₂ loadings of 0 to 0.44 mol/mol alkalinity shows that PZ monocarbamate and unhindered 2MPZ monocarbamate are the main reaction products. The former accounts for more than 50% of CO₂ in the solution, which is roughly 20% to 50% more than total unhindered 2MPZ carbamate. The amount of PZ dicarbamate and hindered 2MPZ carbamate increases with loading and reaches 11% and 7% of the total carbamate at loading of 0.3 mol/mol alkalinity. Quantification of each species at each loading is not feasible due to peak overlap. The current 2MPZ/PZ model cannot properly represent the speciation data and needs to be modified.

Future work

The 2MPZ and 2MPZ/PZ models will be modified to match the speciation data. Kinetic models of absorption/desorption rates in 2MPZ solution are also under development with Aspen Plus[®].

Appendix

C¹³ spectrum at 40 °C (downfield)

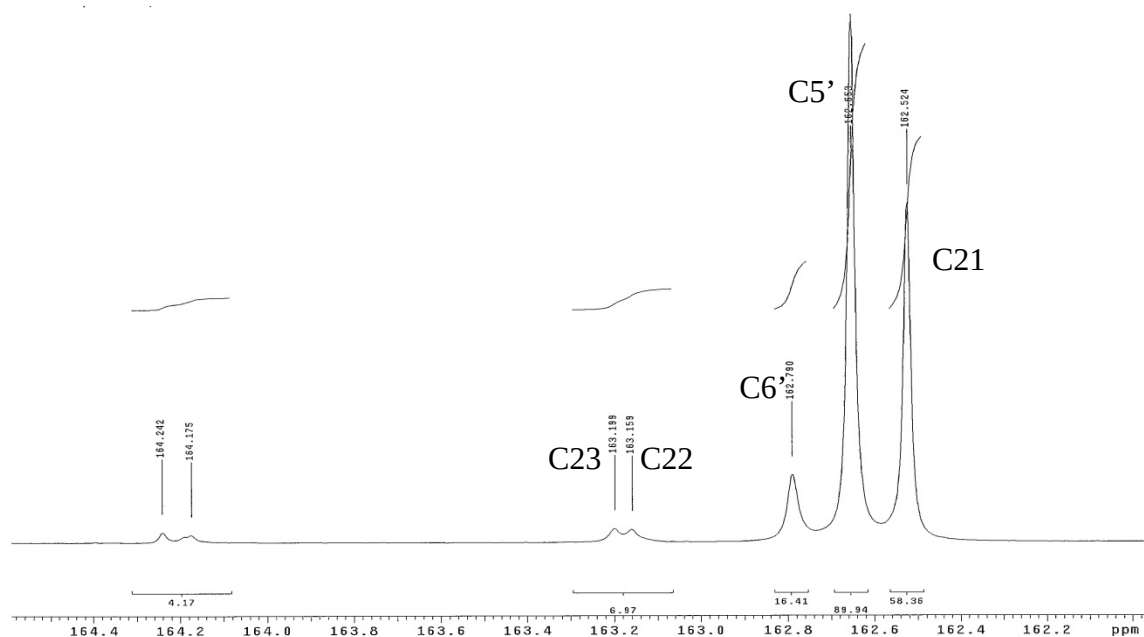


Figure 9: ¹³C NMR Spectrum (downfield) for 4 m 2MPZ/4 m PZ at 40 °C and α = 0.143

XC-2MPZ-PZ-0.2-LDG
temp=40c
Pulse Sequence: s2pu1

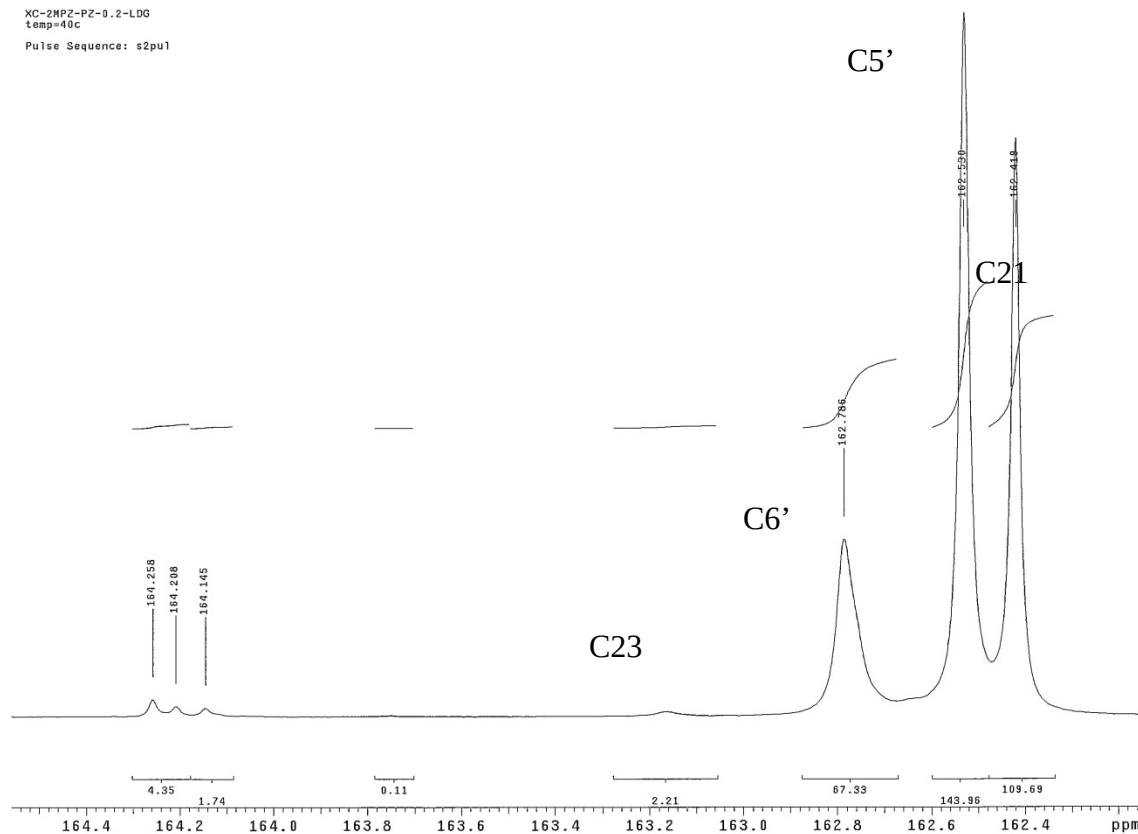


Figure 10: ^{13}C NMR Spectrum (downfield) for 4 m 2MPZ/4 m PZ at 40 °C and $\alpha = 0.219$

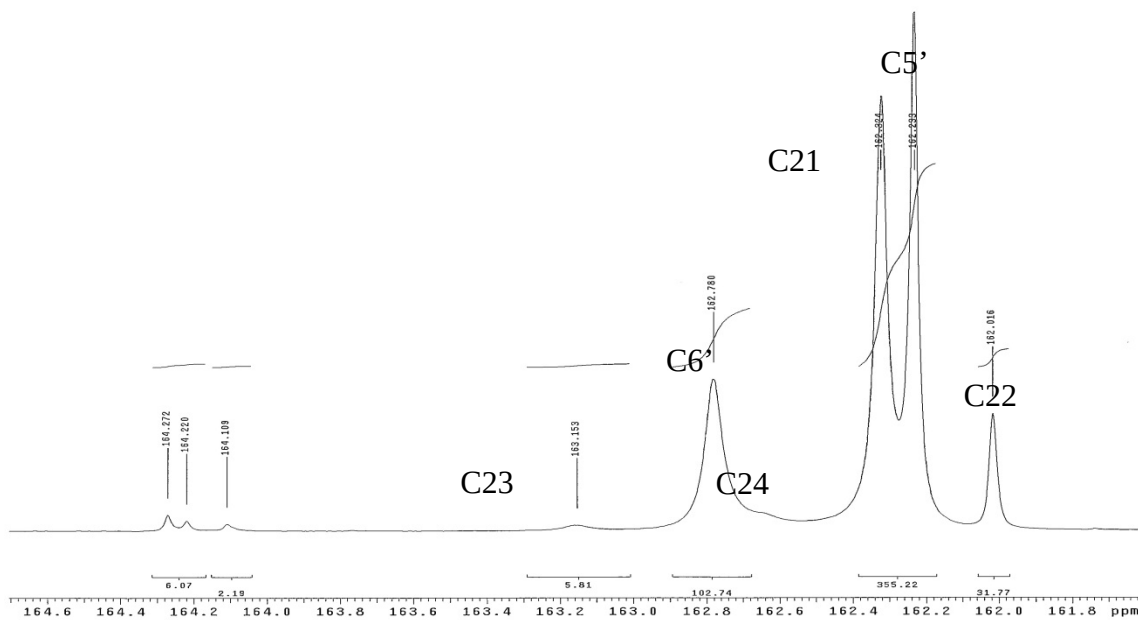


Figure 11: ^{13}C NMR Spectrum (downfield) for 4 m 2MPZ/4 m PZ at 40 °C and $\alpha = 0.300$

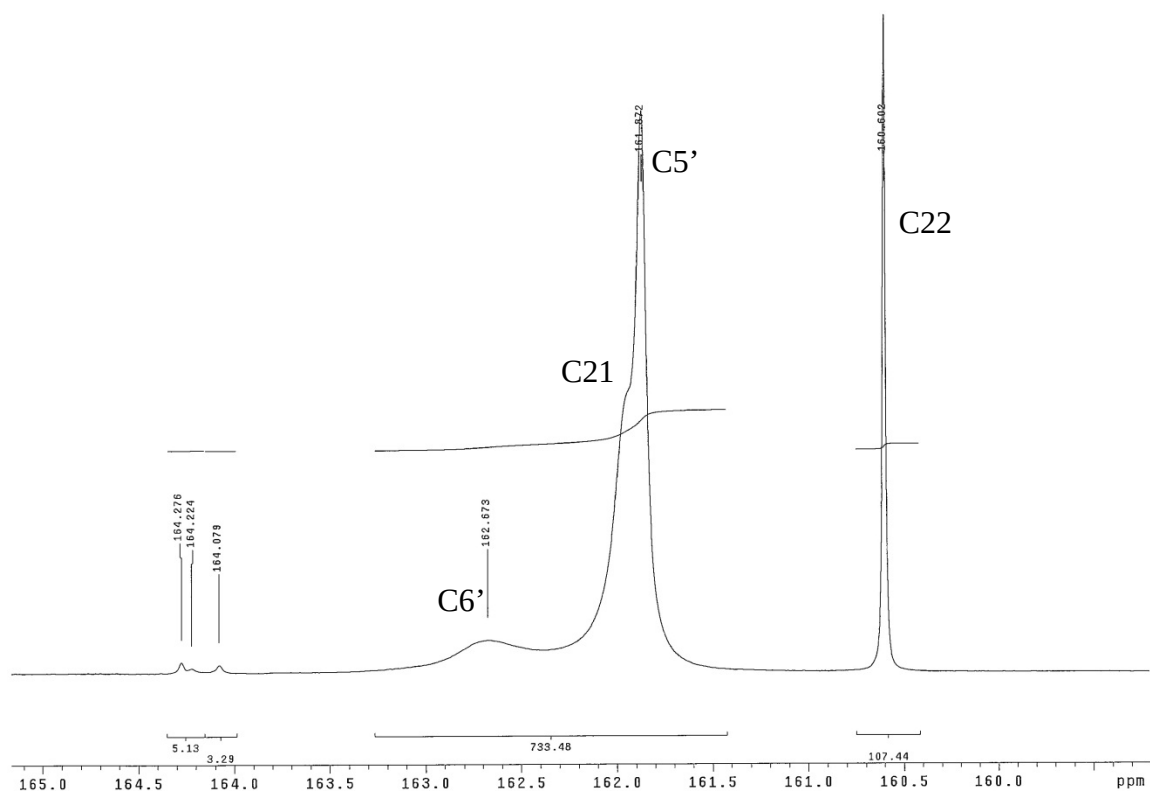


Figure 12: ^{13}C NMR Spectrum (downfield) for 4 m 2MPZ/4 m PZ at 40 °C and $\alpha = 0.440$
 C^{13} spectrum at 40 °C (upfield)

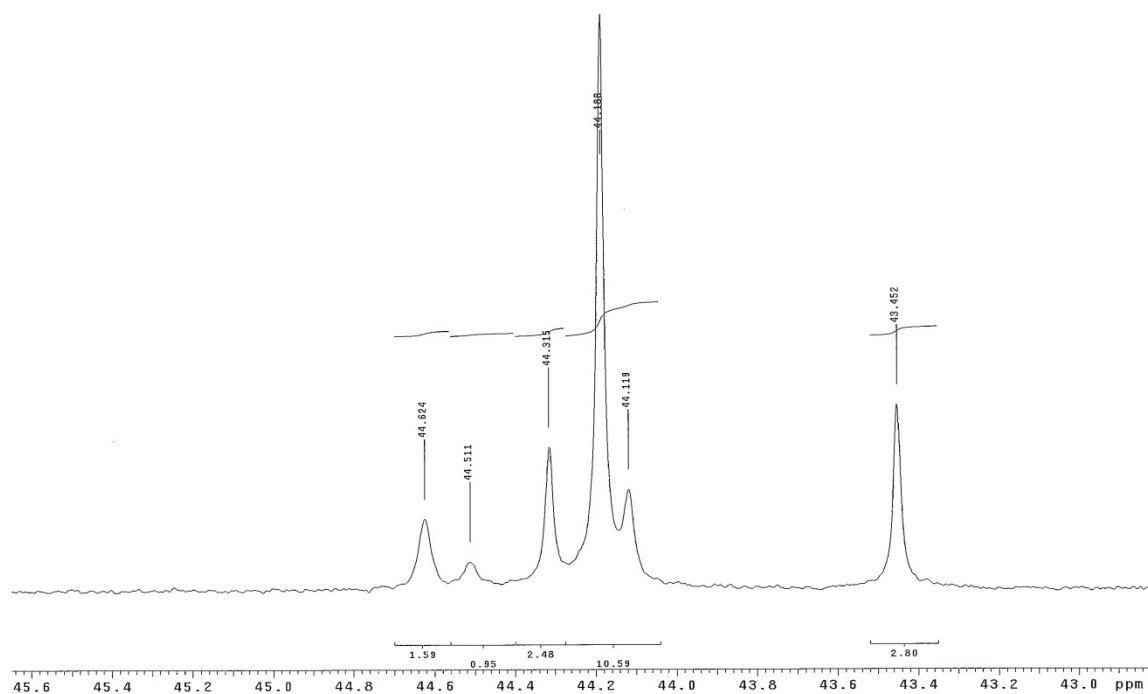


Figure 13: ^{13}C NMR Spectrum for 4 m 2MPZ/4 m PZ at $\alpha = 0.143$ and 40 °C, $\delta = 40-45$

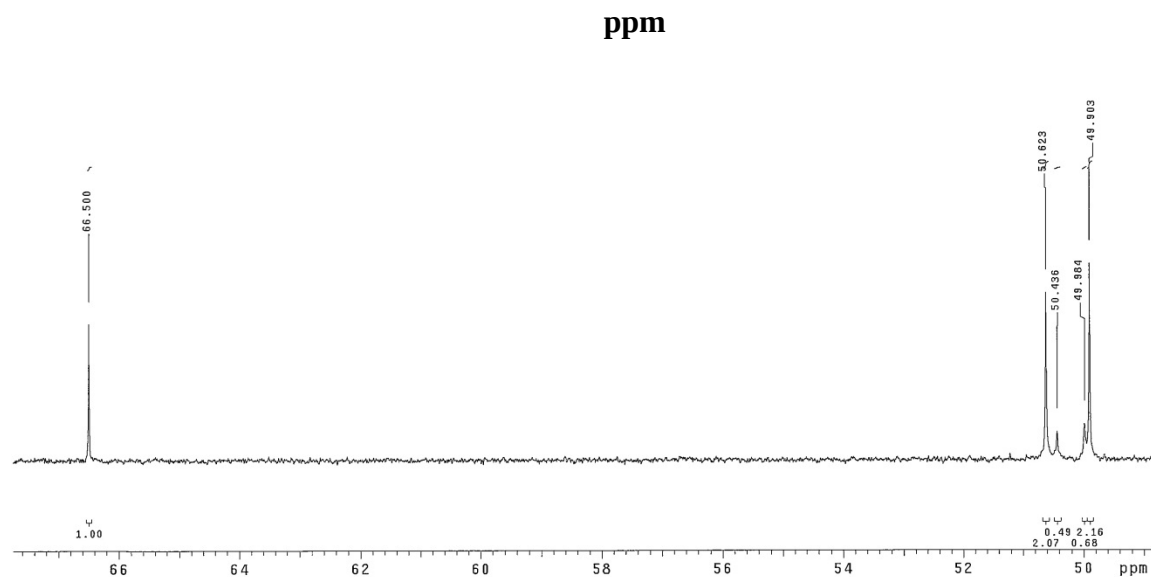


Figure 14: ^{13}C NMR Spectrum for 4 m 2MPZ/4 m PZ at $\alpha = 0.143$ and 40°C , $\delta = 50\text{--}67$ ppm

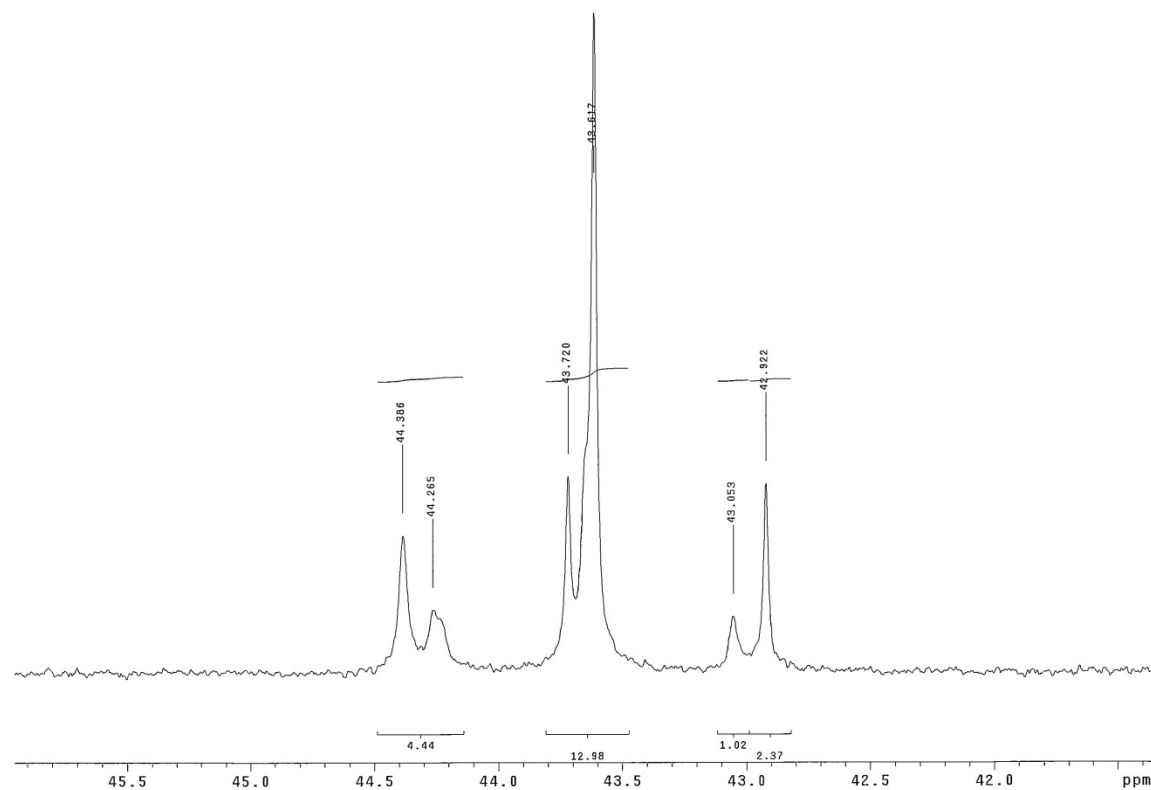


Figure 15: ^{13}C NMR Spectrum for 4 m 2MPZ/4 m PZ at $\alpha = 0.219$ and 40°C , $\delta = 40\text{--}45$ ppm

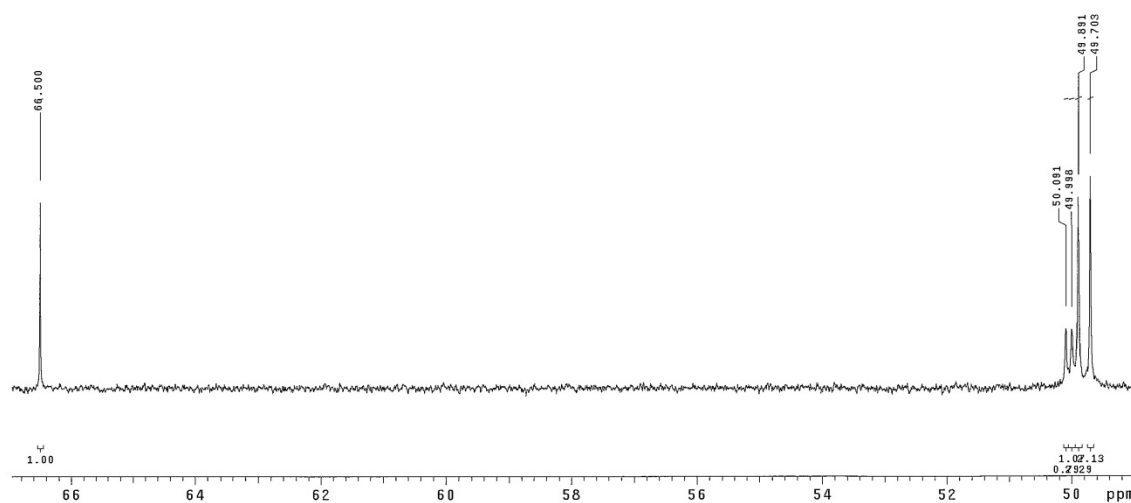


Figure 16: ^{13}C NMR Spectrum for 4 m 2MPZ/4 m PZ at $\alpha = 0.219$ and 40°C , $\delta = 50\text{--}67$ ppm

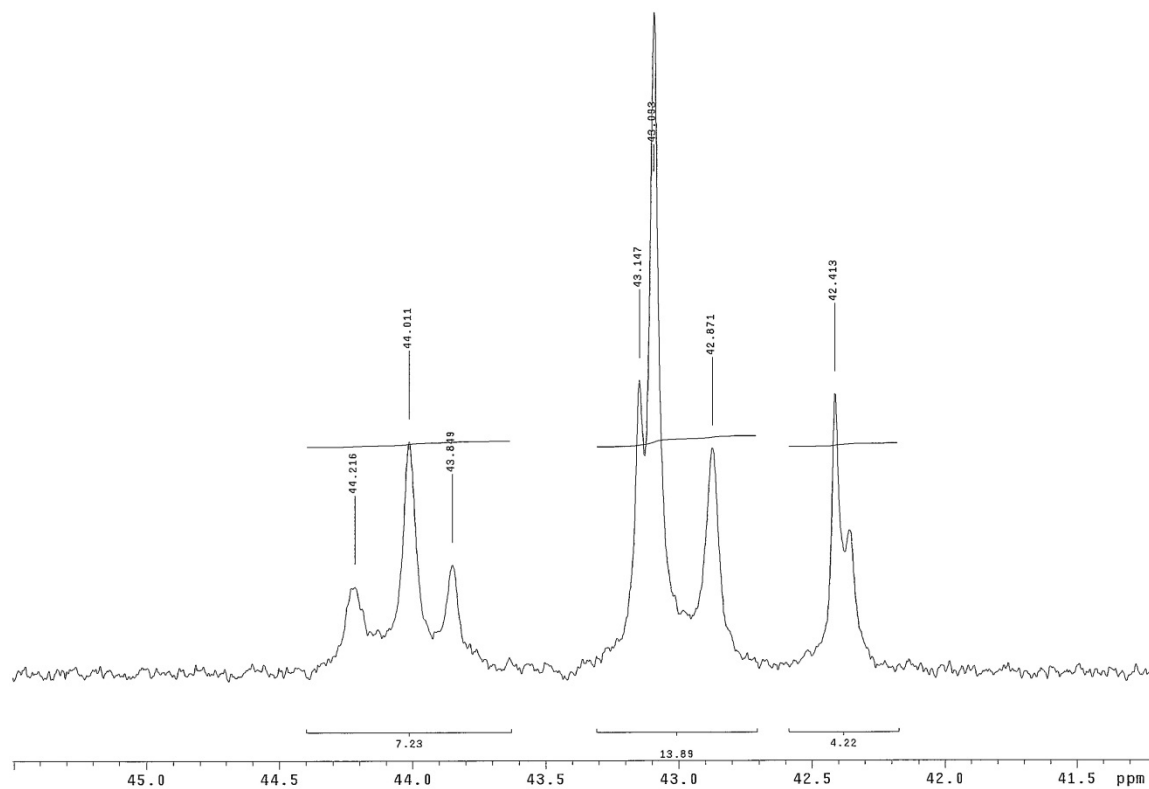


Figure 17: ^{13}C NMR Spectrum for 4 m 2MPZ/4 m PZ at $\alpha = 0.300$ and 40°C , $\delta = 40\text{--}45$ ppm

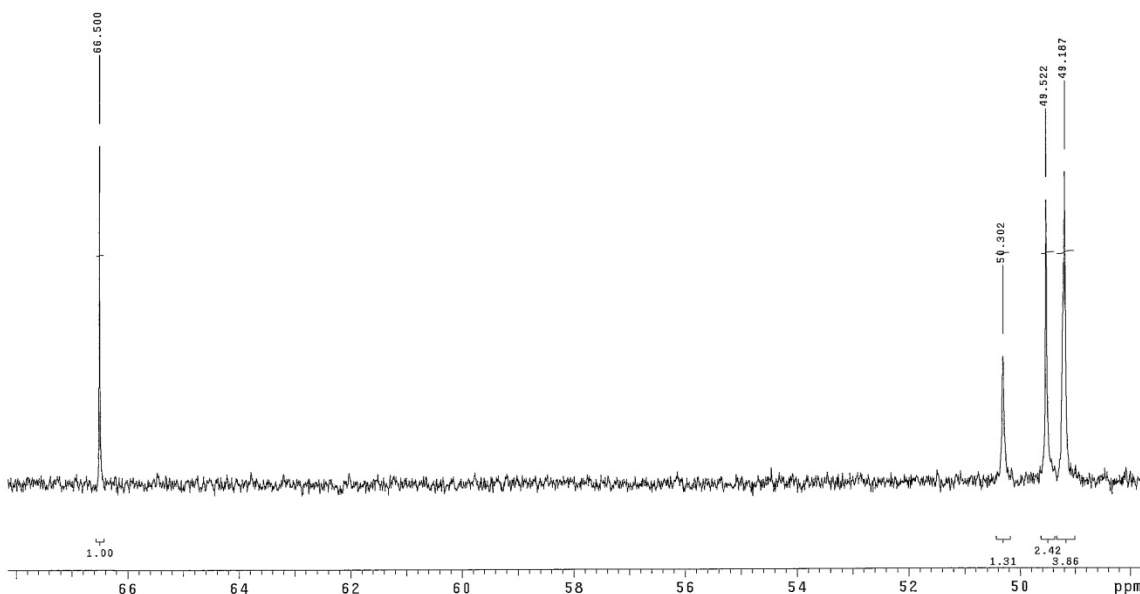


Figure 18: ^{13}C NMR Spectrum for 4 m 2MPZ/4 m PZ at $\alpha = 0.300$ and 40°C , $\delta = 50\text{--}67$ ppm

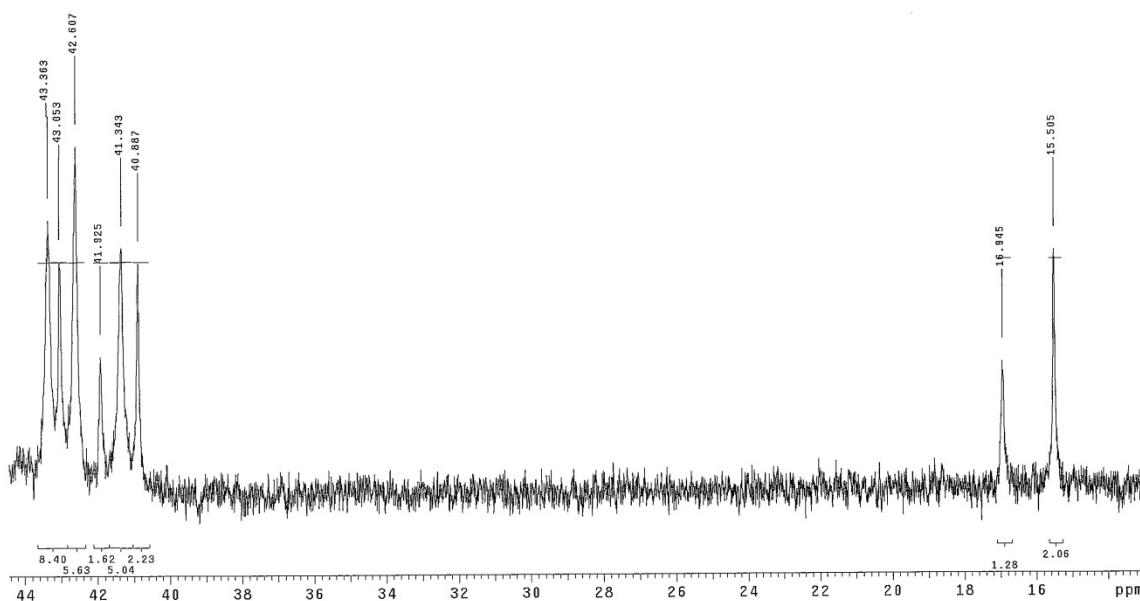


Figure 19: ^{13}C NMR Spectrum for 4 m 2MPZ/4 m PZ at $\alpha = 0.440$ and 40°C , $\delta = 15\text{--}45$ ppm

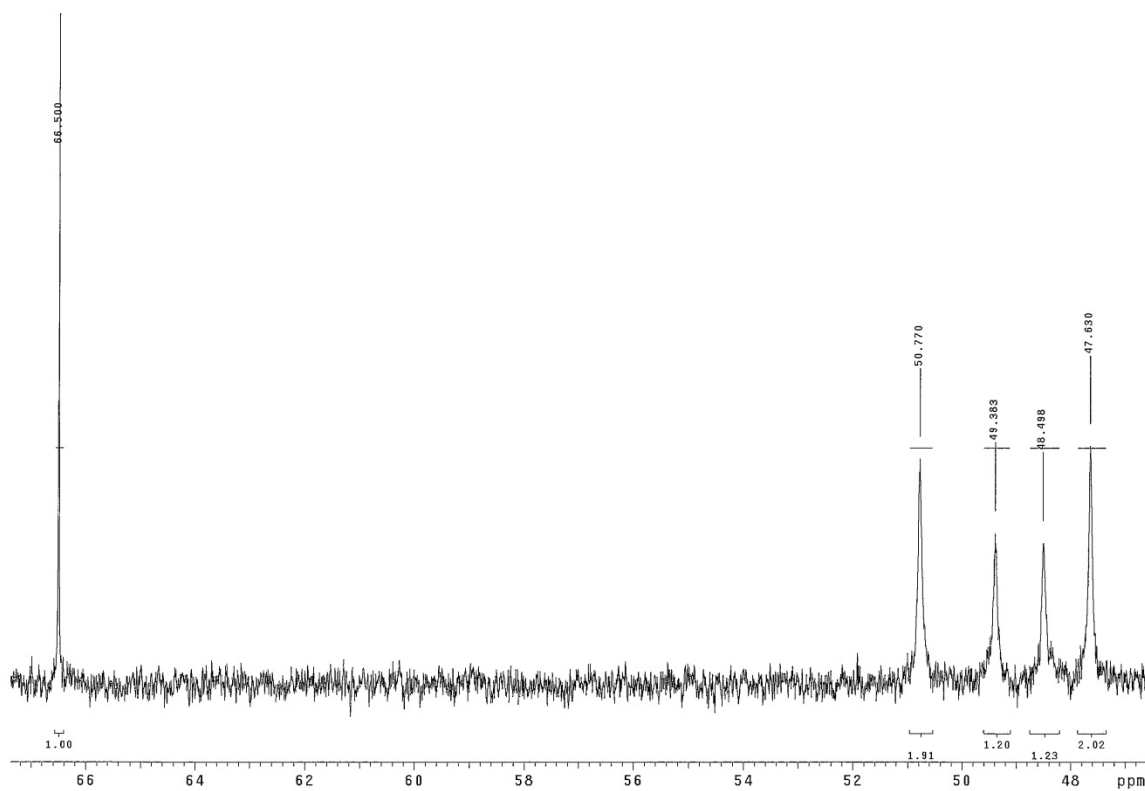


Figure 20: ^{13}C NMR Spectrum for 4 m 2MPZ/4 m PZ at $\alpha = 0.440$ and 40°C , $\delta = 47\text{--}67$ ppm

Solvent Screening Using the Wetted Wall Column

Quarterly Report for January 1 – March 31, 2011

by Le Li

Supported by the Luminant Carbon Management Program

and the

Industrial Associates Program for CO₂ Capture by Aqueous Absorption

Department of Chemical Engineering

The University of Texas at Austin

April 15, 2011

Abstract

The CO₂ absorption performance for 4.5 m SarNa and a blend of 2 m amine X/6 m PZ was tested using the wetted wall column. 4.5 m SarNa is the first sodium neutralized amino acid solvent tested in the group and was chosen due to the attractive results of 6 m SarK. The sodium-based sarcosine solvent is less soluble than the potassium form. The capacity of 4.5 m SarNa is less than 6 m SarK due to the lower solvent concentration. The CO₂ solubility of sarcosine does not change with the choice of neutralizing base, and is also independent of solvent concentration. The absorption rate of 4.5 m SarNa is lower than 6 m SarK at high loading, but is competitive with 7 m MEA and faster than other amino acid solvents. The heat of absorption for 4.5 m SarNa is lower than 7 m MEA by approximately 40%. The blend of 2 m amine X/6 m PZ aimed to combine the expected high heat of absorption and thermal stability of amine X with the fast rate and high capacity of piperazine (PZ). However, measured rate and CO₂ solubility results show this blend to have performance similar to 7 m MEA and 8 m PZ. The absorption rate and capacity of 2 m amine X/6 m PZ were much lower than 8 m PZ, while the heat of absorption of the blend is higher than 8 m PZ. The wetted wall column was used to obtain rate and $P_{CO_2}^*$ measurements at 30 °C, beyond the temperature range of previous experiments. The absorption rates of 7 m MDEA/2 m PZ was tested and shown to be similar to rates at 40 °C and 60 °C. The apparatus is shown to be stable at 30 °C.

Introduction

Two solvents were tested using the wetted wall column during this quarter: 4.5 m SarNa and 2 m amine X/6 m PZ. Previous studies on amino acid solvents have used potassium (K⁺) as the neutralizing salt. Using a different base will change the ionic interactions of the species in solution, which can alter the absorption rate, amino acid solubility, viscosity, and other physical properties of the solvent. Sodium (Na⁺) is cheap, available, and environmentally benign, which makes it a good alternative to potassium. Also, sodium has a lower molecular weight (22.9 g/mol) than potassium (39.53 g/mol), which will result in higher capacities at the same solvent concentration. 6 m SarK was tested in the wetted wall column previously, and has high

absorption rates compared to other amino acid solvents (Rochelle, 2010). A solvent using sarcosine and sodium was expected to maintain its good rate performance (Figure 1).

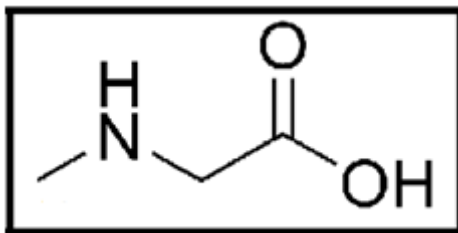


Figure 1: Molecular Structure of Sarcosine

The blend of 2 m amine X/6 m PZ was tested. The blend potentially could combine the high heat of absorption of amine X with the fast rate and high capacity of piperazine (PZ). Absorption rates were measured using the WWC at 30 °C for 7 m MDEA/2 m PZ. Typically, the WWC operates between the temperature ranges of 40 °C and 100 °C. However, rate measurements at lower temperatures are valuable for absorber design and operation in cold regions. Equilibrium partial pressure measurements in the lower temperature range can confirm the temperature dependence of solvent CO₂ solubility. Also, at low temperature the wetted wall column can be used to test rich solvent conditions.

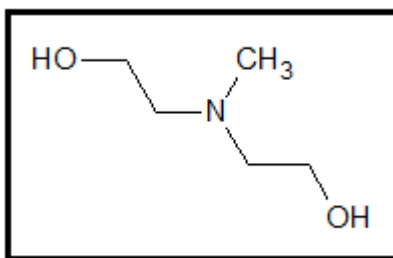


Figure 2: Molecular Structure of Methyldiethanolamine (MDEA)

Experimental Methods

The absorption rate measurements and CO₂ solubility data were obtained using the wetted wall column. The method is identical to that used by Chen (2010).

Materials

Table 1: Chemical Species in 4.5 m SarNa Initial Solution

Chemical Species	Mass (g)	Wt %
Sarcosine	607.5	0.269
Sodium Hydroxide	270.2	0.120
Water	1378.8	0.611
SarNa (salt)	762.9	0.338

Table 2: Chemical Species in 2 m amine X/6 m PZ

Chemical Species	Mass (g)	Wt %
Piperazine	568.6	0.295
Amine X	255.8	0.133
Water	1101.5	0.572

Table 3: Chemical Species in 7 m MDEA/2 m PZ Initial Solution

Chemical Species	Mass (g)	Wt %
Piperazine	137.8	0.086
Methyldiethanolamine	667.5	0.416
Water	800.1	0.498

Table 4: Materials Used for Solvents Preparation

Chemical	Purity	Source
Sarcosine	98.00%	Acros Organics
Sodium Hydroxide (liquid)	40%	Fisher Chemical
Piperazine	98%	Sigma-Aldridge
Methyldiethanolamine	98.5%	Huntsman
DDI Water	100.00%	Millipore, Direct-Q

The 4.5 m SarNa solution was prepared by mixing equimolar amount of sarcosine with sodium hydroxide in water. The chemical species present in each of the three solutions tested are listed in Tables 1–3. The chemicals used to prepare the solutions are listed in Table 4. CO₂ is loaded into the solutions by bubbling gaseous CO₂ (99.99%, Matheson Tri-Gas) into the solvents.

Results and Discussion

Solvent Solubility Observations

SarNa solvents are less soluble in than SarK solvents at a CO₂ loading of 0.5 mol CO₂/mol alk. SarK is soluble at 6.5 m, where SarNa is only soluble up to 4.5 m at 0.5 loading. The highest loading tested for 4.5 m SarK in the WWC was 0.514 mol CO₂/mol alk, which corresponds to P_{CO₂*} of 1.25 kPa. A rich loading (P_{CO₂*} = 5 kPa) was not reached since the solvent precipitated at 0.57 loading.

Absorption/Desorption Rates

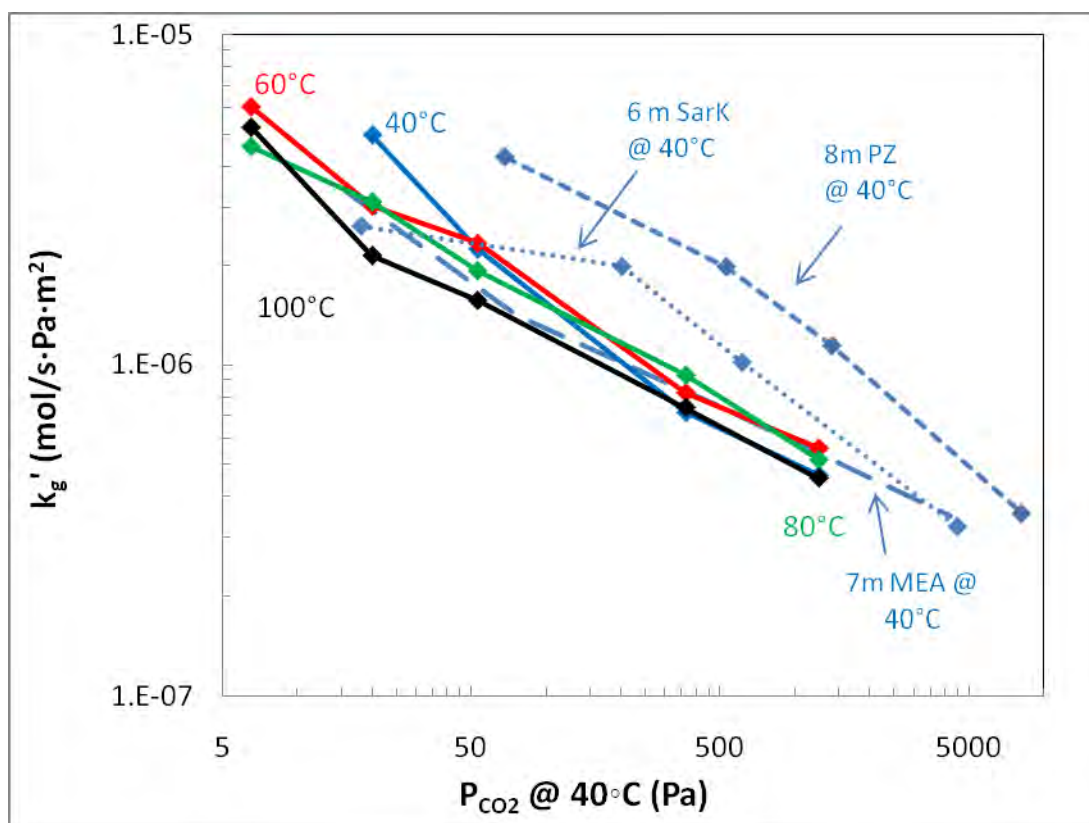


Figure 3: CO₂ Liquid Phase Mass Transfer Coefficient (k_g') in 4.5 m SarNa

Liquid phase mass transfer coefficient (k_g') for 4.5 m SarNa was measured at five lean loadings and four temperatures and compared against 7 m MEA, 8 m PZ, 6 m SarNa at 40 °C (Figure 3). The absorption rate at 40 °C for 4.5 m SarNa is lower than 8 m PZ. 4.5 m SarNa is faster than 7 m MEA at two lower loadings and about the same rate as 7 m MEA at the three higher loadings. Compared to 6 m SarK, 4.5 m SarNa has similar rates at low loadings, but lower rates at high loadings. At low loadings, the absorption rate of 4.5 m SarNa is higher at 40 °C. At the higher loadings, k_g' values changed little at the four different temperature conditions. An average k_g' can be calculated at optimized absorber conditions using this equation:

$$k_{g' \text{ avg}} = \frac{Flux_{CO_2, LM}}{(P_{CO_2, gas} - P_{CO_2}^*)_{LM}} = \frac{(Flux_{CO_2, top} - Flux_{CO_2, bottom}) / \ln(Flux_{CO_2, top} / Flux_{CO_2, bottom})}{[(P_{CO_2, top} - P_{CO_2, lean}^*) - (P_{CO_2, bottom} - P_{CO_2, rich}^*)] / \ln\left(\frac{P_{CO_2, top} - P_{CO_2, lean}^*}{P_{CO_2, bottom} - P_{CO_2, rich}^*}\right)} \quad (1)$$

An average is calculated using coal flue gas conditions and natural gas for the sarcosine solvents and compared to 7 m MEA (Table 5). 4.5 m SarNa has the same absorption rates as 7 m MEA at both coal and gas conditions. However, this solvent precipitates at rich loadings for coal and the $k_{g' \text{ avg}}$ value is a theoretical prediction only. The absorption rate of 6 m SarK in an optimized absorber is higher than 4.5 m SarNa and 7 m MEA at both conditions with no precipitation observed.

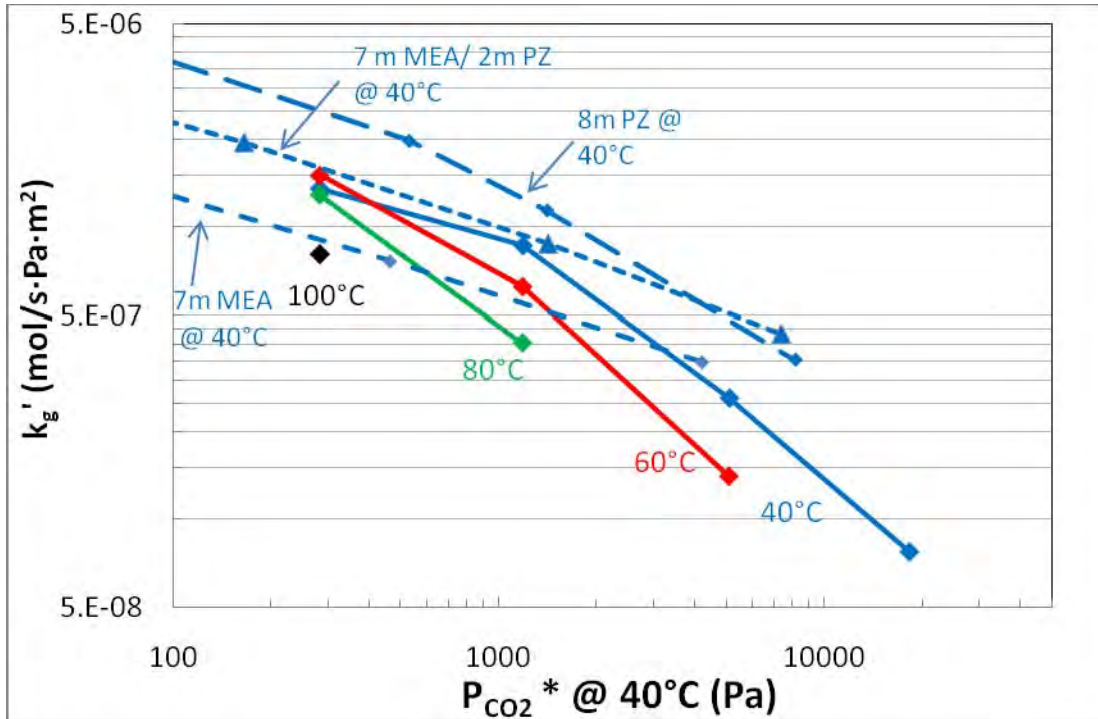


Figure 4: CO₂ Liquid Phase Mass Transfer Coefficient (k_g') in 2 m amine X/6 m PZ

The absorption rates of 2 m X/6 m PZ were measured at four loadings across the lean and rich loading range. The measured k_g' results are compared against 40 °C results of 7 m MEA, 8 m PZ, and the blend of 7 m MEA/2 m PZ (Figure 4). The absorption rate of the blend decreased quickly with increasing $P_{CO_2}^*$. At the low loading condition, the rate of the blend was not affected by temperature from 40 °C to 80 °C, but decreased significantly at 100 °C. At the higher loadings, the absorption rate decreased consistently with increase in temperature. The rate of the blend is slower than 8 m PZ across the loading range. Compared to 7 m MEA, the blend is faster at lean loadings but slower at rich loadings. The amine X/PZ blend has similar rates to 7 m MEA/2 m PZ at two low loadings, but the rate of X/PZ decreased at a faster rate than MEA/PZ and is much slower at rich loadings. The $k_{g' \text{ avg}}$ value calculated for X/PZ using Equation 1 is compared to the values for MEA/PZ, 7 m MEA, and 8 m PZ (Table 6). At coal flue gas conditions, the rates for X/PZ is slightly higher than 7 m MEA, but much slower than 8 m PZ and MEA/PZ.

The k_g' of 7 m MDEA/2 m PZ was measured at 30 °C and compared with results at 40 °C, 60 °C, 80 °C, and 100 °C (Figure 5). Five CO₂ loadings across the lean and rich loading range were tested. The absorption rate of this blend at 30 °C is about the same as its rate at 40 °C and 60 °C when compared at the same $P_{CO_2}^*$ (40 °C).

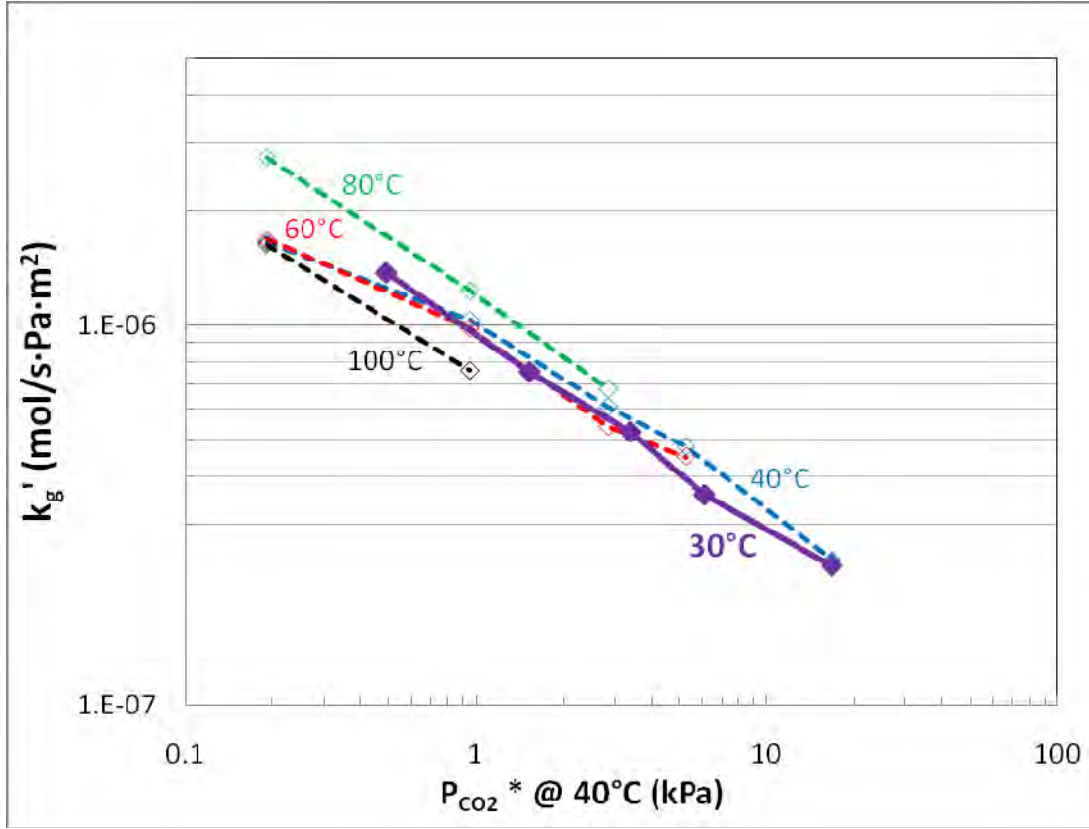


Figure 5: CO₂ Liquid Phase Mass Transfer Coefficient (k_g') in 7 m MDEA/2 m PZ at 30 °C

CO₂ Solubility

A semi-empirical thermodynamic model is generated for each solvent by fitting the experimental CO₂ solubility data to Equation 1, which relates $P_{CO_2}^*$ to temperature and CO₂ loading:

$$\ln(P) = a + b/T + c \cdot \alpha + d \cdot \alpha/T + e \cdot \alpha^2 \quad (2)$$

This thermodynamic model is used to calculate the CO₂ capacity and heat of absorption for each solvent. The capacity is calculated using the rich and lean loadings of a solvent, which corresponds to $P_{CO_2}^*$ (40 °C) at 0.5 and 5 kPa for coal flue gas, and 0.1 and 1 kPa for gas:

$$Capacity = mol\ CO_2 / kg\ solvent = \frac{(\alpha_{rich} - \alpha_{lean}) \cdot mol\ alkalinity}{kg\ solvent} \quad (3)$$

Solubility curves with small slopes will result in a large difference between rich and lean loading, and large capacity for the solvent. A high solvent concentration also increases the capacity of the solvent. The heat of absorption of a solvent is calculated by applying the Gibbs-Helmholtz equation to its thermodynamic model (Equation 2):

$$\Delta H_{Abs} = -R \frac{d \ln P}{d(1/T)} = -R(b + d \cdot \alpha) \quad (4)$$

The final expression relates the heat of absorption of the solvent to its CO₂ loading only and independent of temperature.

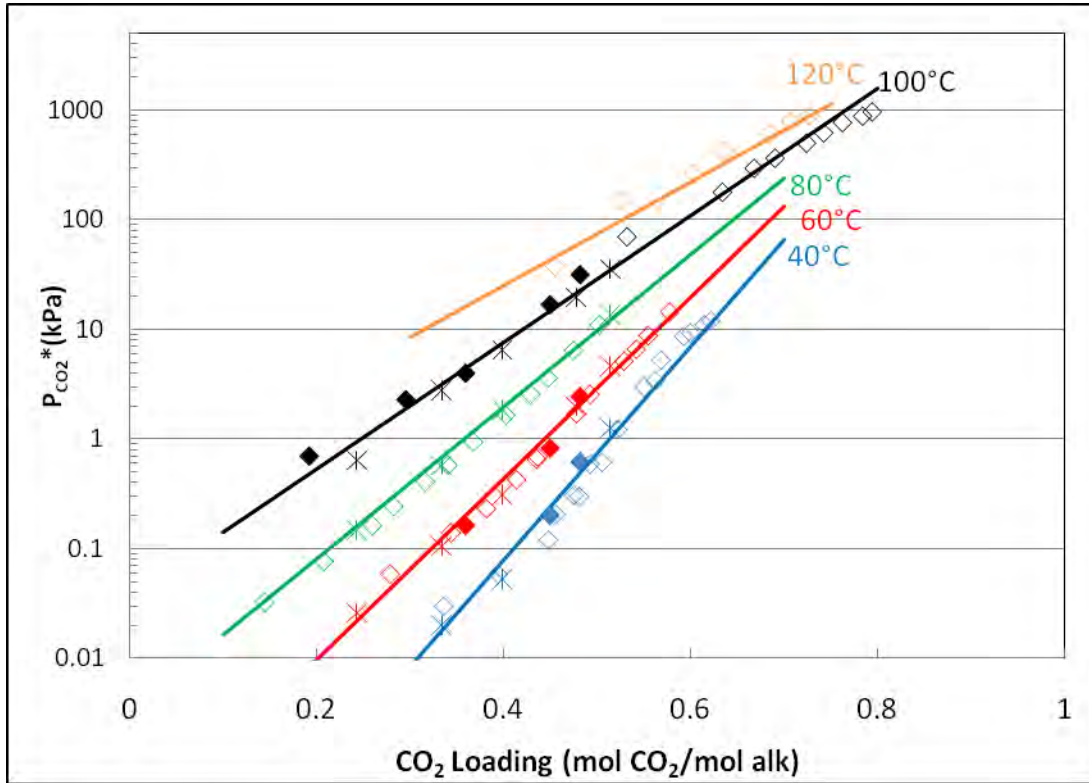


Figure 6: CO₂ Solubility for Sarcosine [Empty points: 3 M SarK (Aronu, 2011). Filled points: 6 m SarK (Rochelle, 2010). Asterisk: 4.5 m SarNa. Lines: model (Eq. 2)]

The measured equilibrium partial pressure of CO₂ for 4.5 m SarNa is compared against the equilibrium results of two SarK solvents (Figure 6). CO₂ solubility in SarNa is the same as the SarK solvents as the three data sets follow the same trend. Thus, for sarcosine solvents, the choice of base does not affect the thermodynamic equilibrium of CO₂. One thermodynamic model was regressed to fits all three sets of experimental data, and the result fits the data relatively well. The thermodynamic model is used to calculate the capacity and heat of absorption for 4.5 m SarNa and 6 m SarK at both coal flue gas condition and natural gas condition, and results are compared to 7 m MEA (Table 5). The capacity of the sarcosine solvents are lower than 7 m MEA at both coal and gas conditions, with 4.5 m SarNa having a lower capacity than 6 m SarK. Even though using Na⁺ as the neutralizing salt decreases the solvent mass per mole of sarcosine in solution, its capacity is still lower than potassium due to the low solvent concentration of SarNa at 4.5 m. The heats of absorption of the two sarcosine solvents are the same, and are both much lower than 7 m MEA.

Table 5: Measured Properties of Sarcosine Solvents

Property	Operation condition	SarNa 4.5 m	SarK 6 m	MEA 7 m (Dugas, 2009)
$k_g'_{avg}$ ($\times 10^7$ mol/s·Pa·m ²)	Coal	4.47	5.01	4.3
	Gas	11.4	18.9	11.7
Capacity (mol CO ₂ /kg solvent)	Coal	0.307	0.348	0.47
	Gas	0.307	0.348	0.55
ΔH_{abs} (kJ/mol)	Coal (@P* _{CO2} =1500)	54.4		82
	Gas (@P* _{CO2} =500)	61.7		83

The $P_{CO_2}^*$ of 2 m amine X/6 m PZ were measured at four loadings and data was fitted using the semi-empirical model (Equation 2). The results are compared with CO₂ solubility of 8 m PZ (Figure 7). The semi-empirical model fits the experimental data well over the loading range of the experiment. The CO₂ solubility of the blend exhibits significantly different behavior than 8 m PZ. The solubility curve of the blend has a much higher slope, which will contribute to a lower capacity. Also, since CO₂ is much more soluble in the blend at lean loadings than 8 m PZ, the operation lean/rich loading of the blend is much richer.

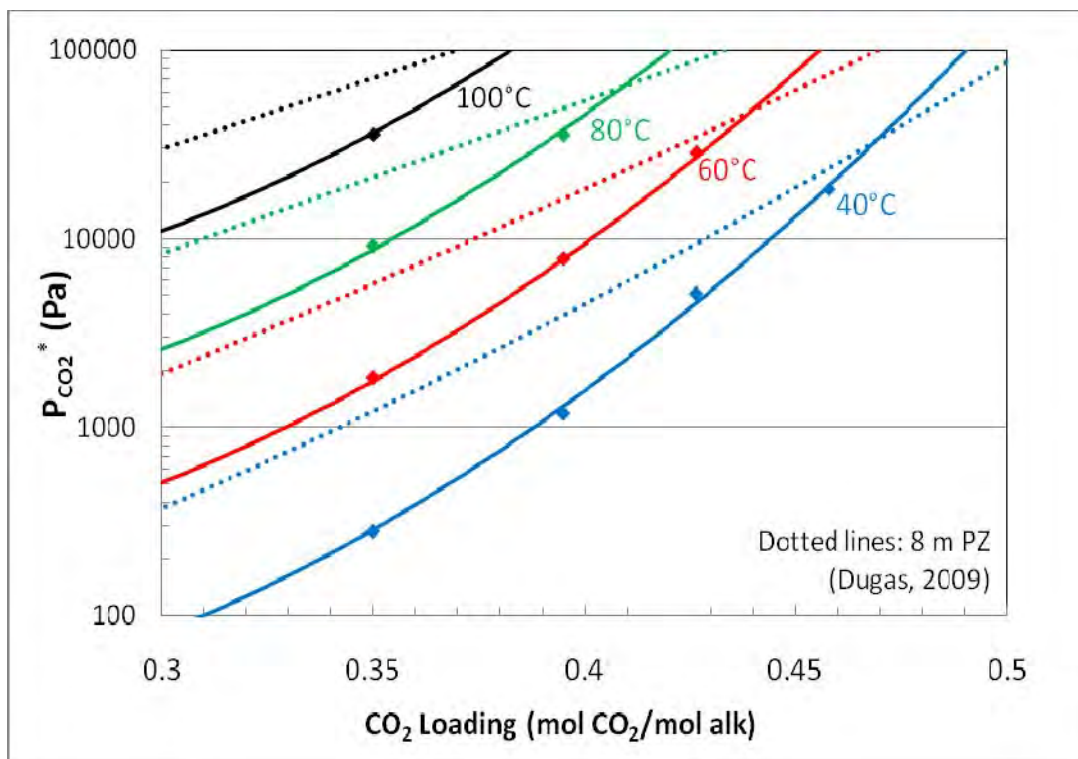


Figure 7: CO₂ Solubility for 2 m X/6 m PZ

The capacity and heat of absorption of the blend were calculated at coal flue gas conditions and compared to 8 m PZ, 7 m MEA/2 m PZ, and 7 m MEA (Table 6). The capacity of the X/PZ blend is slightly higher than 7 m MEA, but lower than 7 m MEA/2 m PZ and much lower than 8

m PZ. The heat of absorption of the blend is much higher than 8 m PZ, but still lower than 7 m MEA and 7 m MEA/2 m PZ. The overall performance of the X/PZ blend in terms of rate, capacity, and heat of absorption is very similar to 7 m MEA, and very different from 8 m PZ. Even though the blend contains almost 30 wt % PZ, the attractive rate and capacity of PZ do not affect the performance of the blend significantly.

Table 6: Measured Properties of 2 m amine X/6 m PZ

Property	2 m X/ 6 m PZ	7 m MEA/ 2 m PZ	8 m PZ	7 m MEA
		(Dugas, 2009)		
$k_g'_{avg}$ ($\times 10^7 \text{ mol/s}\cdot\text{Pa}\cdot\text{m}^2$)	4.88	7.2	8.46	4.3
Capacity (mol CO ₂ /kg solvent)	0.55	0.62	0.79	0.47
ΔH_{abs} (kJ/mol) (@P* _{CO2} =1500)	77.4	79.7	70	82

The measured k_g' values and corresponding P_{CO2}* for the three solvents are listed in Tables 7–9. The detailed wetted wall column results for all experiments are included in the Appendix.

Table 7: CO₂ Solubility and k_g' Measured for 4.5 m SarNa

CO ₂ loading	Temperature	k_g'	P _{CO2} *
mol CO ₂ /mol alk	°C	$\times 10^7 \text{ (mol/s}\cdot\text{Pa}\cdot\text{m}^2)$	(kPa)
0.243	40	/	0.0065
0.333	40	49.75	0.020
0.398	40	22.45	0.053
0.477	40	7.19	0.365
0.514	40	4.64	1.252
0.243	60	60.50	0.026
0.333	60	30.30	0.106
0.398	60	23.33	0.312
0.477	60	8.23	1.977
0.514	60	5.58	4.611
0.243	80	45.87	0.148
0.333	80	31.22	0.577
0.398	80	19.29	1.851
0.477	80	9.31	6.676
0.514	80	5.16	13.66
0.243	100	52.35	0.638
0.333	100	21.40	2.772
0.398	100	15.65	6.496
0.477	100	7.42	19.48
0.514	100	4.53	35.31

Table 8: CO₂ Solubility and k_g' Measured for 2 m amine X/2 m PZ

CO ₂ loading	Temperature	k _g '	P _{CO2} *
mol CO ₂ /mol alk	°C	×10 ⁷ (mol/s·Pa·m ²)	(kPa)
0.35	40	13.60	0.28
0.40	40	8.66	1.19
0.43	40	2.62	5.11
0.46	40	0.78	18.22
0.35	60	15.09	1.82
0.40	60	6.27	7.82
0.43	60	1.41	28.66
0.35	80	12.93	9.18
0.40	80	4.03	35.70
0.35	100	8.09	35.49

Table 9: CO₂ Solubility and k_g' Measured for 7 m MDEA/2 m PZ at 30 °C

CO ₂ loading	Temperature	k _g '	P _{CO2} *
mol CO ₂ /mol alk	°C	×10 ⁷ (mol/s·Pa·m ²)	(kPa)
0.133	30	13.70	0.217
0.195	30	7.53	0.732
0.249	30	5.23	2.175
0.298	30	3.58	4.154
0.356	30	2.33	8.262
0.356	40	2.42	16.712

Conclusions

Sarcosine is less soluble in its sodium salt (4.5 m) form than its potassium salt form (> 6 m). 4.5 m SarNa has the same CO₂ solubility as SarK solvents. The capacity of 4.5 m SarNa is less than 6 m SarK, and is approximately 30–40% less than 7 m MEA. 4.5 m SarNa has low heat of absorption (about 40% less than 7 m MEA), but good absorption rates (about the same as 7 m MEA). The blend of 6 m amine X/2 m PZ has slightly higher capacity and absorption rates than 7 m MEA, but not competitive with 8 m PZ. The heat of absorption for the X/PZ is lower than 7 m MEA, but higher than 8 m PZ. The overall performance of the blend is more similar to 7 m MEA than 8 m PZ in terms of rate, capacity, and heat of absorption. Long chain diamine with primary amine groups shows less attractive CO₂ absorption rates and capacity than mono-primary amines both when used alone in a solvent and in blends. The absorption rate of 7 m MDEA/2 m PZ at 30 °C is the same as at 40 °C and 60 °C. The wetted wall column can operate with stable conditions at 30 °C with the current set up.

Future Work

A sarcosine solvent neutralized using both potassium and sodium will be tested next. Using two different bases could maximize the solvent concentration and thus the capacity of the solvent. A series of enzyme-based rate measurements will test the effect of a carbonic anhydrase enzyme on the absorption rate of several amine solvents. Effort will also be invested in upgrading the wetted wall column apparatus to allow measurements at lower temperatures ranges.

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Appendix

Table A-1: Detailed Wetted Wall Column Data for 4.5 m K

SarNa	CO ₂ Idg	P* _{CO2}	Temp	Pressure	Gas _{Dry}	Gas _{wet}	P _{CO2in, dry}	P _{CO2in, wet}	P _{CO2out, dry}	P _{CO2out, wet}	CO ₂ flux	K _G	k _g	K _G /k _g	k _g '
m	mol CO ₂ /mol alk	Pa	°C	psig	Std L/min	Std L/min	Pa	Pa	Pa	Pa	mol/s cm ²	mol/s Pa cm ²	mol/s Pa cm ²		mol/s Pa cm ²
4.5	0.243	6.5	40	20	5	5.16	0	0	3.83	3.71	-1.545E-09	4.59E-10	4.57E-10	1.00	/
							3.35	3.25	5.02	4.87	-6.758E-10				
							5.50	5.33	6.22	6.03	-2.896E-10				
							12.68	12.29	8.37	8.11	1.738E-09				
							14.59	14.14	9.09	8.81	2.22E-09				
							17.70	17.15	9.57	9.27	3.282E-09				
4.5	0.243	26	60	20	5	5.45	0	0	12.68	11.62	-5.116E-09	2.686E-10	4.83052E-10	0.56	6.05E-10
							7.89	7.24	17.46	16.01	-3.861E-09				
							14.35	13.16	20.57	18.86	-2.51E-09				
							39.23	35.96	33.72	30.91	2.22E-09				
							45.92	42.10	38.75	35.52	2.896E-09				
							52.14	47.80	40.66	37.27	4.634E-09				
4.5	0.243	148	80	40	5	5.72	0	0	79.56	69.56	-2.037E-08	1.889E-10	3.2117E-10	0.59	4.59E-10
							46.00	40.22	104.06	90.99	-1.487E-08				
							87.85	76.81	127.06	111.10	-1.004E-08				
							247.34	216.26	210.39	183.95	9.461E-09				
							291.07	254.50	229.62	200.77	1.574E-08				
							331.04	289.45	255.63	223.51	1.931E-08				
4.5	0.243	637	100	40	5	6.84	0	0	391.37	286.20	-1.002E-07	2.189E-10	3.76225E-10	0.58	5.23E-10
							198.32	145.03	545.20	398.69	-8.881E-08				
							466.02	340.79	635.69	464.86	-4.344E-08				
							1333.21	974.94	1118.30	817.78	5.503E-08				
							1559.43	1140.37	1229.53	899.12	8.447E-08				
							1729.10	1264.45	1340.75	980.46	9.943E-08				
4.5	0.333	20	40	20	5	5.16	0	0	10.52	10.20	-4.248E-09	2.383E-10	4.57375E-10	0.52	4.98E-10
							9.33	9.04	13.87	13.44	-1.834E-09				
							13.39	12.98	15.31	14.84	-7.723E-10				
							40.90	39.64	31.57	30.60	3.765E-09				
							53.10	51.46	37.31	36.16	6.371E-09				
							64.82	62.82	47.12	45.66	7.144E-09				

Table A-2: Detailed Wetted Wall Column Data for 4.5 m K

SarNa	CO ₂ Idg	P* _{CO2}	Temp	Pressure	Gas _{Dry}	Gas _{wet}	P _{CO2in, dry}	P _{CO2in, wet}	P _{CO2out, dry}	P _{CO2out, wet}	CO ₂ flux	K _G	k _g	K _G /k _g	k _g '
m	mol CO ₂ /mol alk	Pa	°C	psig	Std L/min	Std L/min	Pa	Pa	Pa	Pa	mol/s cm2	mol/s Pa cm2	mol/s Pa cm2		mol/s Pa cm2
4.5	0.333	106	60	20	5	5.45	0	0	40.18	36.83	-1.622E-08	1.862E-10	4.83052E-10	0.39	3.03E-10
							30.62	28.06	59.56	54.59	-1.168E-08				
							57.16	52.40	78.45	71.91	-8.592E-09				
							160.01	146.68	141.84	130.02	7.337E-09				
							187.04	171.45	164.80	151.06	8.978E-09				
							212.39	194.69	179.15	164.22	1.342E-08				
4.5	0.333	577	80	40	5	5.72	0	0	279.39	244.28	-7.153E-08	1.583E-10	3.2117E-10	0.49	3.12E-10
							113.11	98.90	338.58	296.04	-5.773E-08				
							218.31	190.88	401.55	351.09	-4.692E-08				
							701.67	613.51	684.70	598.67	4.344E-09				
							798.19	697.90	741.26	648.12	1.458E-08				
4.5	0.333	2772	100	40	5	6.84	0	0	1129.99	826.33	-2.893E-07	1.364E-10	3.76225E-10	0.36	2.14E-10
							1379.96	1009.13	2235.84	1635.02	-2.191E-07				
							2786.32	2037.57	3143.38	2298.67	-9.142E-08				
							5583.95	4083.40	5058.74	3699.33	1.345E-07				
							6914.90	5056.69	5842.98	4272.82	2.745E-07				
							8219.46	6010.68	6781.81	4959.36	3.681E-07				
4.5	0.398	53	40	20	5	5.16	0	0	19.37	18.78	-7.819E-09	1.506E-10	4.57375E-10	0.33	2.25E-10
							29.18	28.28	34.92	33.84	-2.317E-09				
							56.93	55.17	55.01	53.31	7.723E-10				
							109.78	106.40	93.04	90.17	6.758E-09				
							135.14	130.97	110.74	107.32	9.847E-09				
							159.77	154.84	128.92	124.94	1.245E-08				
4.5	0.398	312	60	20	5	5.45	0	0	110.74	101.51	-4.47E-08	1.573E-10	4.83052E-10	0.33	2.33E-10
							109.55	100.42	176.04	161.37	-2.684E-08				
							213.11	195.35	242.05	221.88	-1.168E-08				
							409.00	374.92	385.32	353.21	9.557E-09				
							500.85	459.11	459.47	421.18	1.67E-08				
4.5	0.398	1851	80	40	5	5.72	0	0	739.00	646.15	-1.892E-07	1.205E-10	3.2117E-10	0.38	1.93E-10
							542.94	474.72	1021.78	893.40	-1.226E-07				
							1063.25	929.66	1451.60	1269.22	-9.943E-08				
							2560.10	2238.43	2409.28	2106.57	3.861E-08				
							3114.34	2723.04	2756.16	2409.86	9.171E-08				
							3619.58	3164.80	3129.43	2736.23	1.255E-07				

Table A-3: Detailed Wetted Wall Column Data for 4.5 m K

SarNa	CO ₂ Idg	P* _{CO2}	Temp	Pressure	Gas _{dry}	Gas _{wet}	P _{CO2in, dry}	P _{CO2in, wet}	P _{CO2out, dry}	P _{CO2out, wet}	CO ₂ flux	K _G	k _R	K _G /k _R	k _R '
m	mol CO ₂ /mol alk	Pa	°C	psig	Std L/min	Std L/min	Pa	Pa	Pa	Pa	mol/s cm ²	mol/s Pa cm ²	mol/s Pa cm ²		mol/s Pa cm ²
4.5	0.398	6496	100	40	5	6.84	0	0	2439.44	1783.90	-6.246E-07	1.105E-10	3.76225E-10	0.29	1.56E-10
							3461.22	2531.10	4931.67	3606.41	-3.765E-07				
							6929.98	5067.72	7420.13	5426.16	-1.255E-07				
							13603.58	9947.95	12208.53	8927.79	3.572E-07				
							16733.00	12236.42	14772.40	10802.68	5.02E-07				
							19862.43	14524.89	16846.12	12319.14	7.723E-07				
4.5	0.477	365	40	20	5	5.16	0	0	58.12	56.33	-2.346E-08	6.216E-11	4.57375E-10	0.14	7.19E-11
							152.36	147.66	181.54	175.94	-1.178E-08				
							281.28	272.60	287.02	278.16	-2.317E-09				
							621.16	601.99	586.24	568.14	1.409E-08				
							745.77	722.76	699.61	678.02	1.863E-08				
							884.97	857.66	813.22	788.12	2.896E-08				
4.5	0.477	1977	60	20	5	5.45	0	0	325.29	298.18	-1.313E-07	7.032E-11	4.83052E-10	0.15	8.23E-11
							681.67	624.86	901.72	826.57	-8.881E-08				
							1360.95	1247.53	1468.58	1346.20	-4.344E-08				
							4135.46	3790.83	3836.48	3516.77	1.207E-07				
							4786.03	4387.20	4398.56	4032.01	1.564E-07				
							5443.79	4990.13	4965.42	4551.63	1.931E-07				
4.5	0.477	6676	80	40	5	5.72	0	0	1674.05	1463.72	-4.286E-07	7.219E-11	3.2117E-10	0.22	9.31E-11
							2741.08	2396.67	3721.38	3253.81	-2.51E-07				
							5531.17	4836.20	5983.61	5231.80	-1.158E-07				
							10960.53	9583.40	10319.57	9022.97	1.641E-07				
							13562.10	11858.10	12393.28	10836.13	2.993E-07				
							19858.66	17363.52	17068.57	14923.99	7.144E-07				
4.5	0.477	19478	100	40	5	6.84	0	0	4494.31	3286.57	-1.151E-06	6.195E-11	3.76225E-10	0.16	7.42E-11
							9037.63	6608.99	11714.61	8566.60	-6.854E-07				
							17030.86	12454.24	18425.91	13474.40	-3.572E-07				
							37918.84	27729.09	36335.28	26571.07	4.055E-07				
							45987.48	33629.48	42933.46	31396.16	7.819E-07				
							53980.71	39474.73	49380.84	36110.95	1.178E-06				
4.5	0.514	1252	40	20	5	5.16	0	0	124.37	120.54	-5.02E-08	4.216E-11	4.57375E-10	0.09	4.64E-11
							552.51	535.46	626.66	607.32	-2.993E-08				
							1131.33	1096.42	1143.29	1108.01	-4.827E-09				
							1724.50	1671.29	1679.06	1627.24	1.834E-08				
							2150.25	2083.89	2073.71	2009.72	3.089E-08				
							2843.88	2756.12	2693.19	2610.08	6.082E-08				

Table A-4: Detailed Wetted Wall Column Data for 4.5 m K

SarNa	CO ₂ Idg	P* _{CO2}	Temp	Pressure	Gas _{Dry}	Gas _{Wet}	P _{CO2in, dry}	P _{CO2in, wet}	P _{CO2out, dry}	P _{CO2out, wet}	CO ₂ flux	K _G	k _g	K _G /k _g	k _g '
m	mol CO ₂ /mol alk	Pa	°C	psig	Std L/min	Std L/min	Pa	Pa	Pa	Pa	mol/s cm2	mol/s Pa cm2	mol/s Pa cm2		mol/s Pa cm2
4.5	0.514	4611	60	20	5	5.45	0	0	562.08	515.24	-2.269E-07	5.005E-11	4.83052E-10	0.10	5.58E-11
							2901.28	2659.50	3068.71	2812.98	-6.758E-08				
							4240.70	3887.31	4336.37	3975.01	-3.861E-08				
							8330.71	7636.48	8019.78	7351.46	1.255E-07				
							10387.68	9522.03	9837.56	9017.76	2.22E-07				
							12444.65	11407.58	11607.51	10640.21	3.379E-07				
4.5	0.514	13661	80	40	5	5.72	0	0	2345.18	2050.52	-6.005E-07	4.449E-11	3.2117E-10	0.14	5.16E-11
							6277.70	5488.94	7446.53	6510.91	-2.993E-07				
							11971.00	10466.90	12423.44	10862.50	-1.158E-07				
							23206.77	20290.96	22226.47	19433.83	2.51E-07				
							28598.43	25005.19	26713.23	23356.86	4.827E-07				
							34065.50	29785.35	31501.63	27543.62	6.564E-07				
4.5	0.514	35309	100	40	5	6.84	0	0	5708.37	4174.39	-1.462E-06	4.047E-11	3.76225E-10	0.11	4.53E-11
							23240.70	16995.34	25276.71	18484.22	-5.213E-07				
							55439.86	40541.76	54836.59	40100.61	1.545E-07				
							66260.88	48454.91	64262.58	46993.60	5.116E-07				
							71124.69	52011.69	68749.34	50274.65	6.082E-07				

Table B-1: Detailed Wetted Wall Column Data for 2 m amine X/6 m PZ

X	PZ	CO ₂ ldg	P* _{CO2}	Temp	Pressure	Gas _{Dry}	Gas _{Wet}	P _{CO2in, dry}	P _{CO2in, wet}	P _{CO2out, dry}	P _{CO2out, wet}	CO ₂ flux	K _G	k _g	K _G /k _g	k _g '
m		mol CO ₂ /mol alk	Pa	°C	psig	Std L/min	Std L/min	Pa	Pa	Pa	Pa	mol/s cm2	mol/s Pa cm2	mol/s Pa cm2		mol/s Pa cm2
2	6	0.349	282	40	20	5	5.16	0	0	69.4	67.2	-2.8E-08	1.05E-10	4.57E-10	0.23	1.36E-10
								103.1	99.9	137.5	133.3	-1.39E-08				
								192.8	186.8	216.0	209.3	-9.364E-09				
								445.8	432.1	414.0	401.2	1.2839E-08				
								531.2	514.8	479.3	464.5	2.0948E-08				
								607.0	588.3	533.9	517.4	2.954E-08				
2	6	0.349	1820	60	20	5	5.45	0	0	466.2	427.3	-1.881E-07	1.15E-10	4.83E-10	0.24	1.51E-10
								449.9	412.4	775.4	710.8	-1.314E-07				
								1007.0	923.0	1258.1	1153.3	-1.014E-07				
								2523.4	2313.1	2396.6	2196.9	5.1164E-08				
								3023.3	2771.3	2762.6	2532.3	1.0522E-07				
								3544.7	3249.3	3202.6	2935.8	1.3805E-07				
2	6	0.349	9180	80	40	5	5.72	0	0	3016.3	2637.3	-7.723E-07	9.22E-11	3.21E-10	0.29	1.29E-10
								4166.3	3642.8	5768.7	5043.9	-4.103E-07				
								8238.3	7203.2	8690.8	7598.8	-1.158E-07				
								10877.6	9510.9	10689.1	9346.0	4.8268E-08				
								14874.2	13005.3	13856.2	12115.2	2.6065E-07				
								19888.8	17389.9	17362.7	15181.1	6.4679E-07				
2	6	0.349	3549 2	100	40	5	6.84	0	0	9139.4	6683.4	-2.34E-06	6.66E-11	3.76E-10	0.18	8.09E-11
								22448.9	16416.3	26181.6	19145.9	-9.557E-07				
								43638.5	31911.8	43864.8	32077.2	-5.792E-08				
								58946.3	43106.0	57174.2	41810.1	4.5372E-07				
								64526.5	47186.6	62000.3	45339.3	6.4679E-07				
								66487.1	48620.3	63772.4	46635.2	6.9506E-07				
2	6	0.396	1187	40	20	5	5.16	0	0	215.0	208.4	-8.679E-08	7.28E-11	4.57E-10	0.16	8.66E-11
								465.7	451.3	576.0	558.2	-4.45E-08				
								897.4	869.7	935.0	906.1	-1.516E-08				
								1519.5	1472.6	1464.5	1419.3	2.2203E-08				
								1708.5	1655.8	1631.9	1581.6	3.0892E-08				
								1899.8	1841.2	1806.5	1750.8	3.7649E-08				
2	6	0.396	7824	60	20	5	5.45	0	0	1128.9	1034.9	-4.557E-07	5.55E-11	4.83E-10	0.11	6.27E-11
								2829.5	2593.7	3451.4	3163.8	-2.51E-07				
								5508.4	5049.3	5771.5	5290.5	-1.062E-07				
								13329.6	12218.8	12731.7	11670.7	2.4134E-07				
								15984.5	14652.5	15123.5	13863.2	3.4753E-07				
								18567.7	17020.4	17419.6	15968.0	4.6337E-07				

Table B-2: Detailed Wetted Wall Column Data for 2 m amine X/6 m PZ

X	PZ	CO ₂ ldg	P* _{CO2}	Temp	Pressure	Gas _{Dry}	Gas _{wet}	P _{CO2in, dry}	P _{CO2in, wet}	P _{CO2out, dry}	P _{CO2out, wet}	CO ₂ flux	K _G	k _g	K _G /k _g	k _g '
m		mol CO ₂ /mol alk	Pa	°C	psig	Std L/min	Std L/min	Pa	Pa	Pa	Pa	mol/s cm ²	mol/s Pa cm ²	mol/s Pa cm ²		mol/s Pa cm ²
2	6	0.396	35669	80	40	5	5.72	0	0	5553.8	4856.0	-1.422E-06	3.58E-11	3.21E-10	0.11	4.03E-11
								11925.8	10427.3	14866.7	12998.7	-7.53E-07				
								22671.4	19822.8	24066.4	21042.6	-3.572E-07				
								54418.1	47580.7	52608.3	45998.3	4.6337E-07				
								64937.5	56778.4	62411.3	54569.7	6.4679E-07				
								75192.9	65745.3	71460.3	62481.7	9.5571E-07				
2	6	0.426	5110	40	20	5	5.16	0	0	337.2	326.8	-1.361E-07	2.48E-11	4.57E-10	0.05	2.62E-11
								1399.2	1356.0	1614.5	1564.7	-8.688E-08				
								2858.2	2770.0	2977.8	2885.9	-4.827E-08				
								5584.9	5412.6	5537.1	5366.2	1.9307E-08				
								6972.2	6757.0	6876.5	6664.3	3.8615E-08				
								8263.7	8008.7	8120.2	7869.6	5.7922E-08				
2	6	0.426	28662	60	40	5	5.28	0	0	2571.4	2435.5	-6.584E-07	1.97E-11	2.98E-10	0.07	2.11E-11
								6217.4	5888.7	7838.6	7424.3	-4.151E-07				
								11986.1	11352.4	12891.0	12209.5	-2.317E-07				
								39170.6	37099.9	38416.5	36385.7	1.9307E-07				
								44750.8	42385.1	43619.7	41313.7	2.8961E-07				
								50067.0	47420.3	48709.7	46134.7	3.4753E-07				
								55270.2	52348.4	53724.3	50884.2	3.958E-07				
2	6	0.458	18221	60	20	5	5.16	0	0	545.3	528.5	-2.201E-07	7.63E-12	4.57E-10	0.02	7.76E-12
								6005.9	5820.5	6269.0	6075.5	-1.062E-07				
								11531.0	11175.1	11626.6	11267.9	-3.861E-08				
								27484.4	26636.3	27317.0	26474.0	6.7575E-08				
								32818.2	31805.4	32579.0	31573.6	9.6536E-08				
								38271.5	37090.5	38056.3	36881.9	8.6883E-08				
								43414.0	42074.2	43126.9	41796.1	1.1584E-07				

Table C-1: Detailed Wetted Wall Column Data for 7 m MDEA/2 m PZ

MDEA	PZ	CO ₂ ldg	P* _{CO2}	Temp	Pressure	Gas _{Dry}	Gas _{wet}	P _{CO2in, dry}	P _{CO2in, wet}	P _{CO2out, dry}	P _{CO2out, wet}	CO ₂ flux	K _G	k _g	K _G /k _g	k _g '
m		mol CO ₂ / mol alk	Pa	°C	psig	Std L/min	Std L/min	Pa	Pa	Pa	Pa	mol/s cm ²	mol/s Pa cm ²	mol/s Pa cm ²		mol/s Pa cm ²
7	2	0.1335	217	30	20	5	5.09	0	0	51.9	51.0	-2.1E-08	1.05E-10	4.5E-10	0.23	1.37E-10
								43.8	43.0	82.8	81.3	-1.6E-08				
								113.6	111.6	137.5	135.1	-9.7E-09				
								287.0	281.9	266.9	262.2	8.11E-09				
								334.9	328.9	310.7	305.2	9.75E-09				
								382.7	375.9	348.5	342.3	1.38E-08				
7	2	0.195	732	30	20	5	5.09	0	0	110.7	108.8	-4.5E-08	6.46E-11	4.5E-10	0.14	7.53E-11
								210.2	206.5	290.6	285.5	-3.2E-08				
								382.5	375.7	432.0	424.3	-2E-08				
								892.4	876.6	862.7	847.4	1.2E-08				
								1058.4	1039.6	1012.7	994.7	1.84E-08				
								1205.5	1184.1	1145.4	1125.1	2.42E-08				
7	2	0.249	2750	30	20	5	5.09	0	0	275.1	270.2	-1.1E-07	4.06E-11	4.51E-10	0.09	4.46E-11
								1062.0	1043.1	1219.8	1198.2	-6.4E-08				
								2004.3	1968.8	2088.1	2051.0	-3.4E-08				
								3085.4	3030.7	3052.0	2997.8	1.35E-08				
								3525.5	3463.0	3470.5	3409.0	2.22E-08				
								3936.9	3867.1	3836.5	3768.5	4.05E-08				
7	2	0.245	2175	30	20	5	5.09	0	0	251.1	246.7	-1E-07	4.69E-11	4.51E-10	0.10	5.23E-11
								684.1	671.9	839.5	824.6	-6.3E-08				
								1408.8	1383.8	1487.7	1461.3	-3.2E-08				
								4180.9	4106.8	3982.4	3911.8	8.01E-08				
								4860.2	4774.0	4573.2	4492.1	1.16E-07				
								5506.0	5408.3	5147.2	5055.9	1.45E-07				
7	2	0.298	4154	30	20	5	5.09	0	0	344.4	338.3	-1.4E-07	3.32E-11	4.51E-10	0.07	3.58E-11
								1370.5	1346.2	1581.0	1553.0	-8.5E-08				
								2800.8	2751.2	2896.5	2845.1	-3.9E-08				
								9426.2	9259.0	9043.5	8883.1	1.54E-07				
								10741.7	10551.2	10239.4	10057.8	2.03E-07				
								12081.1	11866.9	11459.2	11256.0	2.51E-07				

Table C-2: Detailed Wetted Wall Column Data for 7 m MDEA/2 m PZ

MDEA	PZ	CO ₂ ldg	P* _{CO2}	Temp	Pressure	Gas _{Dry}	Gas _{wet}	P _{CO2in, dry}	P _{CO2in, wet}	P _{CO2out, dry}	P _{CO2out, wet}	CO ₂ flux	K _G	k _g	K _G /k _g	k _g '
m		mol CO ₂ / mol alk	Pa	°C	psig	Std L/min	Std L/min	Pa	Pa	Pa	Pa	mol/s cm ²	mol/s Pa cm ²	mol/s Pa cm ²		mol/s Pa cm ²
7	2	0.356	8262	30	20	5	5.09	0	0	459.2	451.1	-1.9E-07	2.22E-11	4.51E-10	0.05	2.33E-11
								2829.5	2779.4	3114.2	3058.9	-1.1E-07				
								5580.1	5481.2	5699.7	5598.6	-4.8E-08				
								13425.3	13187.2	13210.0	12975.8	8.69E-08				
								16199.8	15912.6	15769.3	15489.7	1.74E-07				
								18759.1	18426.4	18208.9	17886.1	2.22E-07				
7	2	0.356	16712	30	20	5	5.09	0	0	1470.5	1441.7	-3.8E-07	2.23E-11	2.87E-10	0.08	2.42E-11
								5625.4	5515.3	6530.3	6402.5	-2.3E-07				
								11054.8	10838.4	11394.1	11171.1	-8.7E-08				
								21461.1	21040.9	21234.9	20819.2	5.79E-08				
								26701.9	26179.2	25947.8	25439.9	1.93E-07				
								31905.1	31280.5	30623.1	30023.6	3.28E-07				

Piperazine/Amine X for use in CO₂ Capture

Quarterly Report for January 1 – March 31, 2011

By Omkar Namjoshi

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Department of Chemical Engineering

The University of Texas at Austin

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Abstract

A blend of proprietary amine X and piperazine (PZ) was evaluated as a potential CO₂ capture solvent. A total amine strength of 8 m was used (6 m PZ and 2 m amine X) and compared to the performance of 8 m PZ. In this quarter, the solubility window, CO₂ working capacity, heats of absorption, and rates of absorption were evaluated. The wetted wall column and the total pressure apparatus were used to acquire these data.

The data suggest that the lower solubility limit is somewhere between a loading of 0.3 and 0.35 mol CO₂/mol alkalinity at room temperature. There is no upper solubility limit. In addition, the data suggest that the working capacity of the solvent is about 85% that of 8 m PZ, with an operating lean and rich loading of about 0.35 and 0.42, respectively. Amine rates of absorption of the blend are between 50 and 75% that of 8 m PZ, and the heat of absorption is about 14% greater than that of 8 m PZ.

Goals for the next quarter include evaluating thermal and oxidative degradation of the amine blend as well as evaluating the amine volatility.

Background and Motivation

PZ is currently considered to be a “state of the art” solvent for use in CO₂ capture from flue gas, with high absorption rates, high working capacities, and negligible oxidative and thermal degradation compared to other solvents. However it has a limited solubility window somewhat close to its operating range and can cause precipitation issues and problems for plant operators. Because of this limitation it is desirable to develop a new amine blend that has most of the performance characteristics of PZ but with a wider solubility window.

To establish the viability of a solvent for use in CO₂ capture applications it is necessary to determine solid solubility, amine capacity and absorption rates, thermal and oxidative degradation rates and degradation products, and amine volatility over a range of expected operating conditions in a CO₂ capture system. The data obtained in the screening can then be used in modeling studies and pilot plant studies prior to commercialization.

In this quarter the wetted wall column was used to determine the equilibrium partial pressure of CO₂ at a given solvent CO₂ loading. The data obtained can be used to estimate solvent CO₂ capacity, operating range, amine heat of absorption of CO₂, and CO₂ absorption rates. These data can, in turn, be used to estimate the energy duty of a CO₂ capture plant and effective absorber mass transfer area in any future modeling work.

Experimental

Solid Solubility of PZ/Amine X

The experiments were conducted by preparing blends of PZ and amine X over a range of loading conditions. Solutions were prepared gravimetrically. The amine blend was then sparged with CO₂ and the amount of CO₂ dissolved in the solvent was determined gravimetrically.

Wetted wall column

The wetted wall column was used to determine equilibrium CO₂ partial pressures, rates of absorption of CO₂, and heats of absorption. The experimental methods and apparatus are the same as described by Chen (2010).

Total Pressure Apparatus

The total pressure apparatus was used to estimate equilibrium CO₂ pressure at higher temperatures (and thus pressures). The apparatus and experimental methods were the same as Fulk (2010).

Materials

Piperazine (99 wt % purity) was supplied by Sigma-Aldrich.

Results and Discussion

Solid Solubility

Solubility data were taken at room temperature (roughly 23–25 °C) as a rough measure to determine the absolute minimum and maximum loading. The following observations were made:

Table 1: Solubility window for 6 m PZ/2 m amine X

6 m PZ/2 m amine X, loading 0.25	Solution crystallized at room temperature
6 m PZ/2 m amine X, loading 0.30	Solution turbid at room temperature
6 m PZ/2 m amine X, loading 0.35+	No solubility issues noted at room temperature.
6 m PZ/2 m amine X, loading 0.55	Maximum loading. No solubility issues noted at room temperature.

CO₂ Amine CO₂ Working Capacity

The wetted wall column can be used to find the equilibrium partial pressure of CO₂ at a given solvent CO₂ loading. This data can be used to determine the working capacity of the solvent.

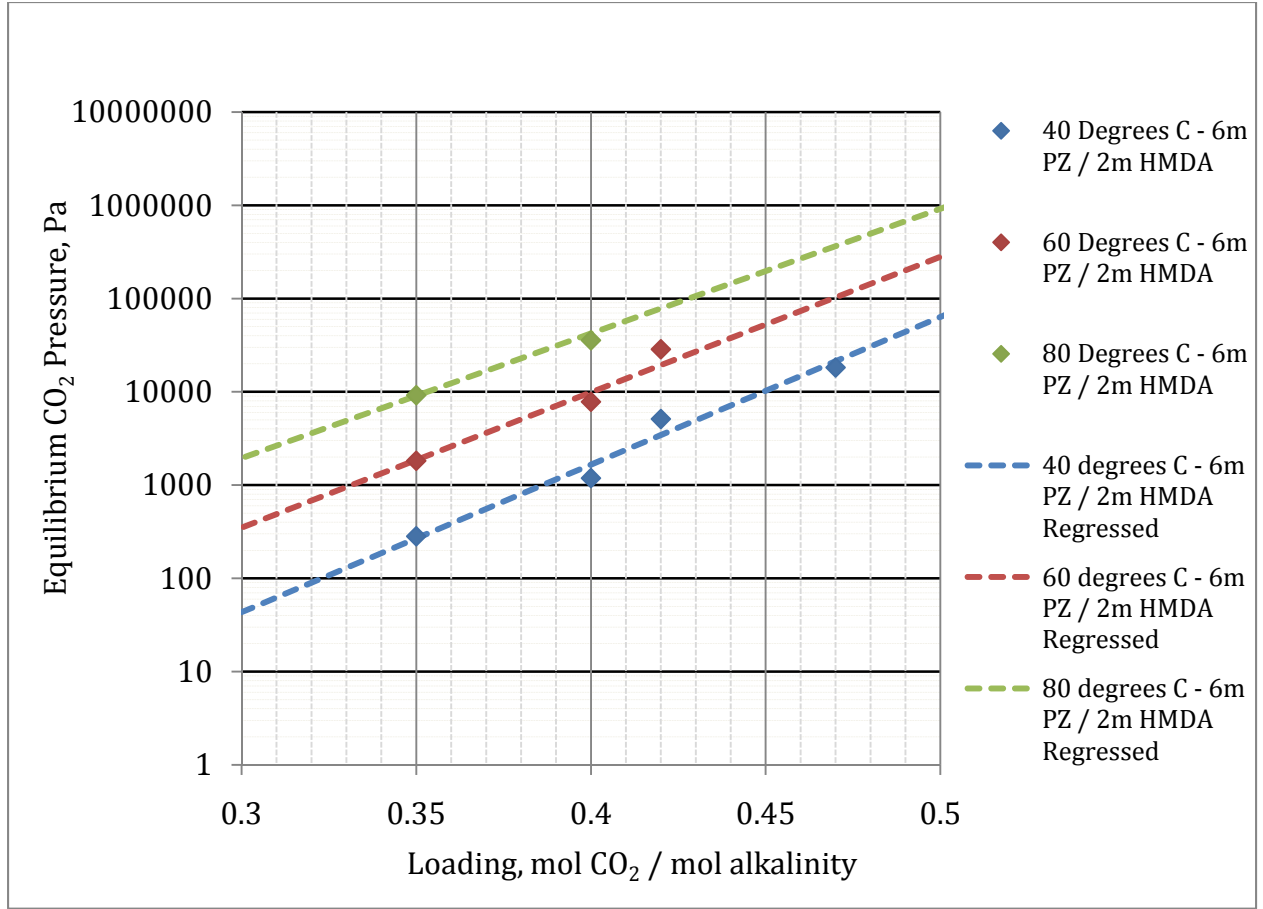


Figure 1: Equilibrium CO₂ Pressure and Solvent Amine Loading

Nominal CO₂ capacity is found by taking the difference of equilibrium amine loading at 40 °C and CO₂ partial pressures of 5000 kPa and 500 kPa (corresponding to loadings of roughly 0.42 mol CO₂/mol alkalinity and 0.35 mol CO₂/mol alkalinity). Interpolating between the regressed expression and experimental values gives a nominal solvent capacity of about 0.64 mol CO₂/kg amine. This is somewhat less than that of PZ (0.76 mol CO₂/kg amine) (Frailie, 2010).

A semi-empirical relationship correlating the CO₂ partial pressure, loading, and temperature can be used as a means to estimate capacity beyond the experimental data; these regressions are included in the plot as dashed lines. The relationship is given by the following expression (Li, 2010):

$$\ln(P_{CO_2}^*) = A + \frac{B}{T} + C * \alpha + \frac{D}{T} * \alpha + \frac{E}{T^2}$$

The equilibrium CO₂ partial pressure is given in pascals, the amine CO₂ loading α is given in mol CO₂/mol alkalinity, and T is given in Kelvins. For the 6 m PZ/ 2 m amine X blend they were found to be the following:

Table 2: Regression Coefficients for Semi-Empirical Model

A	21.7537
B	-2114.85
C	-13.5516
D	15649.7
E	-2171271

CO₂ Absorption Rates

The overall rate of CO₂ absorption can be determined by analyzing the liquid film mass transfer coefficient (k_g) as it is particularly dependent on CO₂ absorption kinetics. The rate is directly proportional to the liquid film mass transfer coefficient.

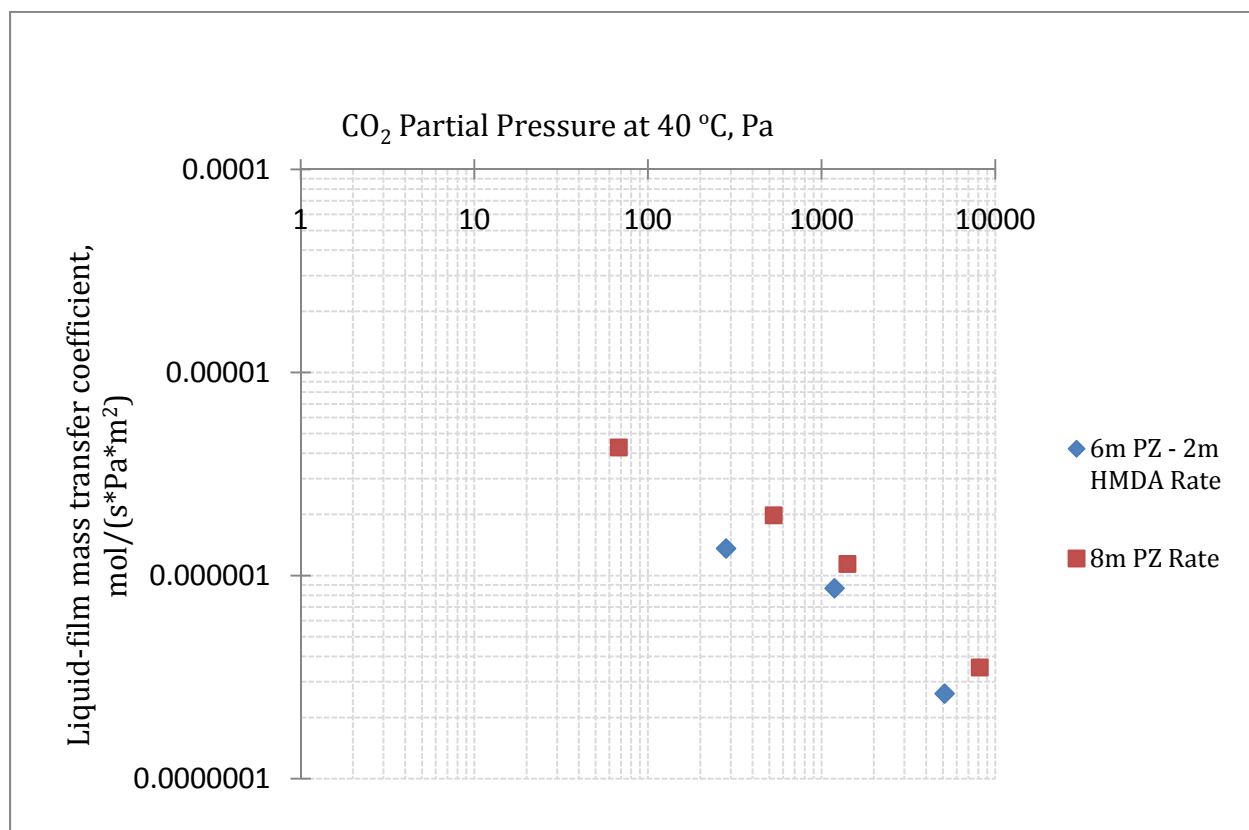


Figure 2: Rate of CO₂ Absorption

Amine absorption rates of this system are less than those of 8 m PZ. This was not initially expected as the pKa of amine X is higher than that of 8 m PZ. The solution was noted to be more viscous in this example compared to 8 m PZ from qualitative observations. The increased viscosity of the system would reduce the diffusivity of the CO₂ into the bulk liquid as shown in the relationship below (Dugas, 2009):

$$(D_{CO_2}\mu)_{\text{Amine}} = (D_{CO_2}\mu)_{\text{Water}}$$

where $\mathcal{D}_{CO_2}$ is the diffusivity of CO_2 and μ is the viscosity in the system.

Furthermore, the rate of amine absorption can be related to the flux of CO_2 and liquid-film mass transfer, which can help explain why the increased viscosity can impact the diffusivity and correspondingly the rate of absorption (Dugas, 2009):

$$k'_g = \frac{N_{CO_2}}{P_{CO_2,i} - P_{CO_2,b}^*} = \frac{\sqrt{\mathcal{D}_{CO_2} * k_2 [\text{Amine}]_b}}{H_{CO_2}}$$

With N_{CO_2} equivalent to the CO_2 flux, P_{CO_2} corresponding to the partial pressure of CO_2 in the gas (at the interface and equilibrium pressure in the bulk gas), $\mathcal{D}_{CO_2}$ corresponding to the diffusivity of CO_2 in the liquid, k_2 corresponding to the pseudo-first-order rate constant of absorption, $[\text{Amine}]$ corresponding to the concentration of amine in the bulk liquid, and H_{CO_2} corresponding to the Henry's law constant for equilibrium CO_2 in the liquid phase.

Heat of CO_2 Absorption

The heat of CO_2 absorption was determined using the Gibbs-Helmholtz relationship:

$$\left(\frac{\partial \ln p}{\partial 1/T} \right)_{P,x} = \frac{\Delta H_{abs}}{R} \approx \frac{\ln p_2 - \ln p_1}{\frac{1}{T_2} - \frac{1}{T_1}}$$

The total pressure apparatus can also help confirm the heat of absorption measurement from the wetted wall column. The total pressure of CO_2 at a given temperature can be estimated by assuming ideal conditions in both the liquid and vapor phases and accounting for the partial pressures of the nitrogen and water vapor in the headspace.

For the total pressure experiment temperatures were ramped up from ambient conditions to temperature set points ($T = 373$ K, $T = 393$ K, $T = 413$ K, $T = 433$ K) and held at the setpoint until the system achieved a steady pressure. The system was then ramped down ($T = 413$ K, $T = 393$ K, $T = 373$ K) and held at individual setpoints until the system achieved a steady pressure. The system was then ramped back down to ambient conditions. Data at $T = 373$ K, $T = 393$ K, $T = 413$ K is averaged from the data taken while ramping up and ramping down.

For the 6 m PZ/2 m amine X blend the following data were obtained at a loading of 0.35:

Table 3: CO_2 VLE Estimates from the Total Pressure Apparatus

Temperature, Kelvins	Pressure (bar)	Saturation Pressure, H_2O , bar	Partial Pressure, N_2 , bar	Partial Pressure, H_2O , bar	Partial Pressure, CO_2 , bar
373	2.33	1.01	1.26	0.89	0.19
393	4.06	1.98	1.32	1.73	1.00
413	7.77	3.61	1.39	3.15	3.22
433	15.45	6.17	1.46	5.39	8.60

Taking one point at $T = 433$ K (from the total pressure experiment), $P_{CO_2} = 8.6$ bar and the other at $T = 313$ K, P_{CO_2} at 0.00282 bar, the heat of CO_2 absorption is roughly -74 kJ/mol at a loading

of 0.35. At a loading of 0.42 and taking points at $T = 313.15\text{ K}$, $P_{\text{CO}_2} = 0.0511\text{ bar}$ and $T = 333.15\text{ K}$, $P_{\text{CO}_2} = 0.287\text{ bar}$ the heat of absorption is roughly -75 kJ/mol .

For comparison purposes the heat of CO_2 absorption of 8 m PZ is -65 kJ/mol (Frailie, 2010).

Conclusions

The data suggest the following for a blend of 6 m PZ/2 m amine X:

- A lean solubility limit between 0.3 and 0.35, with no real rich solubility limit;
- A working capacity of about $0.64\text{ mol CO}_2/\text{kg}$ solvent (compared to $0.76\text{ mol CO}_2/\text{kg}$ solvent for 8 m PZ);
- Enthalpy of absorption equal to about -74 to -75 kJ per mol CO_2 absorbed (compared to -65 kJ per mol CO_2 absorbed for 8 m PZ);
- A CO_2 absorption rate between 50 and 75% of that of 8 m PZ.

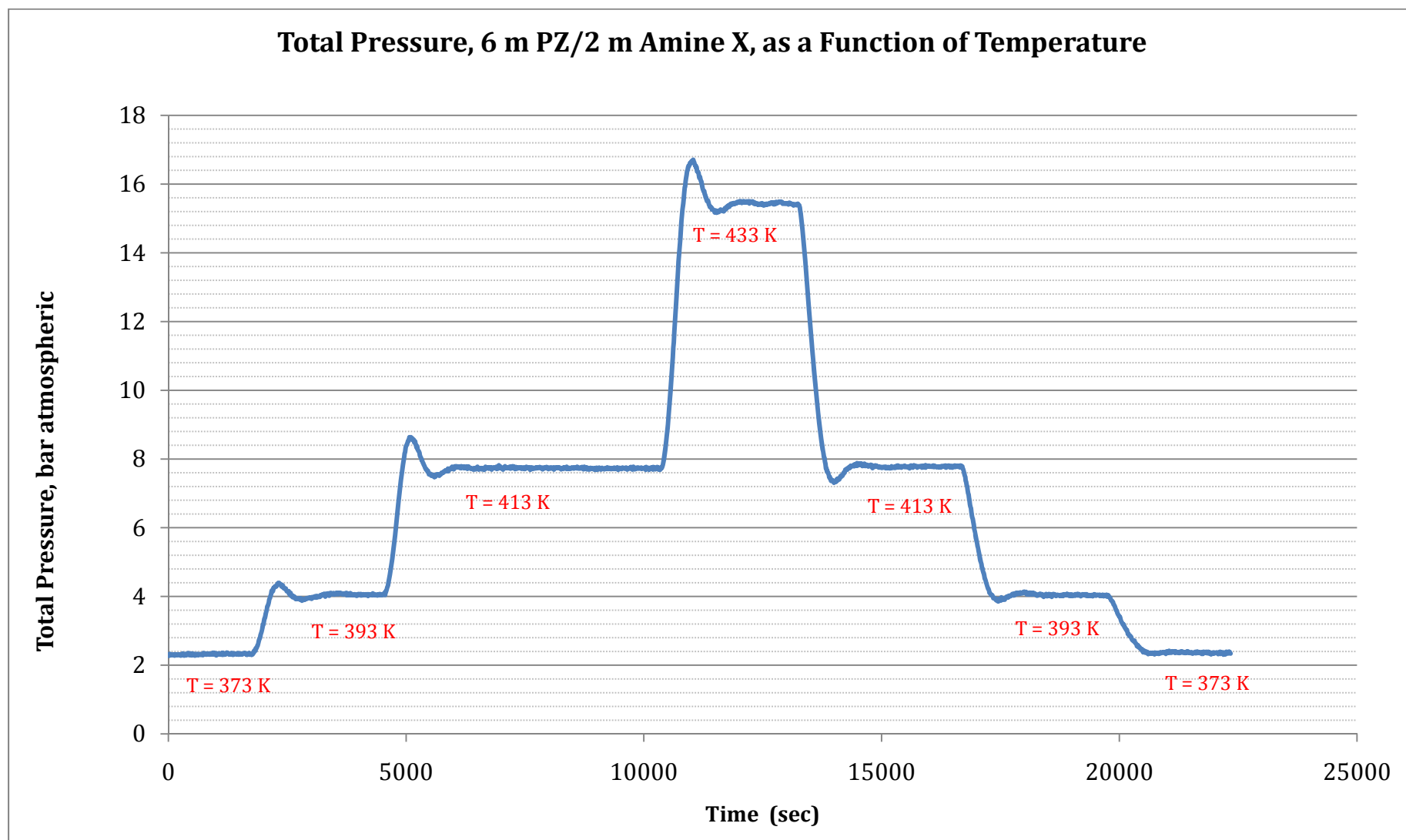
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Appendix – Wetted Wall Column Data (Raw)

P(CO ₂), Pascal	Loading, mol CO ₂ /mol alk	Temperature (Kelvins)	Rates (mol/s*Pa*cm ²)
282	0.35	313	1.36E-10
1187	0.4	313	8.66E-11
5110	0.42	313	2.62E-11
18221	0.47	313	
1820	0.35	333	1.51E-10
7824	0.4	333	6.27E-11
28662	0.42	333	2.11E-11
9180	0.35	353	1.29E-10
35699	0.4	353	4.03E-11
35492	0.35	373	8.09E-11

Appendix – Total Pressure as a function of Temperature (graph)



Vapor-Liquid Equilibrium of CO₂ Loaded MEA and PZ

Quarterly Report for January 1 – March 31, 2011

by Qing Xu

Supported by the Luminant Carbon Management Program

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Abstract

In this period total pressure was measured with 10 m PZ and 8 m 2MPZ at 100–160 °C in an autoclave. CO₂ partial pressure was derived from the total pressure data and semi-empirical models were correlated. According to the Gibbs-Helmholtz Equation, CO₂ heat of absorption was derived from CO₂ partial pressure models. The updated models are as follows:

0.9–13 m PZ:

$$\ln P_{CO_2} = 35.5 + \frac{-11067}{T} - 21.5 \cdot \alpha^2 + 4710 \cdot \frac{\alpha}{T} + 11419 \frac{\alpha^2}{T}$$
$$\Delta H_{abs} = -R(-11067 + 4710\alpha + 11419\alpha^2) \text{ (J/mol CO}_2\text{)}$$

8 m 2MPZ:

$$\ln P_{CO_2} = 40.1 + \frac{-12513}{T} - 22.1 \cdot \alpha^2 + 14099 \cdot \frac{\alpha}{T}$$
$$\Delta H_{abs} = -R(-12513 + 14099\alpha) \text{ (J/mol CO}_2\text{)}$$

Pilot plant work by Eric Chen showed that fogging might occur in the condenser of the 2-stage flash and cause solid formation and clogging in the pipe. Therefore an apparatus has been set up at bench scale to test fogging. One experiment with 8 m PZ was conducted and fogging was observed at 150 °C, 7.3–7.7 bar. The condensate accumulated from 7.3–12.3 bar contains 2.84 wt % PZ and 0.92 wt % CO₂. In future, more experiments will be done at various temperature and pressure values in order to find the boundary condition of fogging formation.

In the next quarter the electrolyte-NRTL thermo model of CO₂-MEA-H₂O will be improved with more experimental data and fewer parameters.

Introduction

With concentrated aqueous piperazine (PZ) thermal degradation is negligible up to 150 °C (Freeman et al., 2008). Better energy performance may be obtained by increasing stripper temperature without degradation of PZ (Rochelle et al., 2008). Multi-stage flashes instead of a simple stripper show a better performance by flashing at elevated temperature. Some other

configurations for stripping at elevated temperature also give better energy performance than the simple stripper (Rochelle et al., 2010a).

For thermally resistant amines such as PZ and PZ derivatives, the stripper temperature can be increased. With amines of relatively high thermal degradation rates, for instance, MEA, stripper temperature is limited but the thermal reclaimer operating temperature is up to 150 °C. Measurements of CO₂ solubility at high temperature expand the temperature range to 160 °C to get the temperature dependence of CO₂ solubility and the heat of absorption. The data are also important for the design of the high temperature processes.

The operation of a 2-stage flash in the pilot plant by Eric Chen indicated that there might be fogging of PZ and water inside the condenser which would cause solids to clog the pipes. In order to control fogging and avoid clogging in the pipes, the boundary condition of fogging needs to be found.

Total Pressure Measurements

A description of the total pressure apparatus and procedures can be found in Rochelle et al. (2010c).

Results

In this period, the total pressure of 10 m PZ and 8 m 2MPZ at rich loading has been measured.

CO₂ partial pressure was calculated by subtracting the partial pressure of N₂ and water from the total pressure. P_{water} was assumed following Raoult's Law and P_{amine} was ignored for amines except MEA. The calculation example is in Appendix 4 in the section by Xu in Rochelle et al. (2009).

The liquid composition has been corrected with measurements at 100–160 °C because the real CO₂ loading in the liquid phase is less than that measured at room temperature, and this difference becomes significant at high temperature and high loading.

Total Pressure and CO₂ Partial Pressure

Table 1 lists the new CO₂ partial pressure and total pressure of 10 m PZ generated in this quarter.

Table 1: Total Pressure and CO₂ Partial Pressure in 10 m PZ

T (°C)	Loading in liq.	P _t (kPa)	P _{CO2} (kPa)	T (°C)	Loading in liq.	P _t (kPa)	P _{CO2} (kPa)
100	0.379	293	205	140	0.362	1462	1148
110	0.376	486	361	150	0.355	1976	1561
120	0.372	731	558	160	0.348	2569	2030
130	0.368	1061	825				

Based on all the CO₂ partial pressure data in PZ at both high (Xu et al., 2010) and low temperature (Hilliard, 2008; Dugas et al., 2008; Ermatchkov et al., 2006), the empirical CO₂ partial pressure model was updated:

$$\ln P_{\text{CO}_2} = (35.5 \pm 0.3) + \frac{-11067 \pm 125}{T} + (-21.5 \pm 3.1) \cdot \alpha^2 + (4710 \pm 411) \cdot \frac{\alpha}{T} + (11419 \pm 1337) \frac{\alpha^2}{T} \quad (1)$$

$$r^2 = 0.9933$$

α - CO₂ loading.

T - Temperature (K).

According to the Gibbs-Helmholtz Equation, the heat of absorption can be derived from the empirical CO₂ partial pressure model.

$$\Delta H_{abs} = -R \frac{\partial \ln P_{CO_2}}{\partial (\frac{1}{T})} = -R(-11067 + 4710\alpha + 11419\alpha^2) \text{ (J/mol CO}_2\text{)} \quad (2)$$

R – 8.314 J/(mol·K).

α - CO₂ loading.

Figure 1 gives the CO₂ partial pressure over 0.9–12 m PZ from 40 to 160 °C at various loadings. The model fairly predicts the data and the new data are comparable with previous measured data.

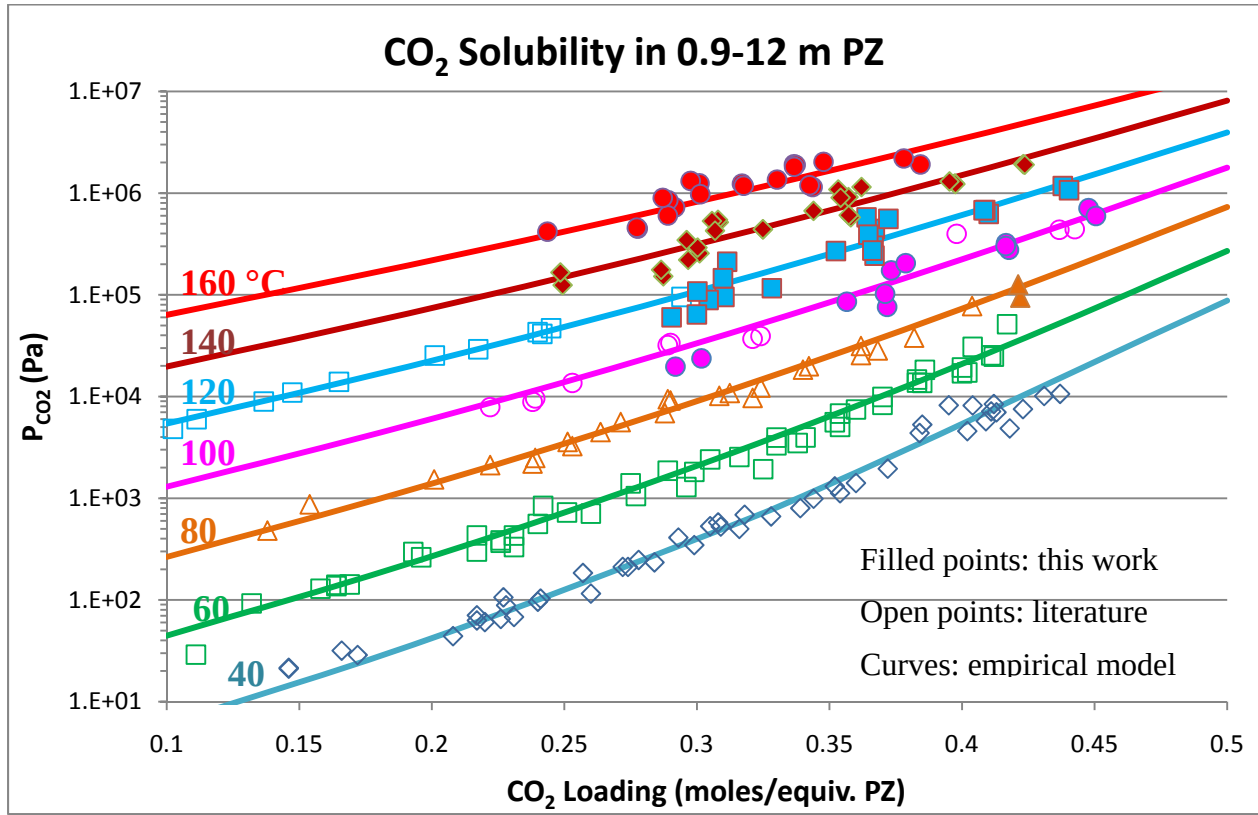


Figure 1: CO₂ Solubility in 0.9–12 m PZ

Table 2 lists the new CO₂ partial pressure and total pressure of 8 m 2MPZ generated in this quarter.

Table 2: Total Pressure and CO₂ Partial Pressure in 8 m 2MPZ

T (°C)	Loading in liq.	P _t (kPa)	P _{CO₂} (kPa)	T (°C)	Loading in liq.	P _t (kPa)	P _{CO₂} (kPa)
100	0.392	392	303	140	0.362	1893	1575
110	0.387	640	514	150	0.351	2513	2093
120	0.380	958	783	160	0.337	3263	2718
130	0.373	1354	1116				

Based on all the CO₂ partial pressure data in 2MPZ at both high (Xu et al., 2010) and low temperature (Rochelle et al., 2010a), the empirical CO₂ partial pressure model was updated:

$$\ln P_{CO_2} = (40.1 \pm 0.9) + \frac{-12513 \pm 298}{T} + (-22.1 \pm 2.8) \cdot \alpha + (14099 \pm 1010) \cdot \frac{\alpha}{T} \quad (3)$$

$$r^2 = 0.9988$$

α - CO₂ loading.

T - Temperature (K).

According to the Gibbs-Helmholtz Equation, the heat of absorption can be derived from the empirical CO₂ partial pressure model.

$$\Delta H_{abs} = -R \frac{\partial \ln P_{CO_2}}{\partial (\frac{1}{T})} = -R(-12513 + 14099\alpha) \text{ (J/mol CO}_2\text{)} \quad (4)$$

R – 8.314 J/(mol·K).

α - CO₂ loading.

Figure 2 gives the CO₂ partial pressure over 8 m 2MPZ from 40 to 160 °C at various loadings. The model fairly predicts the data and the new data are comparable with previous measured data.

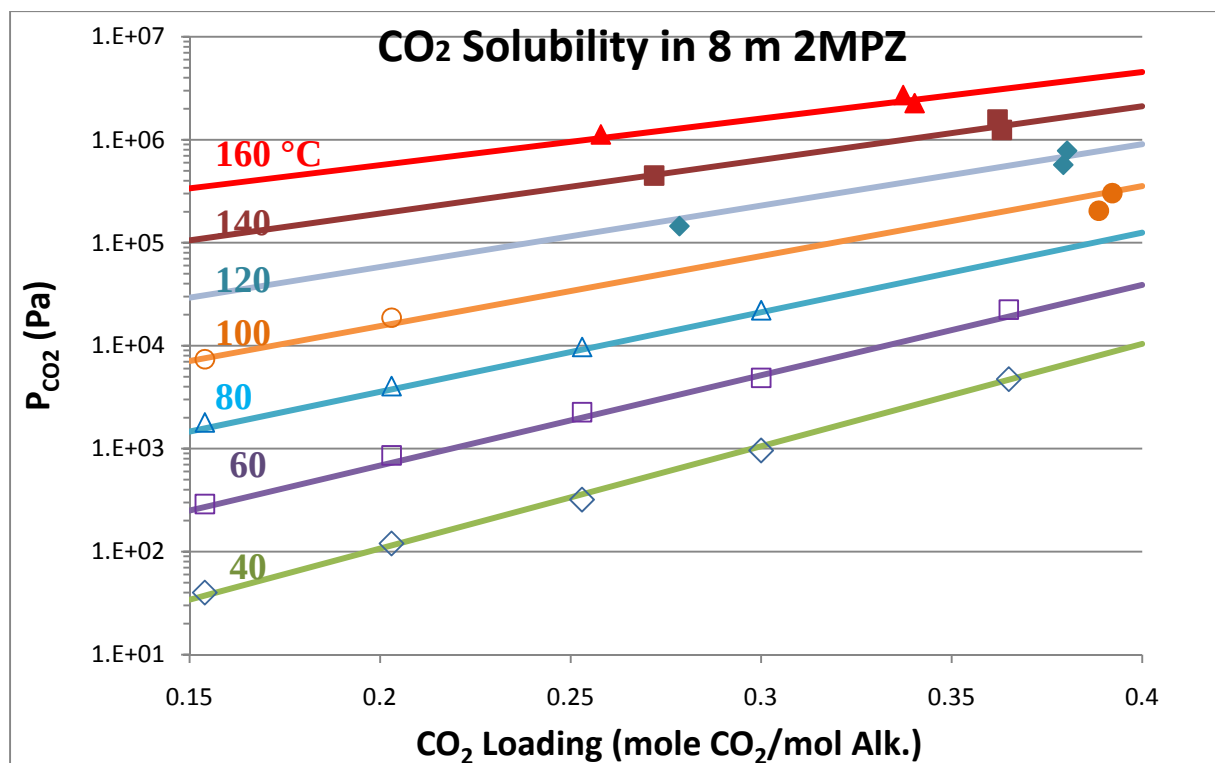


Figure 2: CO₂ Solubility in 8 m 2MPZ

Comparison of Heat of Absorption

Table 3 compares the heat of absorption of CO₂ in 9 screened solvents. The other empirical models are from previous regression work (Rochelle et al., 2010a). The loadings are defined as moles of CO₂ per mole alkalinity. Therefore for MEA, MDEA, and DGA[®], the loading $\alpha = \frac{CO_2(mol)}{MEA \text{ or } DGA^{\circ}(mol)}$; for PZ and PZ derivatives, $\alpha = \frac{CO_2(mol)}{amine(mol) \cdot 2}$.

MEA, DGA[®], and 7 m/2 m MDEA/PZ have the highest ΔH_{abs} , while PZ and 2MPZ have similar lower ΔH_{abs} . 7 m/2 m MDEA/PZ has a constant ΔH_{abs} in the investigated loading range.

Table 3: Comparison of the Heat of Absorption of CO₂

Solvent	ΔH_{abs} (J/mol CO ₂)	ΔH_{abs} (kJ/mol CO ₂)*	Mid-loading**
3.5–13 m MEA	$-R(-12030 + 1086\alpha + 12030\alpha^2)$	72±4	0.486
9.6–10 m DGA [®]	$-R(-7572 - 25209\alpha + 50113\alpha^2)$	73±3	0.447
7/2 MDEA/PZ	7.2E4	72±1	0.202
PZ/1MPZ/1,4-DMPZ	$-R(-10597 + 7627\alpha)$	70±1	0.278
7.7–8 m 1MPZ	$-R(-10344 + 9741\alpha)$	69±3	0.207
5/5 MDEA/PZ	$-R(-11063 + 11098\alpha)$	69±3	0.271

Solvent	ΔH_{abs} (J/mol CO ₂)	ΔH_{abs} (kJ/mol CO ₂)*	Mid-loading**
0.9–12 m PZ	$-R(-11067 + 4710\alpha + 11412\alpha^2)$	66±2	0.353
6.7–8 m 2MPZ	$-R(-12513 + 14099\alpha)$	67±4	0.315
4/4 m PZ/2MPZ	$-R(-12998 + 14684\alpha)$	66±3	0.341

* The heat of absorption of CO₂ at mid-loading.

** The loading where P_{CO₂} is 1.5 kPa at 40 °C, calculated from the 40–160 °C empirical models.

Fogging Test

The 2-stage flash pilot plant operation indicated that there might be fogging inside the condenser of the flashes, causing solids to form after the condenser and clog the pipe. Therefore, a fogging device has been set up, adapted to the high temperature/pressure VLE apparatus, and a fogging test was performed to 8 m PZ at 150 °C.

The 2-stage flash was at 150 °C, with one stage at high pressure and the other at low pressure. According to the previous study (Rochelle et al., 2010b), PZ volatility is higher at lean loading than at rich loading. Higher PZ volatility is more likely to cause fogging. So the vapor exiting the low pressure flash, which corresponds to leaner loading and higher PZ volatility, is easier to form fogging. According to Eric Chen, the pressure of the low pressure flash is about 80–120 psig (6.5–9.3 bar). Therefore the experimental condition of this run was set within this pressure range, at 150 °C.

Apparatus

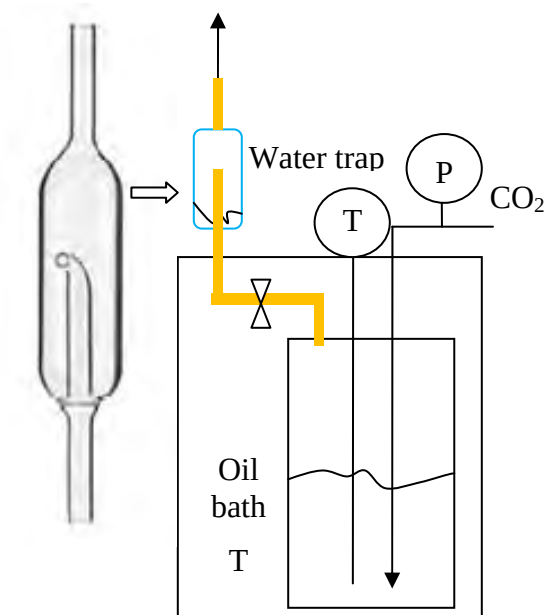


Figure 3: Experimental Setup for Fogging Tests

The testing setup is shown in Figure 3. A transparent glass water trap was used as the condenser. The bottom of the water trap is connected to the vapor sampling line of the high

temperature/pressure VLE apparatus (Rochelle et al., 2011). The orange lines are the vapor flow lines. The tube above the oil level was made of glass and the other tubes are stainless steel.

Temperature of the equilibrium cell was measured by a K-type thermocouple and read by an HH506RA data logger from Omega[®].

A pressure transducer (Druck[®] PTX 611, 0–30 bar absolute) was connected to a signal converter and data logger NI USB 6009. LabView[®] SignalExpress[®] software was used for data recording. The pressure reading system was calibrated by a dead weight pressure tester (S/N 19189/278, by Budenberg Volumetrics, Inc.).

Procedures

About 300 mL of 8 m PZ with 0.32 CO₂ loading was prepared and filled into a 600 mL SS pressure vessel (Parr Instrument Co.). N₂ was used to purge air and the vessel was sealed and placed in the oil bath. The oil bath was heated to 150 °C and CO₂ at a certain pressure was fed into the vessel. After about 30–40 min, when the system reached equilibrium, the metering valve (Swagelok) was opened and vapor flowed through the water trap. The vapor pressure dropped to about 1 atm after exiting the metering valve and the vapor was cooled in the water trap by air. Fogging can be observed through the glass wall of the water trap. Some of the vapor exited from the top, and the rest condensed and accumulated inside the water trap. The condensate was collected and analyzed by total inorganic carbon analyzer and titration.

Analytical Methods

Total Inorganic Carbon (TIC)

The concentration of CO₂ in solution was determined by TIC analysis. The liquid samples collected through each run were diluted by a factor of 50. About 10–15 µL diluted sample was injected into a CO₂ analyzer (Model 525, Horiba PIR 2000). Details can be found in Appendix B.2 of Hilliard's dissertation (2008).

Acid Titration

The total alkalinity of each liquid sample was determined by acid titration using a Metrohm-Peak 835 Titrando equipped with an automatic dispenser, Metrohm-Peak 801 stirrer, and 3M KCl pH probe. Details are available in Appendix A.3 of Hilliard (2008) and Appendix F of Sexton (2008).

Results and discussions

Pictures were taken when the total pressure dropped from 12.3 to 7.3 bar, 150 °C. At these conditions there was steam coming out of the top of the water trap. For some conditions fogging can be observed inside the water trap. Figure 4 was taken at around 7.7–7.3 bar and there is white fog inside the water trap.



Figure 4: Fogging Test at 150 °C, 7.3–7.7 bar

During the experiment, the water kept condensing on the inside wall of the water trap, making it harder for fogging observation. To avoid this, the water trap was taken off for condensate collection, washed with DI water, and reinstalled to the vapor line.

Conclusions

1. CO₂ partial pressure and heat of absorption in 0.9–13 m PZ can be expressed as follows:

$$\ln P_{CO_2} = 35.5 + \frac{-11067}{T} - 21.5 \cdot \alpha^2 + 4710 \cdot \frac{\alpha}{T} + 11419 \frac{\alpha^2}{T}$$

$$\Delta H_{abs} = -R(-11067 + 4710\alpha + 11419\alpha^2) \text{ (J/mol CO}_2\text{)}$$

2. CO₂ partial pressure in 8 m 2MPZ and heat of absorption can be expressed as follows:

$$\ln P_{CO_2} = 40.1 + \frac{-12513}{T} - 22.1 \cdot \alpha^2 + 14099 \cdot \frac{\alpha}{T}$$

$$\Delta H_{abs} = -R(-12513 + 14099\alpha) \text{ (J/mol CO}_2\text{)}$$

3. Fogging formed in the outlet vapor stream of 150 °C 7.3–7.7 bar CO₂ loaded 8 m PZ.

Future Work

1. Complete fogging tests at various temperature, pressure, vapor flow rates, and find the boundary conditions of fogging.
2. Add a third equilibrium cell to the high temperature/pressure VLE apparatus and conduct experiments with MEA-H₂O, test with MEA-CO₂-H₂O and PZ-CO₂-H₂O systems.
3. Improve the MEA-CO₂-H₂O model and PZ-CO₂-H₂O model in Aspen Plus[®].
4. Specific heat capacity measurement with 8 m PZ.
5. Dissertation writing.

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Binary Amine-Water Modeling and MDEA/PZ C_p

Quarterly Report for January 1 – March 31, 2011

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Supported by the Luminant Carbon Management Program

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Abstract

The partition coefficient, or the ratio of the amine concentration in water near infinite dilution to its concentration in the vapor, of 21 amines (12 amines from this work and 9 alkylamines) were successfully modeled by using a group contribution approach by Hine and Mookerjee (1974). The residual errors between measured and predicted values were less than 5%. The empirical expression used to predict the amine partition coefficient at infinite dilution in water at 25 °C is: $\log K_{\text{amine}, 25\text{ }^{\circ}\text{C}} = 0.389 + 3.08 \cdot \text{OH}(\text{C}) - 0.124 \cdot \text{CH}_2(\text{C})(\text{N}) + 1.79 \cdot \text{N}(\text{C}_3) - 0.34 \cdot \text{CH}_3(\text{X}) + 1.37 \cdot \text{C}_{\text{cy}}\text{H}_2(\text{C}_{\text{cy}})(\text{N}_{\text{cy}}) + 0.58 \cdot \text{N}_{\text{cy}}\text{H}(\text{C}_{\text{cy}})_2 + 0.14 \cdot \text{CH}_2(\text{C})(\text{O}) + 3.45 \cdot \text{NH}_2(\text{C}_{\text{cy}}) + 1.39 \cdot \text{C}_{\text{cy}}\text{H}(\text{N}_{\text{cy}})(\text{C}_{\text{cy}})(\text{CH}_3) + 3.45 \cdot \text{NH}(\text{C})_2 - 0.103 \cdot \text{CH}_2(\text{C})_2 - 0.007 \cdot \text{CH}(\text{C})_2(\text{N})$. The subscript cy designates a cyclic structure.

The experimental heat capacity method was validated by benchmarking H₂O and Al₂O₃ C_p measurements to literature values. It was determined that there is a ±10% uncertainty in the data which is well within the margin of error expected for this methodology. C_p for the 7 m MDEA/2 m PZ solution ranges from ~3.06–3.95 J/g*K over the loading range 0.04–0.27 mol CO₂/mol total alkalinity for 40–120 °C. The blend C_p decreases as loading increases as CO₂ appears to have negligible heat capacity. The C_p for the 5 m MDEA/5 m PZ blend ranges from ~2.92–3.56 J/g*K over the loading range 0.19–0.31 mol CO₂/mol total alkalinity for 40–120 °C. The unloaded C_p for the 5/5 blend is less than that of the 7/2 blend at any given temperature because the enthalpy contribution of MDEA to the total enthalpy is less as the MDEA concentration in the 5/5 is less than in the 7/2. MDEA has the greatest C_p of all the components present in the blend.

Introduction

The first part of this report discusses binary amine-water system modeling using the methodology developed by Hine and Mookerjee (1974). This approach predicts the partition coefficient, referred to as the activity coefficient by the authors, in a binary system by summing the contributions of molecular groups in the amine structure similar to UNIFAC methodology. The method under discussion appears to be far less involved, yet is more accurate, than UNIFAC for predicting partition coefficient at infinitely dilute condition. The molecular group parameters for this method were established using data for over 290 compounds, including alkylamines, specifically at infinitely dilute condition in water. This work expands on the existing

methodology to include coverage of amines particularly useful for CO₂ capture, such as MEA and PZ, and presents newly regressed parameters for these amines and alkylamines.

This work also reports preliminary measurements of heat capacities for 7 m MDEA/2 m PZ and 5 m MDEA/5 m PZ. Heat capacity measurements are integrated into Aspen Plus[®] in order to construct a thermodynamically rigorous and consistent model of the blend. The experimental heat capacities were measured using a Differential Scanning Calorimetry technique with Indium metal to calibrate for internal instrument sensitivity and aluminum oxide (Al₂O₃) to calibrate for heat flow fluctuation. Experimental benchmarking was performed in validating the heat capacities of (1) water and (2) 3.7 m MDEA/2.5 m PZ obtained from this method to literature. The blend heat capacities are ultimately modeled using an empirical expression which relates C_p to the individual component heat capacities and loading.

Experimental Methods

Amine Volatility Measurements

Amine volatility was measured in a stirred reactor coupled with a hot gas FTIR analyzer (Fourier Transform Infrared Spectroscopy, Temet Gasmet Dx-4000) as shown in Figure 1.

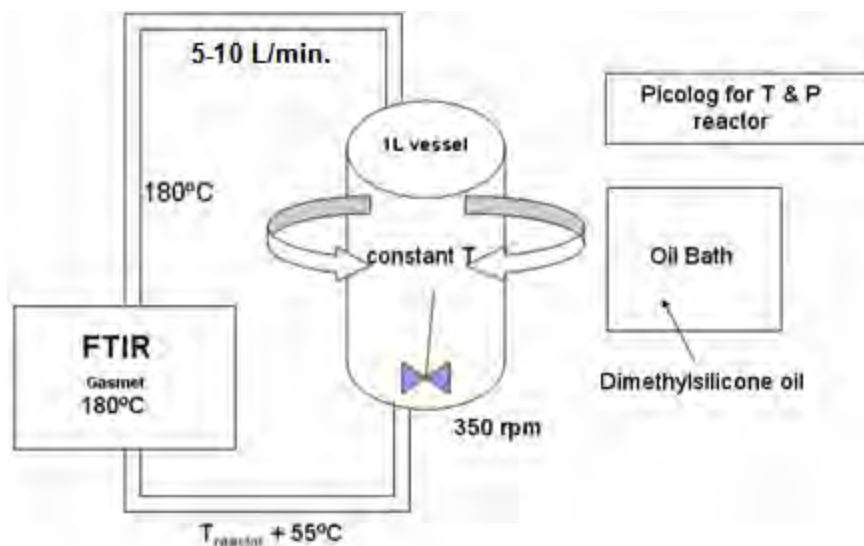


Figure 1: Amine Volatility Experimental Setup

The 1 L glass reactor was agitated at 350 rpm. Temperature in the reactor was controlled by circulating dimethylsilicone oil. The reactor was insulated with thick aluminum insulation material. Vapor from the headspace of the reactor, primarily 5–10 L/min., was circulated by a heated sample pump to the FTIR through a heated Teflon line. Both the line and analyzer were maintained at 180 °C to prevent possible condensation or adsorption of amine. The FTIR measured amine, CO₂, and water concentration in the gas. After the gas passed through the FTIR, it was returned to the reactor through a heated line maintained ~55 °C hotter than the reactor. It was determined that the 55 °C difference is sufficient to ensure that the return gas does not upset the solution that is in equilibrium with the gas inside the reactor, and to prevent potential heat loss at the bottom of the reactor.

Amine Concentration

The amine concentration was determined by acid titration (Hilliard, 2008) with an automatic Titrand series titrator with an automatic equivalence point detection. A 300X diluted sample was titrated with 0.1 N H_2SO_4 to a pH of 2.4. The amount of acid needed to reach the equivalence point at a pH of 3.9 was used to calculate the total amine concentration.

Loading Verification

The CO_2 loading was verified by Total Inorganic Carbon (TIC) analysis. The samples are diluted in H_2O and subsequently dissolved in 30 wt % H_3PO_4 to release aqueous CO_2 -containing products. The CO_2 is carried by an N_2 stream to an infrared detector which analyzes and records the CO_2 composition in terms of voltage. The resulting voltage peaks are integrated and correlated to CO_2 concentrations using a 1000 ppm inorganic carbon standard made from a mixture of potassium carbonate and potassium bicarbonate (Ricca Chemical, Pequannock, NJ).

Heat Capacity Measurement

A 304-stainless steel pan was filled to capacity with 60 μL of solution sample before being sealed with a lid and O-ring. A vapor headspace of roughly 5–10% in volume was estimated to exist in the sealed unit. The sample pan was then placed against an empty reference pan inside a Differential Scanning Calorimeter (DSC) instrument to measure the difference in the amount of heat absorbed by the two pans. This amount of heat differential was subsequently used to determine the heat capacity of the solution. Below is a snapshot inside the DSC sample cell where the differential heat absorbed by a reference versus a sample cell is measured.



Figure 2: Snapshot of DSC Sample Cell

The cell constant and temperature response of the DSC instrument have to be calibrated using Indium metal, which has a known melting point (156.6 $^{\circ}\text{C}$). The cell constant is an internal machine parameter that is used to adjust for subtle differences in the calorimetric response of the unit. In addition, the temperature calibration is done to ensure that the sample thermocouple is reading correctly under experimental conditions.

Theory

Binary Amine-Water System Modeling using Group Contribution

The volatilities of amines infinitely diluted in water are modeled as partition coefficients K . These coefficients are estimated using a group contribution approach established by Hine and Mookerjee (Hine et al., 1974). The partition coefficient, referred to as an activity coefficient by the authors, is:

$$K = c_w / c_g \quad (1)$$

c_w is the concentration of amine in a dilute aqueous solution at 25 °C (moles per liter, or molarity [M])

c_g is the concentration of amine in the gas phase, or its volatility at 25 °C ([M])

Dilute amine solutions (0.3–2 m) were used for experimental volatility measurements as the partition coefficient at these low concentrations is comparable to what it would be at infinite dilution.

MDEA/PZ Blend C_p Determination

The heat flow response of the DSC instrument is calibrated each day by determining the accuracy of measured Al_2O_3 C_p relative to literature values. The relative difference in accuracy between measured and literature values is expressed as the calorimetric constant, E , which is ultimately used in determining C_p for the blend.

$$E = \left[\frac{b}{60 * D_{st}} \right] \left[W_{st} \cdot C_p^{\text{Al}_2\text{O}_3} + \Delta W \cdot C_p^{\text{pan}} \right] \quad (2)$$

D_{st} is the vertical displacement between the empty sample pan and the Al_2O_3 DSC thermal curves at a given temperature,

W_{st} the mass of Al_2O_3 sample, mg,

$C_p^{\text{Al}_2\text{O}_3}$ is the specific heat capacity of Al_2O_3

The C_p of the sample is determined as follows:

$$C_p(s) = \left[\frac{60 \cdot E \cdot D_s}{W_s \cdot b} \right] - \left[\frac{\Delta W \cdot C_p^{\text{pan}}}{W_s} \right] \quad (3)$$

$C_p(s)$ is the specific heat capacity of the sample, kJ/kg-K,

E is the calorimetric sensitivity of the DSC apparatus,

B is the heat rate, 5 °C/min,

D_s is the vertical displacement between the empty sample pan and the sample DSC thermal curves at a given temperature, mW,

W_s is the mass of the sample, mg,

ΔW , is the difference in mass between the reference pan and the sample pan, and

C_p^{pan} is the specific heat capacity of the 304 stainless steel pans.

Data

Table 1 gives the amine Henry's constants and partition coefficients at 25 °C.

Table 1: Henry's Constants and Partition Coefficients of Amines at 25 °C (MEA data from Hilliard)

Amine	$H_{25\text{ °C}}$ (Pa)	$K_{25\text{ °C}}$
MDEA	2.54	5.49E+07
DGA	12.1	7.87E+06
2-MPZ	12.5	1.14E+07
EDA	16.7	1.12E+07
PZ	18.1	4.18E+06
DAP	21.6	8.30E+06
MEA	23.9	6.11E+06
1-MPZ	26.2	6.42E+06
HMDA	27.5	5.36E+06
MAPA	33.3	1.70E+06
AMP	81.6	5.02E+06
1,4-DMPZ	254	5.44E+05

The heat capacity for both 7 m MDEA/2 m PZ and 5 m MDEA/5 m PZ blends at a range of loading is provided in Table 2.

Table 2: Experimental C_p (kJ/kg.K) for MDEA/PZ

T (°C)	7 m MDEA/2 m PZ			
	ldg 0	ldg 0.04	ldg 0.146	ldg 0.27
40	3.70	3.52	3.23	3.06
45	3.74	3.56	3.27	3.10
50	3.77	3.59	3.31	3.13
55	3.80	3.62	3.33	3.15
60	3.83	3.65	3.35	3.17
65	3.86	3.68	3.38	3.20
70	3.89	3.71	3.40	3.23
75	3.92	3.73	3.42	3.26

80	3.95	3.76	3.45	3.29
85	3.98	3.79	3.47	3.32
90	4.01	3.82	3.50	3.36
95	4.04	3.84	3.52	3.38
100	4.06	3.86	3.55	3.42
105	4.09	3.89	3.57	3.45
110	4.11	3.91	3.60	3.48
115	4.13	3.93	3.63	3.51
120	4.13	3.95	3.66	3.54
5 m MDEA/5 m PZ				
T (°C)	ldg 0	ldg 0.186	ldg 0.315	
40	3.50	3.16	2.92	
45	3.53	3.20	2.96	
50	3.57	3.23	2.99	
55	3.60	3.26	3.01	
60	3.63	3.29	3.04	
65	3.66	3.31	3.06	
70	3.69	3.34	3.08	
75	3.72	3.36	3.11	
80	3.75	3.39	3.13	
85	3.77	3.41	3.16	
90	3.80	3.44	3.19	
95	3.82	3.46	3.20	
100	3.85	3.48	3.23	
105	3.87	3.49	3.25	
110	3.89	3.51	3.27	
115	3.91	3.53	3.29	
120	3.93	3.56	3.31	

loading is moles of CO₂/mol of alkalinity

Results

Binary Amine-Water System Modeling

Amine Henry's constants at 25 °C were extrapolated from measured Henry's constants at 40 °C–70 °C using a semi-empirical relationship where $\ln H = a + b \ln(T/298.15) + c(T-298.15)$. Table 3 provides the regressed parameters for the above expression for each amine studied.

Table 3: Regressed Temperature-Dependent Parameters for Amine H Constant Extrapolation

	MDEA			MEA	
	Coefficient	Std. Error		Coefficient	Std. Error

Intercept (a)	0.931	0.110		3.17	0.252
b	155	26.6		68.5	71.1
c	-0.415	0.081		-0.151	0.218
	PZ			1,2-DAP (Diaminopropane)	
Intercept (a)	2.90	0.287		3.08	0.376
b	-64.1	71.1		209	106
c	0.269	0.217		-0.569	0.326
	DGA			1-Methyl PZ	
Intercept (a)	2.50	0.041		3.27	0.247
b	-0.055	8.06		107	69.8
c	0.041	0.024		-0.236	0.215
	2-Methyl PZ			AMP	
Intercept (a)	2.53	0.214		4.40	0.125
b	23.9	51.9		37.5	30.1
c	0.012	0.158		-0.039	0.092
	MAPA			HMDA	
Intercept (a)	3.50	0.254		3.31	0.251
b	-175	71.0		20.9	60.8
c	0.611	0.218		-0.002	0.185
	EDA			1,4-Dimethyl PZ	
Intercept (a)	2.82	0.112		5.54	0.115
b	55.7	37.6		82.7	27.8
c	-0.093	0.116		-0.153	0.085

The R^2 correlation values for these regressed fits are all ~0.99 which indicate highly robust fits despite a number of relatively large standard errors. The H constants and partition coefficients predicted at 25 °C are both provided in Table 1.

The activity coefficients of 21 different amines, which consist of 12 measured amines and 9 alkylamines from literature, were fitted using a total of 12 group contribution parameters. The majority of these parameters were extracted from Hine and Mookerjee (1974), with 3 new parameters added to capture the unique structural contribution of cyclic C and N molecules. These additions were necessary to account for PZ and PZ derivatives. The partition coefficient at 25 °C is estimated using group contributions as follows:

$$\log K_{\text{amine}, 25^\circ\text{C}} = \text{intercept} + \sum \text{coefficient}_i(\text{no. of group } i) \quad (4)$$

where i represents a particular group. The group notation used is such that the group of interest is connected to adjoining groups enclosed in parentheses. The subscript cy designates a group on a cyclic structure. The symbol X stands for any atom C, O, or N.

Table 4 shows the regressed parameter values of the group contributions and standard errors.

Table 4: Group Contribution Parameters used in Estimating Partition Coefficients

Group	Coefficient	Standard error
Intercept	0.389	0.254
OH(C)	3.076	0.128
CH ₂ (C)(N)	-0.124	0.082
N(C ₃)	1.786	0.328
CH ₃ (X)	-0.340	0.106
C _{cy} H ₂ (C _{cy})(N _{cy})	1.371	0.071
N _{cy} H(C _{cy}) ₂	0.580	0.097
CH ₂ (C)(O)	0.135	0.097
NH ₂ (C)	3.445	0.137
C _{cy} H(N _{cy})(C _{cy})(CH ₃)	1.385	0.203
NH(C) ₂	3.447	0.168
CH ₂ (C) ₂	-0.103	0.027
CH(C) ₂ (N)	-0.007	0.195

Table 5 summarizes the experimental partition coefficients at infinite dilution at 25 °C, the predicted values, and the percent errors between the two sets of values.

Table 5: Summary of Measured and Predicted Amine Partition Coefficients

Amine	log K _{measured, 25 °C}	log K _{predicted, 25 °C}	% Error
MDEA	7.74	7.74	0
PZ	6.90	7.03	2.00
DGA	7.06	7.06	0
2-MPZ	7.05	7.05	0
MAPA	6.62	6.59	-0.46
EDA	6.92	7.03	1.62
MEA	6.79	6.79	0
DAP	6.81	6.81	0
1-MPZ	6.73	6.45	-4.10
AMP	6.23	6.23	0
HMDA	6.70	6.62	-1.21
DMPZ	5.74	5.87	2.40

Ethylamine	3.38	3.37	-0.30
Propylamine	3.3	3.27	-1.01
Butylamine	3.21	3.16	-1.44
Pentylamine	3.00	3.06	2.03
Hexylamine	2.96	2.96	-0.07
Dimethylamine	3.14	3.16	0.49
Diethylamine	2.98	2.91	-2.43
Dipropylamine	2.68	2.70	0.81
Dibutylamine	2.43	2.50	2.71

It appears that the partition coefficients at infinite dilution and 25 °C can be adequately predicted using the group contribution scheme established by Hine and Mookerjee (1974). The use of cyclic parameters greatly enhances the ability to capture the unique structural contributions of PZ and its derivatives with percent errors being less than 5%. The group contribution scheme also adequately models straight chained amines; however, the percent error increases slightly with structural complexity and/or the number of methyl groups present.

MDEA/PZ C_p Method Validation: Benchmarking with Water, Al_2O_3 , and MDEA/PZ

The heat capacity of a given water sample was measured on various days over two months to validate the method and to determine the experimental precision. Figure 3 illustrates the measured water C_p over time.

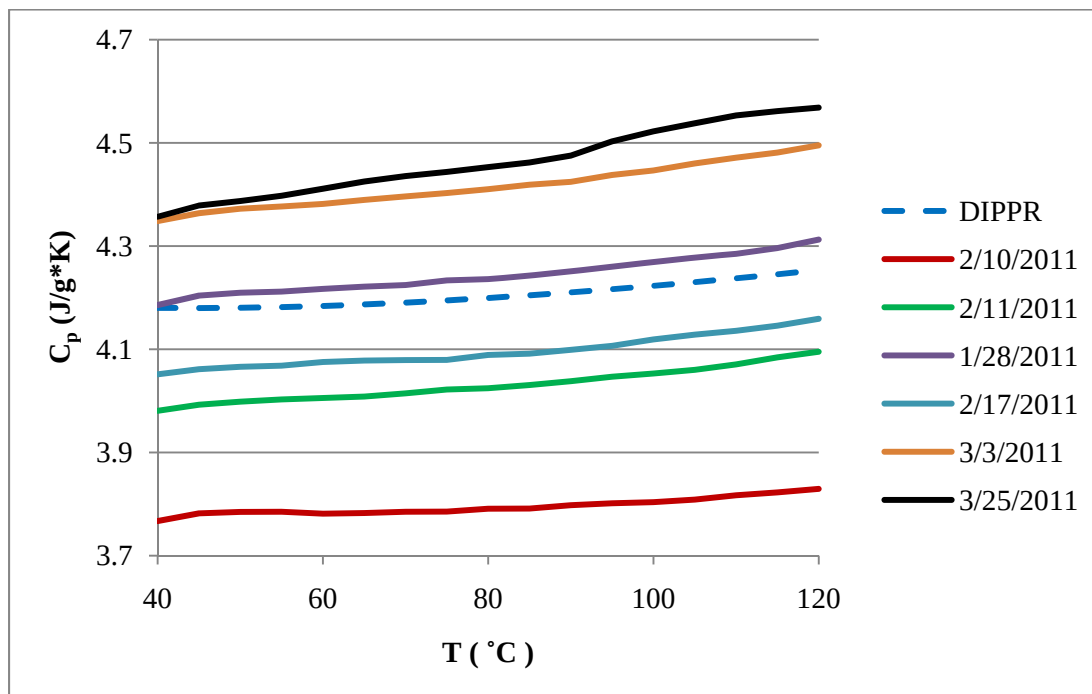


Figure 3: Experimental Validation: Measured C_p for a water sample for 40–120 °C

For the most part, the measured water C_p agrees with literature values obtained from DIPPR (2) except for what appears to be outlier data obtained on 2/10/11. It was determined that both the

experimental accuracy and precision was $\pm 10\%$ from literature. This margin of error is expected historically for this experimental technique.

The heat capacity of Al_2O_3 was also measured and compared against literature values for benchmarking purposes. Figure 4 shows the accuracy of measured Al_2O_3 C_p relative to literature data over a given time period.

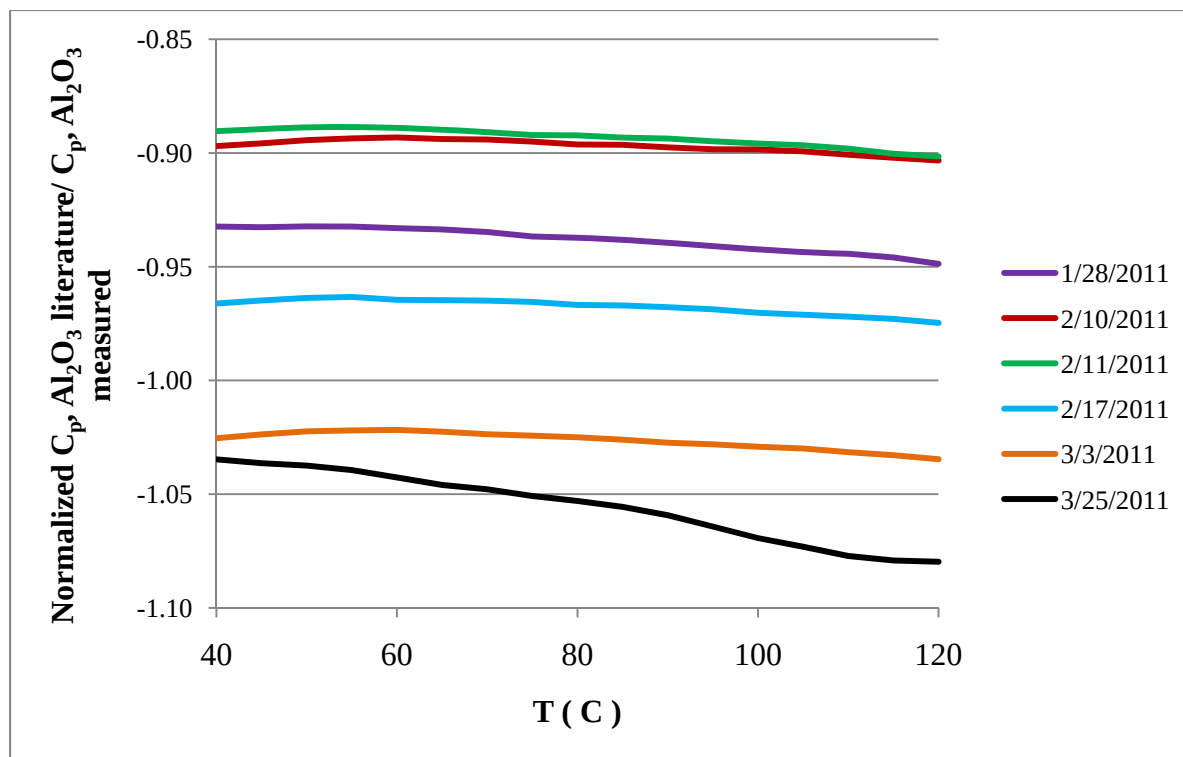


Figure 4: Method Validation: Measured C_p 's for Al_2O_3 sample relative to Literature Values

Similar to the case of the water sample, the measured Al_2O_3 C_p also shows a $\pm 10\%$ margin of error compared to literature values overall. Thus one can conclude that the measured MDEA/PZ C_p will also have a 10% error margin.

The C_p of the 3.7 m MDEA/2.5 m PZ blend was also measured and compared to experimental measurements by Chen et al. (2010). Figure 5 shows the measured C_p from the two works.

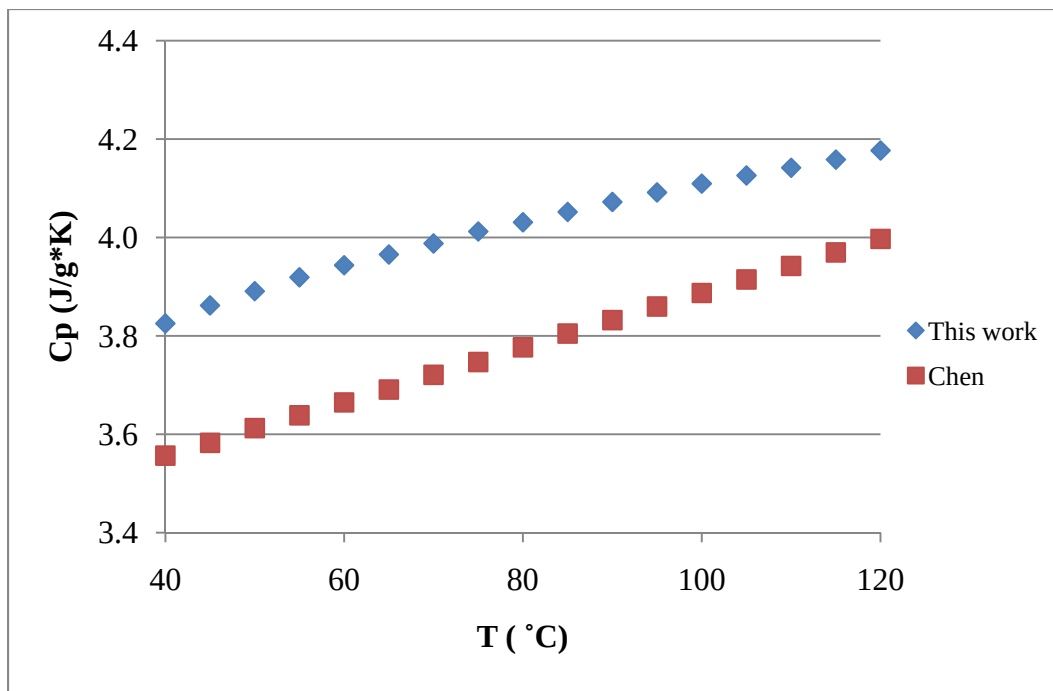


Figure 5: Method Validation: Measured C_p for 3.7 m MDEA/2.5 m PZ Blend Compared to Chen et al. (2010)

The measured C_p for this blend agrees with Chen's data within the expected 10% margin of error.

Preliminary measurements of C_p for the 7 m MDEA/2 m PZ blend are presented in Figure 6.

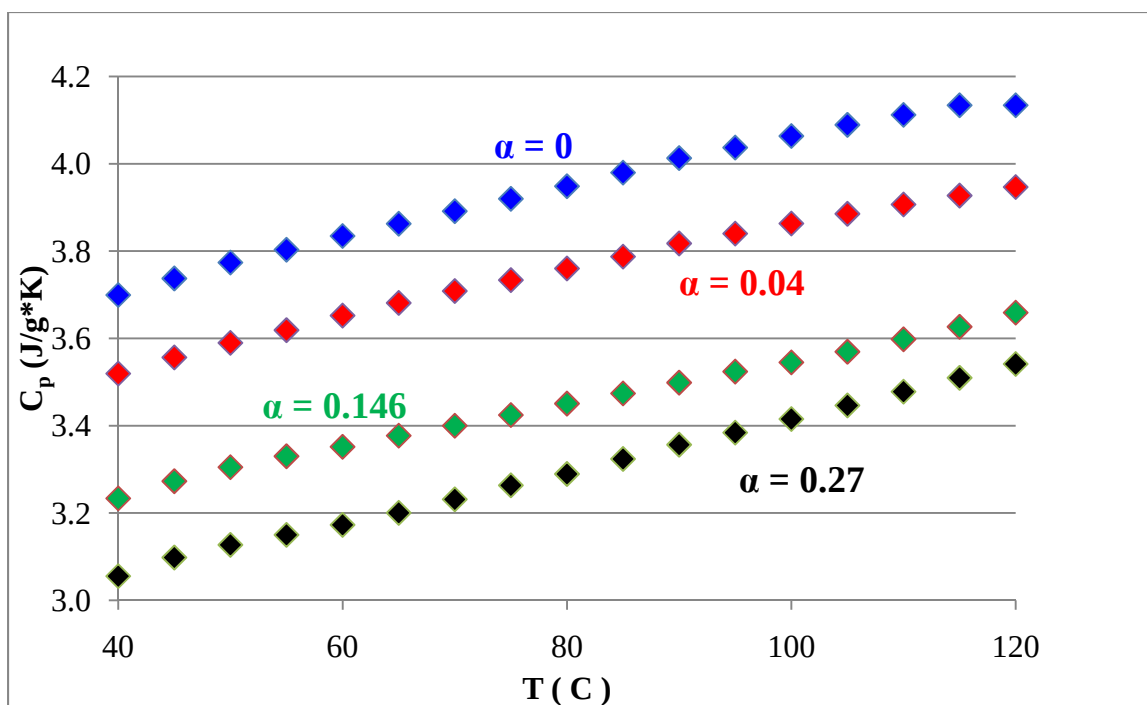


Figure 6: Preliminary C_p for 7 m MDEA/2 m PZ Blend from 40–120 °C

These preliminary C_p measurements will later be corrected for possible CO_2 and H_2O vaporization into the headspace (~1–15% of the total volume) above the solution. This vaporization phenomenon is seen graphically as deviation of the individual curves from linearity starting at ~90 °C and higher as significant vaporization is expected to occur. This issue becomes worse at higher loading due to the greater amounts of CO_2 present. The blend C_p is seen to decrease as loading increases, most likely because liquid CO_2 in solution has negligible heat capacity. The heat contribution of CO_2 , relative to the heat contributions of amines and water, to the total heat of solution is negligible. In other words, no significant change, or increase, in the total amount of heat is required to raise the temperature of an increasingly larger body of solution (due to increasingly greater CO_2 content).

Figure 7 shows preliminary measurements of C_p for the 5 m MDEA/5 m PZ blend.

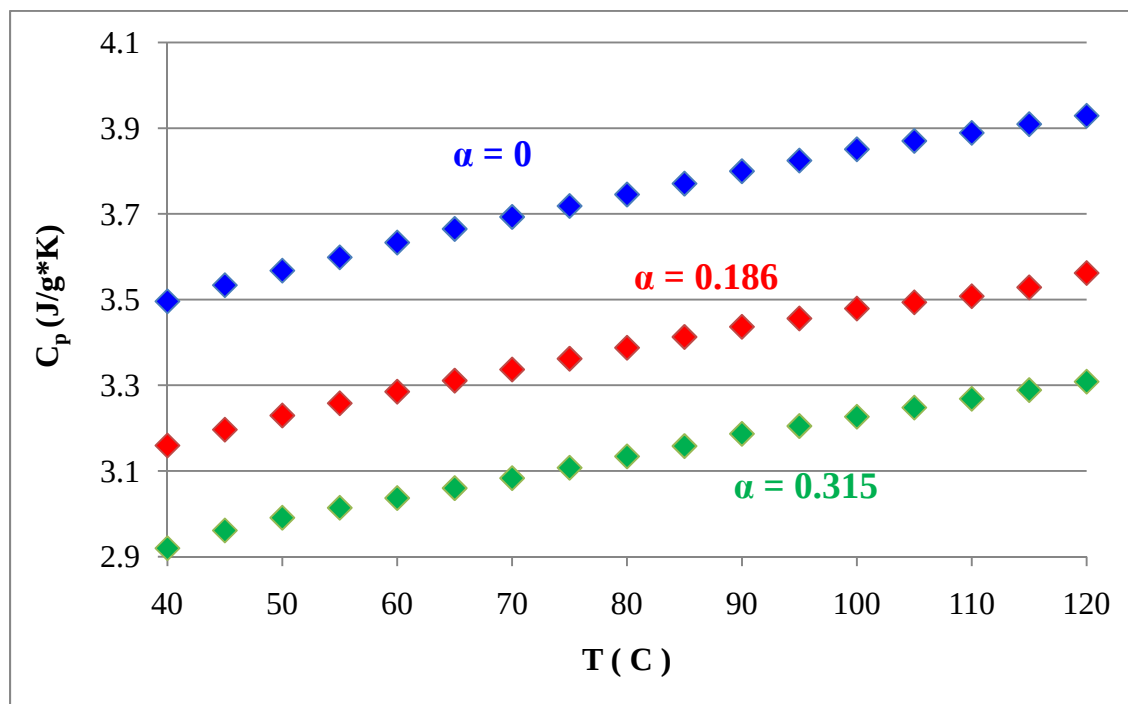


Figure 7: Preliminary C_p for 5 m MDEA/5 m PZ from 40–120 °C

Preliminary C_p for the 5 m MDEA/5 m PZ blend will also have to be corrected for vaporization in the case of the rich loading at 90–120 °C. All of the observations regarding the heat capacity relationship to loading mentioned previously also apply in this case. Finally, at zero loading and any given temperature, the C_p of the 5 m MDEA/5 m PZ blend is less than that of the 7 m MDEA/2 m PZ blend because the heat contribution of MDEA to the total heat is less in the former case due to there being less MDEA present (5 m MDEA compared to 7 m MDEA). The heat contribution from PZ is secondary compared to MDEA because MDEA has a greater intrinsic C_p .

Conclusions

1. The logarithm of amine partition coefficients for amines infinitely diluted in water (at 25 °C) have been adequately predicted using a molecular group contribution scheme established by Hine and Mookerjee with the addition of 3 new parameters used to account for the cyclic

structures of PZ and its derivatives. The percent errors between measured and predicted values are less than 5%.

2. It was determined that C_p measurements for the MDEA/PZ blend have a $\pm 10\%$ margin of error. This error quantification resulted from benchmarking activities that involved measuring water, Al_2O_3 , and MDEA/PZ heat capacities over time and comparing them to literature values.
3. At 40–120 °C, C_p of the unloaded 7 m MDEA/2 m PZ blend ranges from ~ 3.70 – 4.13 J/g*K. Over a range of very lean to very rich loading (~ 0.04 – 0.27 mol CO_2 /mol alkalinity), C_p is ~ 3.06 – 3.95 J/g*K.
4. At 40–120 °C, C_p of the unloaded 5 m MDEA/5 m PZ blend ranges from ~ 3.50 – 3.93 J/g*K. At any given temperature, C_p of the 5/5 blend is less than that of the 7/2 blend due to a smaller contribution of MDEA enthalpy to the total heat of solution. Over a range of lean to rich loading (~ 0.186 – 0.315 mol CO_2 /mol alkalinity), C_p is ~ 2.92 – 3.56 J/g*K.
5. CO_2 appears to have a negligible heat capacity. Therefore, at any given temperature, C_p of the blend decreases as loading is increased.

Future Work

The C_p data for MDEA/PZ blends will be corrected for potential CO_2 and H_2O vaporization into the headspace. An empirical model will be developed to predict the heat capacity for the MDEA/PZ solution as a function of temperature, loading, and amine concentration. NMR analysis at key loadings will also be performed to validate speciation predicted by Aspen[®] Fawkes MDEA-PZ model. This model will also be refined to adequately predict volatility, CO_2 solubility, C_p , and heats of absorption for the blend. Finally, the volatility of 6 m HMDA/2 m PZ blend at nominal loading at 40–70 °C will be measured as part of an ongoing screening effort to identify promising new solvents.

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Modeling MDEA/PZ Thermodynamics, Hydraulics, and Kinetics

Quarterly Report for January 1 – March 31, 2011

by Peter Frailie

Supported by the Luminant Carbon Management Program

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The University of Texas at Austin

April 30, 2011

Abstract

The goal of this study is to evaluate the performance of an absorber/stripper operation that utilizes MDEA/PZ. Before analyzing unit operations and process configurations, thermodynamic, hydraulic, and kinetic properties for the blended amine must be satisfactorily regressed in Aspen Plus[®]. Thermodynamic, hydraulic, and kinetic data have been regressed for 8 m PZ, 7 m MDEA/2 m PZ, and 5 m MDEA/5 m PZ. Heat of absorption predictions have been calculated and compared using Aspen Plus[®] calorimetry and the Gibbs-Helmholtz equation. CO₂ absorption rate data for all solvents were fit using the same set of reactions, rate constants, and binary diffusivities. The CO₂ absorption rate was fit with an average deviation of 6.7% over operational loading and temperature ranges for all solvents. The goal for the next quarter is to begin optimizing an absorption/stripping/compression operation using 7 m MDEA/2 m PZ and 5 m MDEA/5 m PZ.

Introduction

The removal of CO₂ from process gases using alkanolamine absorption/stripping has been extensively studied for several solvents and solvent blends. An advantage of using blends is that the addition of certain solvents can enhance the overall performance of the CO₂ removal system. A disadvantage of using blends is that they are very complex compared to a single solvent, thus making them much more difficult to model.

This study will focus on a blended amine solvent containing piperazine (PZ) and methyldiethanolamine (MDEA). Previous studies have shown that this particular blend has the potential to combine the high capacity of MDEA with the attractive kinetics of PZ (Bishnoi, 2000). These studies have supplied a rudimentary Aspen Plus[®]-based model for an absorber with MDEA/PZ. The report also makes the recommendation that more kinetic and thermodynamic data must be acquired concerning the MDEA/PZ blend before the model can be significantly improved. One of the major goals of this study will be to improve the supplied Aspen Plus[®] absorber model with up-to-date thermodynamic and kinetic data. Another major goal of this study will be to make improvements to the MDEA and PZ thermodynamic models, which should simplify the construction of the blended amine model.

Methods and Discussion

During the past quarter the thermodynamics, hydraulics, and kinetics of MDEA, PZ, and MDEA/PZ were finalized and evaluated. What follows is a description of the sequential regression used to develop the models, as well as a brief discussion of each of the incorporated data sets.

Heat of Absorption

There are two primary ways to calculate the heat of absorption using Aspen Plus[®]: (1) applying the Gibbs-Helmholtz equation to CO₂ solubility predictions and (2) calorimetric predictions. Historically, these two methods have predicted drastically different values for the heat of absorption. Much of this discrepancy has been attributed to thermodynamically inconsistent methodology, by which equilibrium constants and thermodynamic properties were not calculated using a consistent set of parameters. This was the primary motivation for calculating equilibrium constants from Gibbs energies rather than temperature-dependent polynomials. The Guy Fawkes model has corrected these inconsistencies. Figure 1 compares the Gibbs-Helmholtz and Aspen Plus[®] calorimetric predictions for the heat of absorption of CO₂ with 8 m PZ.

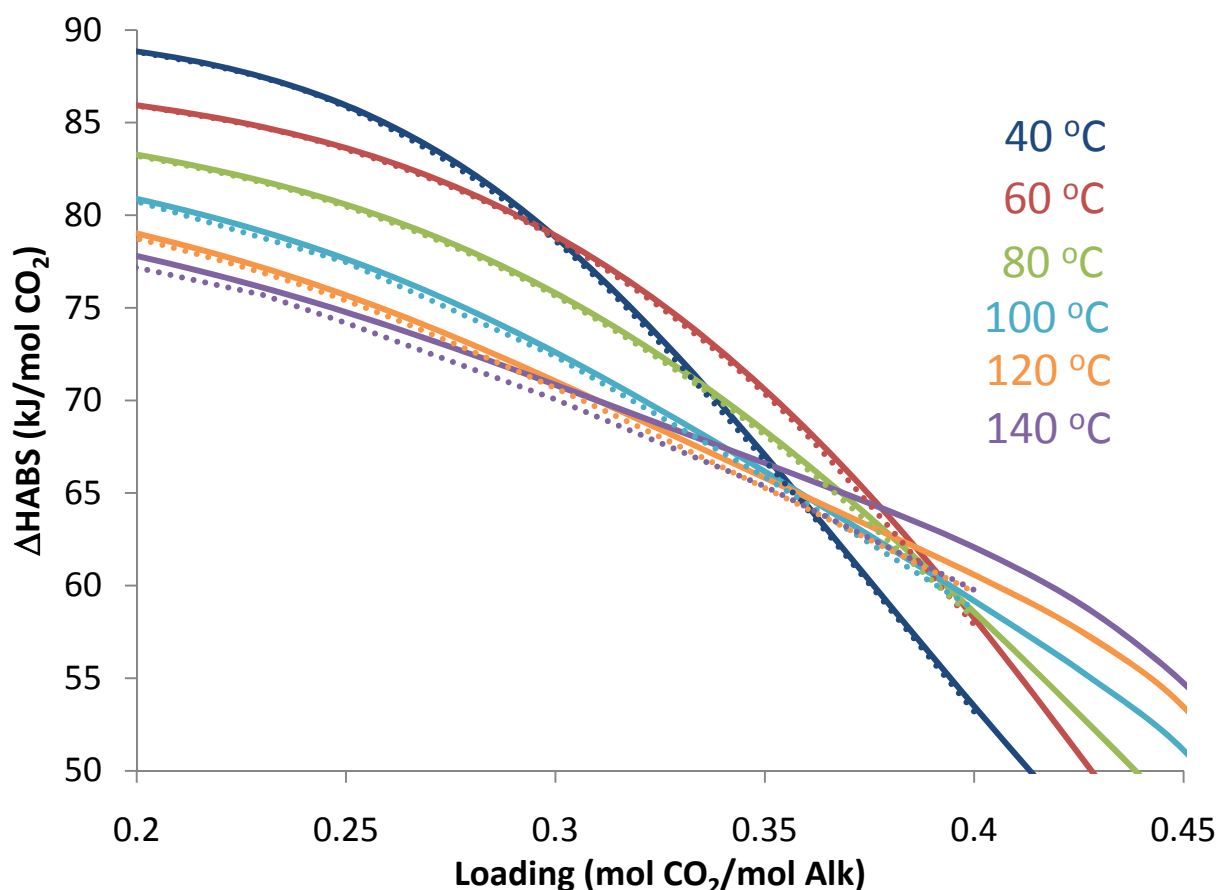
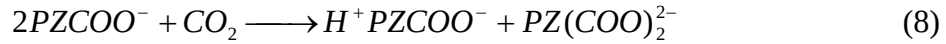
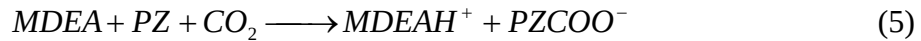
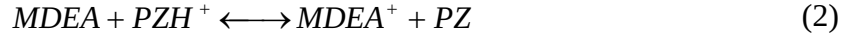


Figure 1: Gibbs-Helmholtz (solid lines) and Aspen Plus[®] calorimetric (dotted lines) predictions for the heat of absorption of CO₂ for 8 m PZ from 40–140 °C.

At low temperatures the two methods have nearly identical predictions for the heat of absorption, but at higher temperatures (>100 °C) Aspen Plus® calorimetry predicts a lower heat of absorption. This discrepancy, though it is relatively small (<5%), is still being investigated.

MDEA/PZ Kinetic Model

Rate data are being incorporated into the model by adjusting reaction rate constants in a wetted wall column (WWC) simulation in Aspen Plus® to match experimental values (Dugas, 2009; Chen, 2010) for the flux of CO₂. Equations 1–8 are the equilibrium and forward kinetic reactions used to model MDEA/PZ.



All reverse rates were calculated using equilibrium constants based on regressed thermodynamic parameters. The ultimate goal is to develop a rate-based model that can predict CO₂ absorption rates in MDEA, PZ, and MDEA/PZ. To accomplish this, all available CO₂ absorption rate data for 8 m PZ, 7 m MDEA/2 m PZ, and 5 m MDEA/5 m PZ were regressed. Because MDEA kinetics are well understood, parameters for Equation 3 were fixed using literature data (Ko, 2000). Parameters for Equations 4–8 were regressed by fitting CO₂ absorption rate data for 8 m PZ (0.20–0.40 loading and 40 °C–100 °C), 7 m MDEA/2 m PZ (0.10–0.26 loading and 40 °C–100 °C), and 5 m MDEA/5 m PZ (0.18–0.37 and 40 °C–100 °C). In the past, the parameters for Equations 4, 6, and 8 would have been fixed by fitting CO₂ absorption rate data for only 8 m PZ. However, under certain conditions these are the primary reactions responsible for CO₂ absorption rate in 5 m MDEA/5 m PZ and, to a lesser extent, 7 m MDEA/2 m PZ.

The first attempt at modeling the kinetics adjusted several rate constants simultaneously for each experimental point. Because the WWC simulation only allows for one adjustable parameter, all forward rates were either fixed or ratioed to another reaction using literature values. Equation 8 was ratioed to Equation 6 using relative CO₂ reaction rates (Cullinane, 2005) and every reaction involving MDEA as the catalyst (5, 7) was ratioed to its PZ counterpart via pKa values (Hetzer, 1968; Hamborg, 2007). Ultimately, the forward rate of Equation 4 was the only independently adjusted parameter.

These forward and reverse reaction rates were adjusted to match CO₂ absorption rate data obtained in the WWC. The data regression tool in Microsoft Excel was used to match these rate constants by adjusting the k_0 and E_A terms in Equation 9 for every forward and reverse reaction.

$$k = k_0 \exp \left[\frac{-E_A}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad (9)$$

Figure 2 compares the predicted and experimental fluxes of CO₂ for 8 m PZ (Δ), 7 m MDEA/2 m PZ (◇), and 5 m MDEA/5 m PZ (□) for both absorption (closed) and desorption (open) experiments from 40 °C–100 °C.

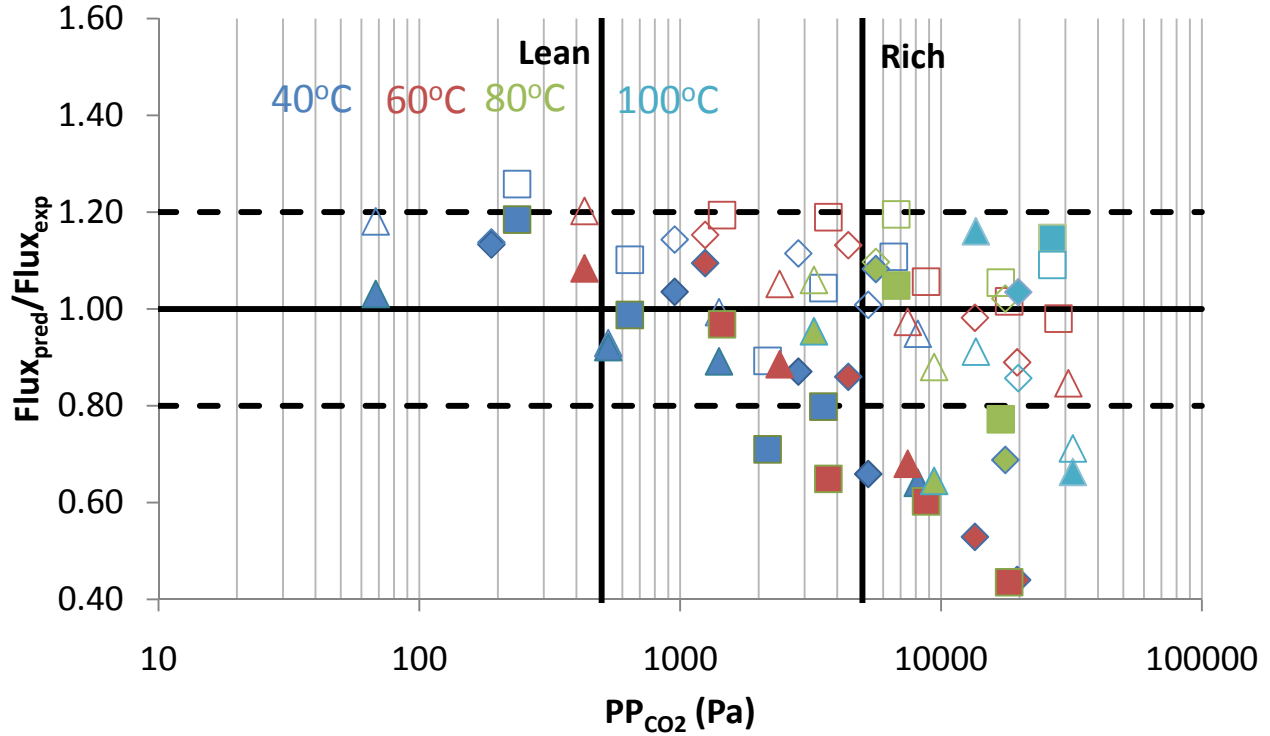


Figure 2: Parity plot comparing predicted and experimental CO₂ flux for 8 m PZ (Δ), 7 m MDEA/2 m PZ (◇), and 5 m MDEA/5 m PZ (□) between 40 °C and 100 °C

The results shown in Figure 2 are unsatisfactory for two reasons: (1) there is a significant discrepancy between the accuracy of absorption and desorption predictions, and (2) the model generally under predicts the flux at higher CO₂ partial pressures. Observation (1) was addressed simply by adjusting the loading (and, thus, equilibrium partial pressure of CO₂) associated with each absorption/desorption pair. Observation (2) required a much more detailed analysis of the effects of reaction rates and binary diffusivities on the overall flux of CO₂. Because kinetic reactions are much faster at higher temperatures (80 °C–100 °C) the absorption of CO₂ is primarily limited by the diffusion of reactants and products between the gas-liquid boundary layer and the bulk liquid. At higher loadings the flux of CO₂ is limited by the diffusion of a dwindling supply of amine between the gas-liquid interface and bulk liquid. It was hypothesized that adjustment of the loadings and diffusion coefficients should eliminate observations (1) and (2), respectively.

Figure 3 compares the predicted and experimental fluxes of CO₂ for 8 m PZ (Δ), 7 m MDEA/2 m PZ (◇), and 5 m MDEA/5 m PZ (□) for both absorption (closed) and desorption (open) experiments from 40 °C–100 °C after adjusting loadings and diffusion coefficients.

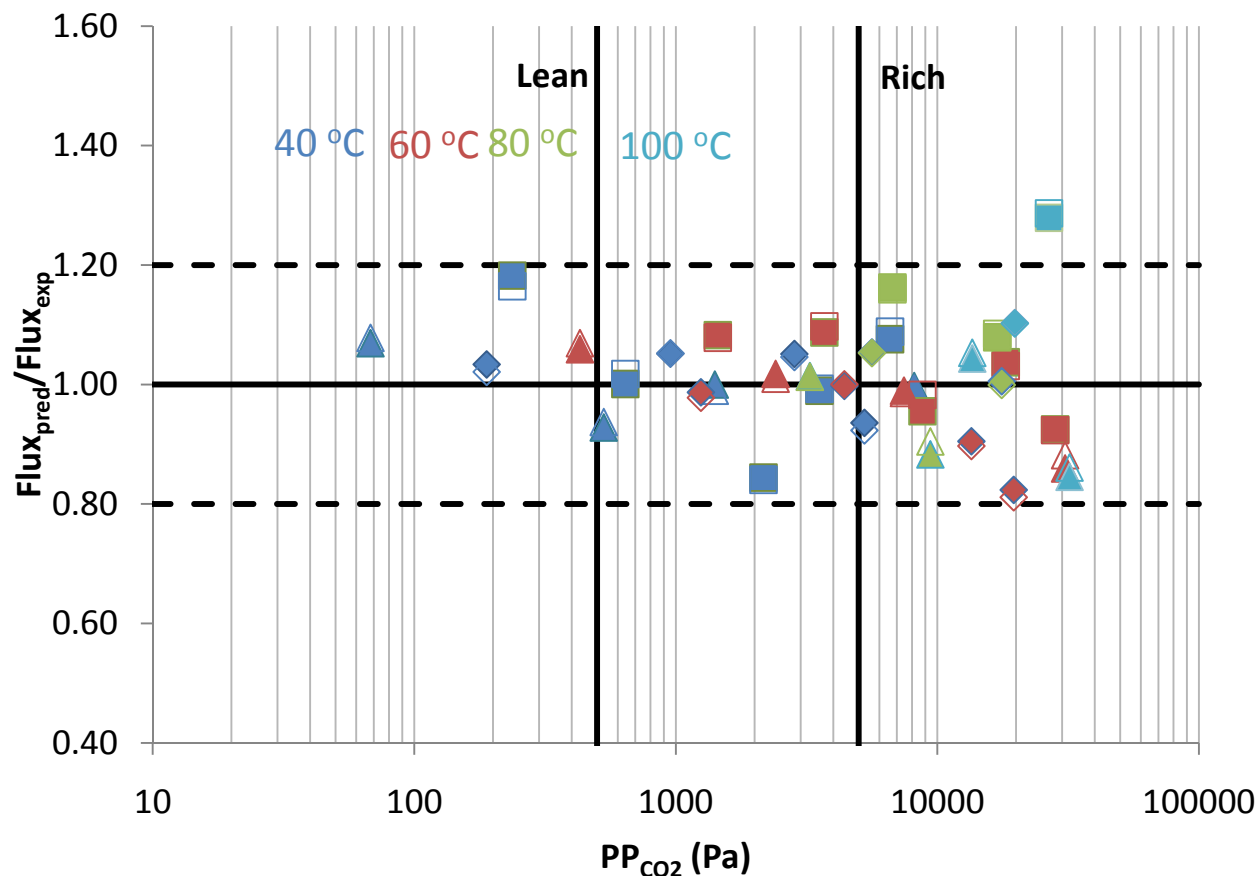


Figure 3: Parity plot comparing predicted and experimental CO₂ flux for 8 m PZ (Δ), 7 m MDEA/2 m PZ ($\diamond$), and 5 m MDEA/5 m PZ ($\square$) between 40 and 100 °C with adjusted loadings and diffusion coefficients.

In addition to correcting the insufficiencies of the earlier kinetic model, the new model has reduced the average error from 16.0% to 6.7%. Rather than adjust the rate constants and binary diffusivity of reactants and products for every point, 7 points were chosen (4 from 8 m PZ and 4 from 7 m MDEA/2 m PZ) to fit the kinetics. Points for 8 m PZ at 40 °C and 80 °C and 0.30 loading were used to regress the k_0 and E_A of Equations 6 and 8. Just as before, the rate constant of Equation 8 was related to the rate constant of Equation 6 using relative CO₂ reaction rates (Cullinane, 2005). Points for 8 m PZ at 40 °C and 100 °C at 0.42 and 0.30 loading, respectively, were fit to determine the diffusivity of reactants and products. The k_0 and E_A values for Equations 5 and 7 were calculated independently using 7 m MDEA/2 m PZ data at 40 °C and 60 °C at loadings of 0.15 and 0.22. The lower loading points were used to fit k_0 and E_A for Equation 5, and the higher loading points were used to fit k_0 and E_A for Equation 7. It should be mentioned that none of the experimental data for 5 m MDEA/5 m PZ was included in the regression, yet the model adequately predicts the flux of CO₂ for this solvent over operationally significant temperature and loading ranges.

Kinetic Model Sensitivity Analysis

It has been assumed that the pseudo first order assumption is valid for every solvent tested in this analysis. This implies that k_g' is related to the reaction rate and diffusivity of CO_2 by Equation 10 (Dugas, 2009).

$$k_g' = \frac{\sqrt{D_{\text{CO}_2} [Am]_b k_2}}{H_{\text{CO}_2}} \quad (10)$$

Derived from a differential analysis, Equation 10 suggests that k_g' should vary as diffusivity (D_{CO_2}) and reaction rate (k_2) to the $\frac{1}{2}$ power. To test this hypothesis, each of these variables was varied in Aspen Plus[®] to determine the sensitivity of k_g' . Figure 4 reports the sensitivity of k_g' for 8 m PZ, 7 m MDEA/2 m PZ, and 5 m MDEA/5 m PZ at 40 °C to the overall rate constant and average diffusivity.

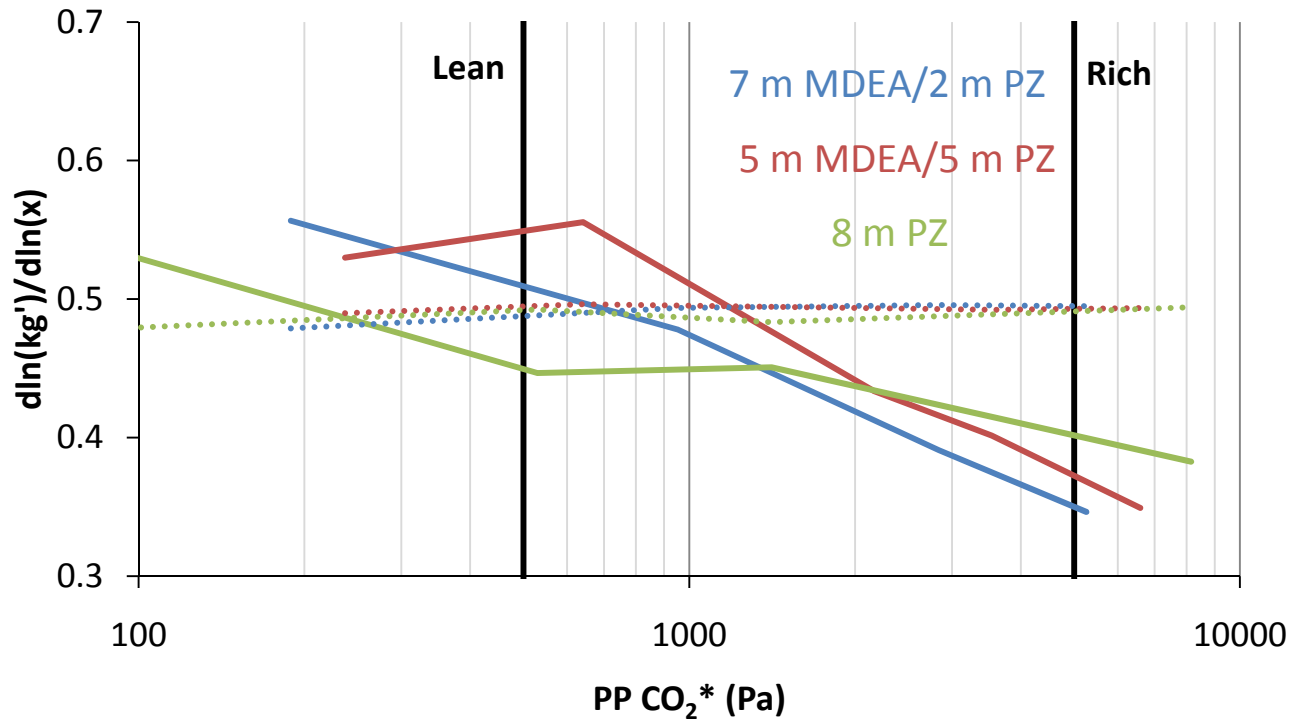


Figure 4: Sensitivity of 8 m PZ, 7 m MDEA/2 m PZ, and 5 m MDEA/5 m PZ to overall rate constant (solid lines) and average diffusivity (dotted lines) at 40 °C

At lower loadings the mass transfer rate varies as both reaction rate and average diffusivity to the $\frac{1}{2}$ power. At higher loadings, however, the sensitivity of mass transfer rate to reaction rate is diminished while sensitivity to diffusivity holds constant.

The diffusivity represented in Figure 4 is not D_{CO_2} from Equation 10, but rather the average diffusivity of all components in the mixture. The FORTRAN subroutine used to calculate binary diffusivities calculates one diffusivity for pairs involving CO_2 (D_{CO_2}) and one diffusivity for everything else (D_{OTHER}). Equation 10 suggests that k_g' should vary as D_{CO_2} to the $\frac{1}{2}$ power. Figure 5 compares the sensitivity of k_g' to D_{CO_2} and D_{OTHER} .

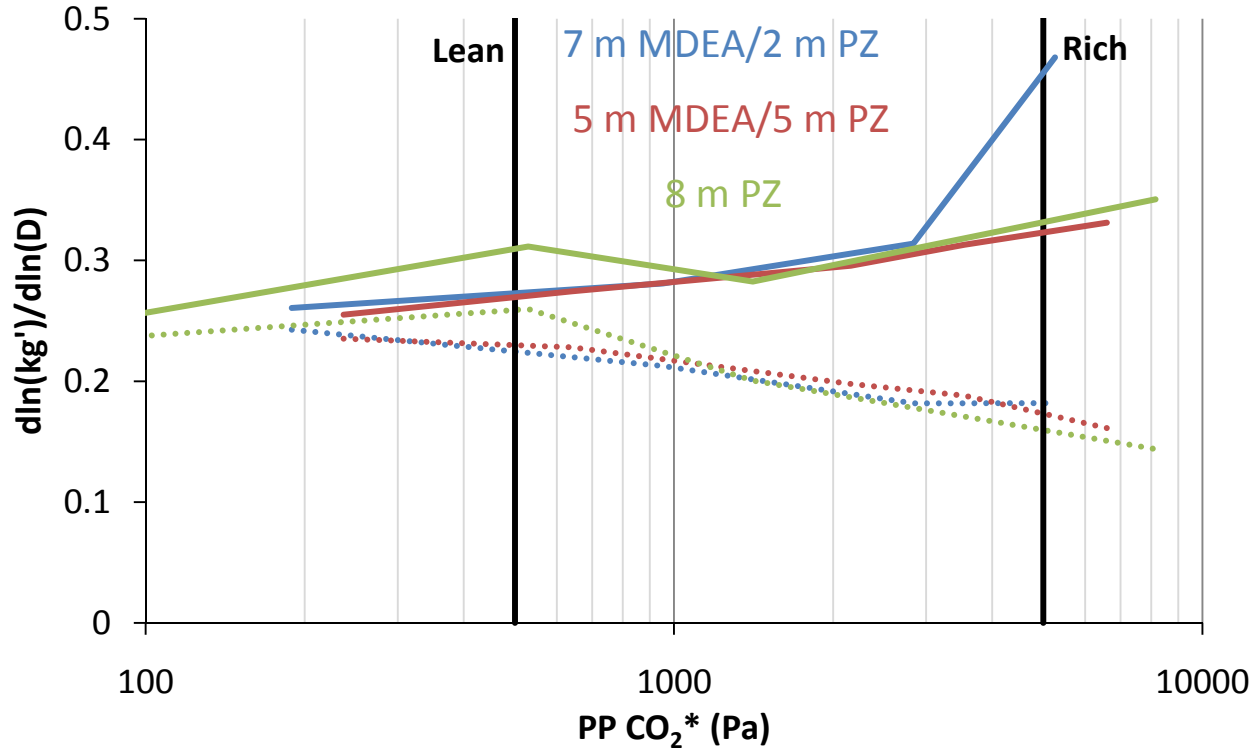


Figure 5: Sensitivity of 8 m PZ, 7 m MDEA/2 m PZ, and 5 m MDEA/5 m PZ to D_{OTHER} (solid lines) and D_{CO_2} (dotted lines) at 40 °C

Though it is still being investigated, it is believed that this hybrid sensitivity to D_{CO_2} and D_{OTHER} is a consequence of the equations used to calculate concentration and flux profiles in the liquid film. If the liquid film is treated as one region and average molar concentrations are used to calculate reaction rates, k_g' varies as D_{OTHER} to the $\frac{1}{2}$ power. Film discretization has the potential to provide much more accurate concentration profiles by calculating reaction and mass transfer rates at several points in the boundary layer. However, it is not a true differential analysis based on an infinitesimal element in the boundary layer, thus yielding this hybrid dependence on D_{CO_2} and D_{OTHER} .

Conclusions

The discrepancy between Aspen Plus[®] and Gibbs-Helmholtz predictions for the heat of absorption has been minimized through the use of thermodynamically consistent methodology. The greatest deviation for 8 m PZ occurred at higher temperatures (>100 °C) and loadings, though it was never greater than 5%. The kinetics of 8 m PZ, 7 m MDEA/2 m PZ, and 5 m MDEA/5 m PZ were fit over operationally significant temperature and loading ranges by adjusting rate constants, loadings, and binary diffusivities. Between 40 °C and 100 °C the average error in predicted CO₂ absorption rates was 6.7%. The sensitivity of the model to the diffusivity of reactants and products was unexpectedly high. The hybrid sensitivity to D_{CO_2} and D_{OTHER} may be a consequence of the numerical method used to determine concentration profiles in the liquid film.

Future Work

The top priority for the next quarter will be the design and optimization of separate absorption and stripping operations that use 7 m MDEA/2 m PZ and 5 m MDEA/5 m PZ. Absorber studies will investigate the possible benefits of lowering the temperature of the absorber. Stripper studies will focus on the performance of various process configurations (ex: 2 stage flash, inter-heated column, etc.).

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Modeling Stripper Performance for CO₂ Capture by Amines

Quarterly Report for January 1 – March 31, 2011

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Abstract

A number of stripper modeling tasks were tackled this quarter. First, two previous concentrated PZ pilot plant campaigns were reconciled. The first campaign with concentrated PZ in November 2008 was simulated with an overall mean absolute percentage error of 4.5%, and the mean absolute percentage error for each run varied between 1.7% and 9.1%. The largest error was in the overhead CO₂ rate, but this was probably due to systematic error in the measurement with the instrument at the pilot plant. The second campaign with concentrated PZ in September 2010 was simulated with an overall mean absolute percentage error of 2.7%, and the mean absolute percentage error for each run varied between 2.0% and 4.1%. The deviation of the overhead CO₂ rate in this campaign was less significant and more stochastic compared to the 2008 campaign, suggesting that there was no systematic error in the new campaign. The next task involved simulating a proposed improvement to the 2-stage flash skid that was operated in December 2010. PZ volatility was a significant issue; solidified PZ resulted in clogging down the line of the overhead CO₂. A cool rich solvent bypass to short packed sections at the top of each flash was evaluated. The most significant improvement was observed with bypass only to the low-pressure flash. The PZ volatility was reduced from 8.8 mol/hour to 3.2 mol/hour, and the energy performance improved from 36.4 kJ/mol CO₂ to 34.0 kJ/mol CO₂. Unlike the initial 2-stage flash configuration, the total heat duty of the rich bypass configuration was less than the heat duty for a simple stripper using 8 m PZ.

The use of geothermal brine to strip CO₂ in an advanced 2-stage flash configuration was evaluated. Even if the temperature of the extracted brine decreased over time, the proposed flowsheet would be capable of stripping to a constant lean loading to ensure adequate absorber performance, but the required brine flow rate would increase slightly. If the brine temperature decreased from 150 °C to 145 °C, the required brine flow rate would increase by 4%. Lastly, an interheated column was optimized using results from an intercooled absorber model. A minimum equivalent work of 31.1 kJ/mol CO₂ was recorded when stripping with 8 m PZ at 150 °C. This value was slightly higher than previous predictions due to the inclusion of the blower and intercooler pump work in the calculation.

Introduction

The pilot plant facility at the J. J. Pickle Research Campus has been used in the past to investigate the feasibility of proposed solvents and verify the accuracy of solvent models in Aspen Plus® (Chen, 2007; Oyeneke, 2007). Generally, agreement between the pilot plant data and Aspen Plus® predictions has proved difficult to attain, especially in the stripper section. Previous thermodynamic models developed for the CO₂ removing amines have only been valid within the range of absorber operating conditions because the data from which they were regressed were in that range.

A solvent model for piperazine (PZ) was finalized in the last year (Rochelle et al., 2010b). The model, named 5deMayo, uses an older model for H₂O-PZ-CO₂ that originally was developed by Hilliard (2008). The older model was regressed using relatively low concentrations of PZ, and it was updated for concentrated PZ solvents, specifically 8 m PZ. The model was updated by making the zwitterion a Henry's component with a zero net charge and near-zero volatility. The parameters used in the regression were revisited to produce the most accurate model possible.

The stripper is generally modeled using steam from the power plant as the energy source for regeneration. However, in some scenarios it may be preferable to use an alternate heat source that provides variable temperature heating. In prior work this effect was analyzed for the application of solar heating. In the current quarter, continued effort has been dedicated to the use of geothermal heating for stripping. The hot brine extracted from the ground could be used to run the stripper. A configuration that runs on multiple temperature levels would most effectively make use of the heat available in brine.

As in previous results, the evaluation of stripper performance was done with equivalent work. The calculation method for this value is shown in Equation 1. The value accounts for the electricity duty required for pumping and compressing as well as the heat duty drawn from steam of a specific temperature. The expression considers the increasing value of steam at increasing temperature; it calculates the amount of electricity that could have been generated from the steam if it had not been used in the reboiler.

$$W_{eq} = \sum_{i=1}^{n_{reboilers}} 0.75Q_i \left(\frac{T_i + 5K - T_{sink}}{T_i + 5K} \right) + W_{pumps} + W_{comps} \quad (1)$$

This work also addressed the use of geothermal brine in an advanced configuration. Unlike condensing steam, the brine changes temperature when it gives up heat, so an integrated form of the equivalent work expression was derived to address the variable temperature nature of brine.

$$W_{eq} = \sum_{i=1}^{n_{reboilers}} 0.75Q_i \left(\frac{T_{i,f} - T_{i,o} - T_{sink} \ln \left(\frac{T_{i,f}}{T_{i,o}} \right)}{T_{i,f} - T_{i,o}} \right) + W_{pumps} + W_{comps} \quad (2)$$

In both Equations 1 and 2, T_{sink} is the sink temperature of cooling water for a steam turbine, assumed to be 40 °C.

Three topics were addressed this quarter. The first topic was the reconciliation of two pilot plant campaigns with concentrated PZ. The second topic was the evaluation of an advanced 2-stage

flash configuration to make efficient use of geothermal brine. The final topic was the optimization of an interheated column using results from a rigorous absorber model.

Methods and Results

PZ Pilot Plant Campaigns

Pilot plant campaigns were run with PZ in November 2008 and September 2010. The 2008 campaign used a typical absorber and stripper configuration, but the 2010 campaign included intercooling in the absorber. The stripper configuration was the same for both, but a later campaign with PZ will use a two-stage flash at high temperature. Aspen Plus[®] was used to analyze the available data from the 2008 and 2010 campaigns. The flow diagram of the stripper is shown in Figure 1.

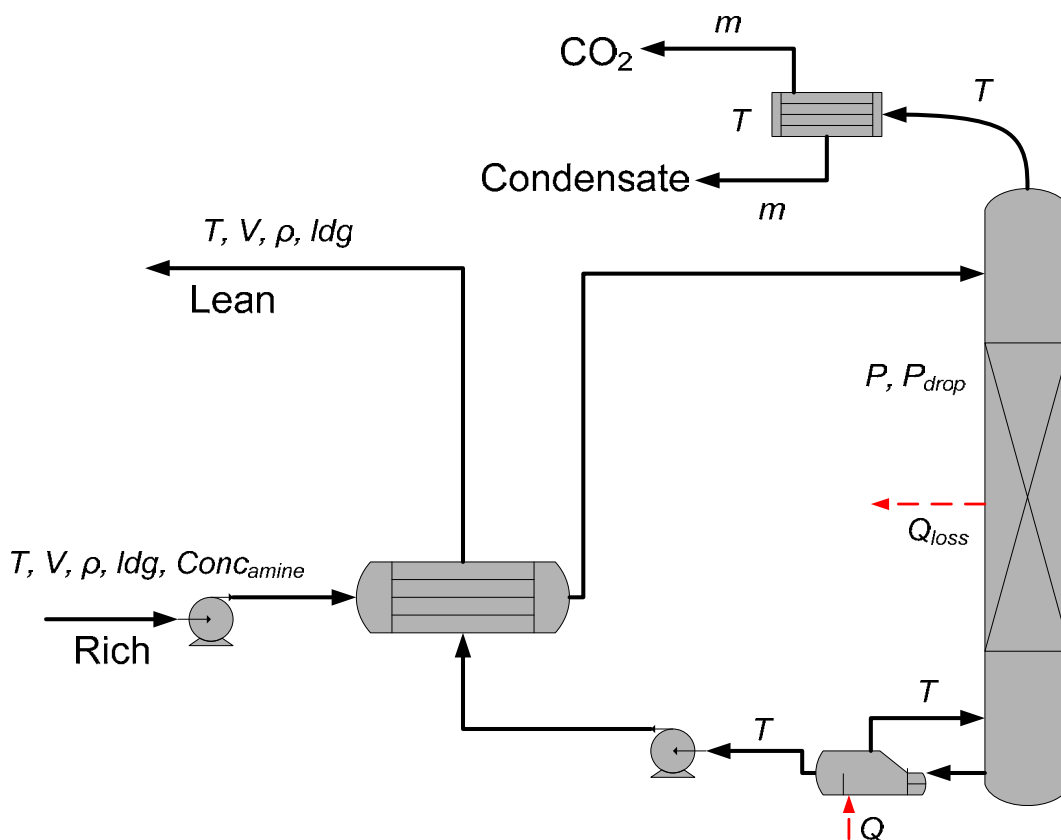


Figure 1: J. J. Pickle Pilot Plant Configuration and Measurements. Measured conditions listed in italics.

At first, the expected route of analysis was to use the Data Fit package in Aspen Plus[®], but most of the fits were unacceptable. Moreover, when rerunning the simulations using the reconciled input values, the values of the calculated results were different than the values given by Data Fit. This outcome suggested that the final input and result values do not necessarily correspond to a fully converged model. Data Fit has the powerful ability to regress one or more solvent or unit operation parameters while simultaneously reconciling the data from all runs. In this work, the goal was only to address the accuracy of the measurements and assess the stripper efficiency.

Therefore, the individual runs were simulated in a stripper model without the use of Data Fit. Measurements from the pilot plant were used for the required input values, and the accuracy of the calculated results was analyzed. The results were better than expected, and no further reconciliation was necessary.

As shown in Figure 1, many measurements were recorded including rich and lean conditions, column conditions, and overhead flow rates. The five interior column temperature measurements were not considered in this analysis. In previous work the temperature profile of the column could only be matched by imposing heat duties throughout the total height of packing, and the resulting heat loss profile was not physically significant or useful for predicting future performance (Plaza et al., 2010).

2008 PZ Pilot Plant Reconciliation

This campaign started in November 2008 and ran into December. It was the first pilot trial with concentrated PZ at the Pickle pilot plant facility. There was significant hesitation and caution to avoid PZ precipitation, which could clog the lines and machinery. The campaign was completed successfully, and there were 14 steady-state runs. The measurements from the pilot plant are displayed below in Tables 1a and 1b. The measurements were analyzed with the 5deMayo thermodynamic model for concentrated PZ. In the Aspen Plus[®] stripper simulation necessary input values were taken directly from the pilot plant measurements. The remaining measured values were compared against the calculated values in the simulation. Compared to the output of the simulation, the pilot plant had redundant measurements of the reboiler temperature; the temperatures of both the liquid and vapor exiting the reboiler were measured. The temperature of the liquid exiting the reboiler was used to compare against the simulation reboiler temperature. The reboiler vapor temperature at the pilot plant was generally higher than expected, which was estimated to be due to superheating. The percent deviation of the variables calculated in the simulation for each of the 14 runs is shown in Table 2a and 2b.

Table 1a: 2008 Concentrated PZ Pilot Plant Campaign - Measurements (Runs 1–7)

<i>Run</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>
Rich flow <i>kg/min</i>	65.7	66.7	66.9	67.4	53.3	79.7	66.7
Rich temp <i>C</i>	47.5	43.9	46.9	37.2	41.6	42.4	43.9
PZ conc <i>m</i>	7.45	7.87	9.18	8.18	7.82	8.21	8.06
Rich loading <i>mol/mol</i>	0.341	0.372	0.330	0.404	0.358	0.361	0.364
Lean flow <i>kg/min</i>	62.1	64.4	62.9	65.5	50.2	76.7	64.0
Lean temp <i>C</i>	49.9	46.5	49.5	39.7	44.1	45.4	48.2
Lean loading <i>mol/mol</i>	0.264	0.308	0.254	0.386	0.284	0.303	0.305
Overhead temp <i>C</i>	95.3	88.6	96.9	71.9	90.9	90.4	107.3
Stripped CO₂ <i>kg/min</i>	1.99	1.58	2.17	0.67	1.70	1.84	1.53
Condensate rate <i>kg/min</i>	1.19	0.48	1.12	0.14	0.65	0.69	0.31
Condenser temp <i>C</i>	14.9	15.5	9.0	22.0	11.3	4.7	19.6
Reboiler duty <i>kW</i>	130.6	101.0	155.5	45.9	111.1	125.3	112.7
Column heat loss <i>kW</i>	13.1	12.1	21.4	14.0	18.9	20.6	21.8
Column pressure <i>kPa</i>	138	138	138	138	138	138	414
Column P_{drop} <i>kPa</i>	0.154	0.144	0.182	0.164	0.127	0.147	0.142

<i>Run</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>
Reboiler liquid temp C	107.2	103.0	108.9	87.5	105.7	104.1	127.5
Reboiler vapor temp C	105.7	100.6	108.6	90.5	105.7	102.3	124.4

Table 1b: 2008 Concentrated PZ Pilot Plant Campaign - Measurements (Runs 8–14)

<i>Run</i>	<i>8</i>	<i>9</i>	<i>10</i>	<i>11</i>	<i>12</i>	<i>13</i>	<i>14</i>
Rich flow <i>kg/min</i>	53.4	79.2	66.7	76.8	76.8	63.8	51.1
Rich temp C	41.1	47.5	41.6	41.0	44.8	42.7	38.9
PZ conc <i>m</i>	7.88	7.84	7.67	4.81	4.95	4.90	4.64
Rich loading <i>mol/mol</i>	0.369	0.338	0.381	0.382	0.362	0.360	0.382
Lean flow <i>kg/min</i>	51.2	75.8	64.6	74.5	73.4	60.8	48.7
Lean temp C	44.9	51.7	45.3	44.8	48.6	46.5	42.6
Lean loading <i>mol/mol</i>	0.298	0.267	0.331	0.316	0.274	0.257	0.262
Overhead temp C	104.8	113.4	96.5	102.1	112.1	111.9	108.4
Stripped CO ₂ <i>kg/min</i>	1.39	1.93	1.05	1.33	1.94	1.84	1.54
Condensate rate <i>kg/min</i>	0.22	0.64	0.77	0.24	0.69	0.60	0.52
Condenser temp C	16.2	20.1	25.2	8.0	11.5	4.8	4.8
Reboiler duty <i>kW</i>	105.6	141.3	79.0	99.8	134.6	129.0	114.5
Column heat loss <i>kW</i>	27.5	26.7	23.1	26.6	30.3	32.3	30.1
Column pressure <i>kPa</i>	414	352	352	352	345	345	345
Column P _{drop} <i>kPa</i>	0.097	0.104	0.168	0.117	0.059	0.029	0.054
Reboiler liquid temp C	127.5	129.0	116.1	119.7	127.6	128.2	127.0
Reboiler vapor temp C	124.3	126.3	111.0	120.1	127.3	128.7	129.5

Table 2a: 2008 Concentrated PZ Pilot Plant Campaign - Simulation Deviations from Measurements (Runs 1–7)

<i>Variable</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>
Lean flow	0.5%	-0.5%	0.5%	1.5%	1.0%	0.1%	0.4%
Lean ldg	-3.3%	-3.5%	-2.1%	-2.9%	-5.5%	-2.8%	-5.8%
Overhead T	4.0%	6.9%	4.1%	18.8%	6.7%	6.1%	13.8%
CO ₂ rate	-0.3%	13.2%	-1.0%	8.2%	0.4%	7.2%	21.2%
Reb. T	0.4%	0.8%	0.9%	2.9%	1.1%	0.3%	4.1%
Average	1.7%	5.0%	1.7%	6.9%	2.9%	3.3%	9.1%

Table 2b: 2008 Concentrated PZ Pilot Plant Campaign - Simulation Deviations from Measurements (Runs 8–14)

<i>Variable</i>	<i>8</i>	<i>9</i>	<i>10</i>	<i>11</i>	<i>12</i>	<i>13</i>	<i>14</i>
Lean flow	0.1%	0.4%	1.0%	0.4%	0.8%	0.7%	0.2%

Lean ldg	-5.0%	-0.9%	0.1%	-1.4%	-2.5%	-0.8%	-2.6%
Overhead T	16.2%	7.7%	17.0%	11.2%	4.8%	5.5%	7.1%
CO₂ rate	17.9%	9.4%	11.9%	9.8%	2.1%	-1.0%	9.9%
Reb. T	4.5%	1.9%	3.8%	2.0%	0.0%	0.6%	1.3%
Average	8.7%	4.0%	6.7%	5.0%	2.0%	1.7%	4.2%

The mean absolute percentage error (MAPE) for the five calculated variables is shown in the final rows of Table 2a and 2b. The smallest MAPE was 1.7%, the largest was 9.1%, and the average was 4.5%. One variable with a consistently large percent deviation was the overhead temperature; the simulation values were always greater than the pilot plant measurements. A reasonable explanation for this observation was that heat loss occurred in the piping before the temperature was measured. Another possibility could be non-equilibrium flashing of the rich feed upon entering the column. The difference could not be explained by the pilot plant failing to reach thermal equilibrium between the liquid and vapor phases in the column because the vapor heated the liquid as it travels up the column, so non-equilibrium would surface as overhead temperatures measured at the pilot plant being consistently higher than the temperatures calculated by the model.

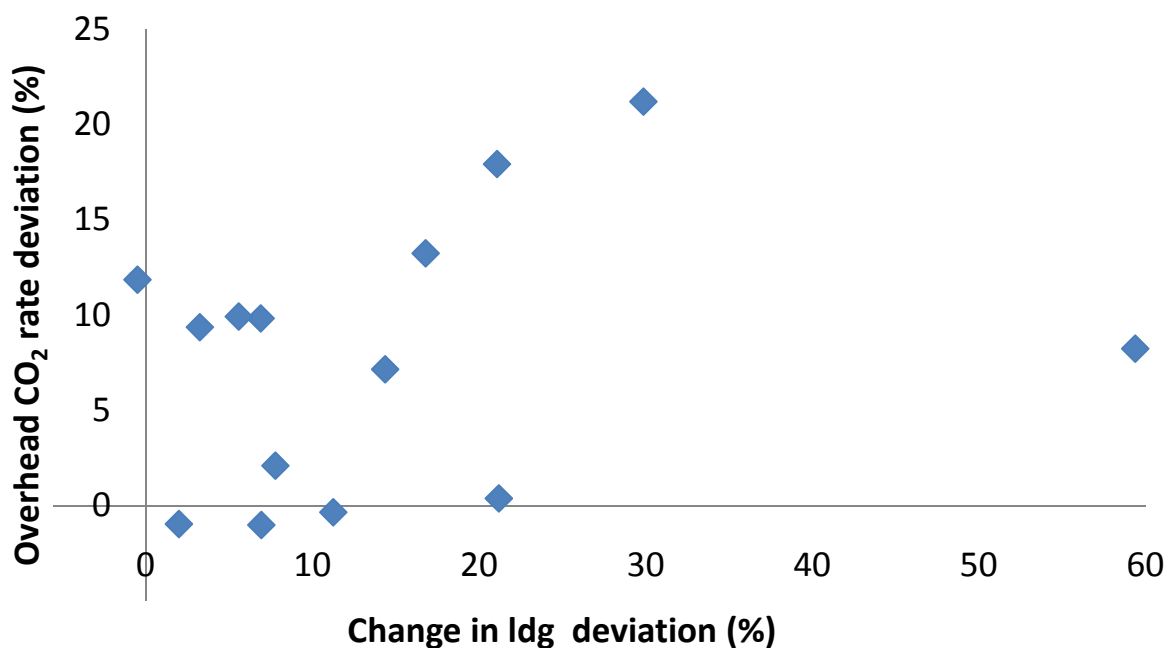


Figure 2: Percent Deviations of Aspen Plus® Simulation Results from Pilot Plant Measurements. A correlation existed between overhead CO₂ rate and change in loading.

A correlation between the CO₂ evolution rate and lean loading percent deviations existed. The correlation was more noticeable when considering the percent deviation in change in loading (the difference between rich and lean loading). The correlation was apparent when plotting the percent deviations of CO₂ evolution rate versus change in loading (Figure 2). However, a parity plot comparing the reported amount of CO₂ stripped based on gas side and liquid side measurements demonstrated that a CO₂ mass balance issue existed in the measurements (Figure 3). This comparison suggested that the measured CO₂ gas rate was consistently low, which was

consistent with the large percent deviations between the simulation and pilot plant measurements. Therefore, the main issue with achieving exact replication of the pilot plant data was the accuracy of the overhead CO₂ gas rate measurement.

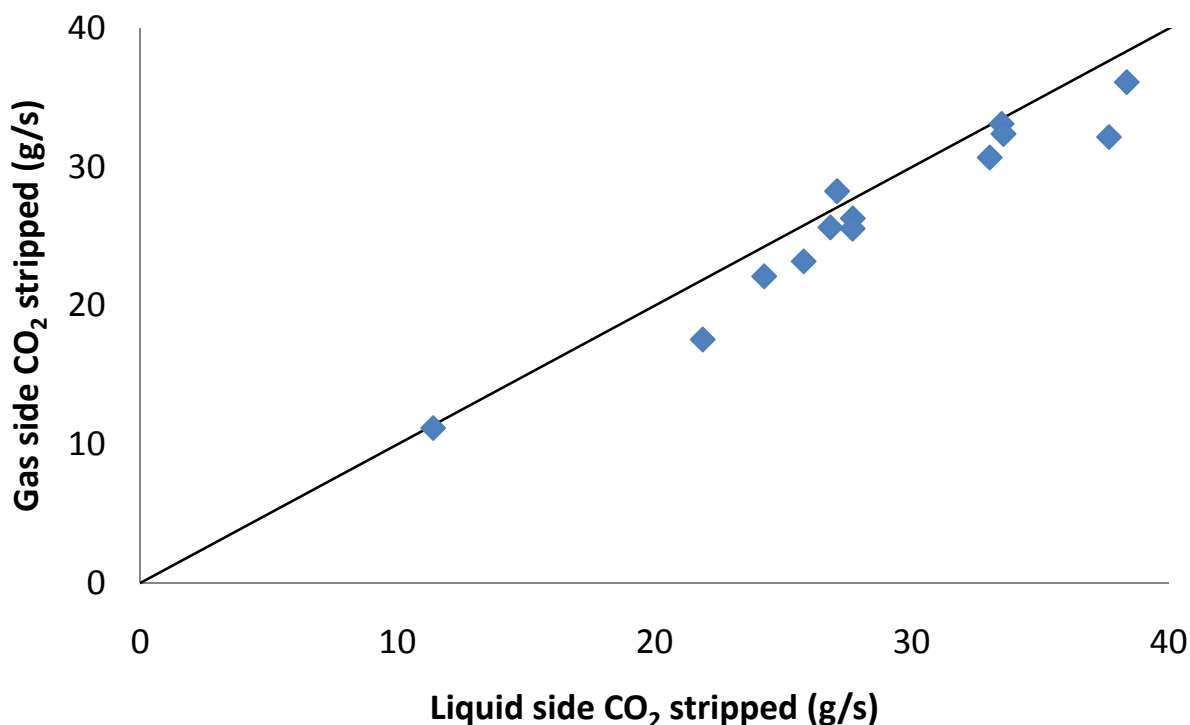


Figure 3: Parity Plot of Measured CO₂ Removal by Gas Side (Measured CO₂ flow rate) and Liquid Side (product of solvent rate and change in loading) Measurements at Pilot Plant.

2010 PZ Pilot Plant Campaign

This campaign was run in September 2010 with 8 m PZ and an intercooled absorber. The intercooling was expected to improve absorber performance and achieve a higher rich loading for any given lean loading. This campaign still used a simple stripper configuration identical to the 2008 campaign, but another campaign later in 2010 used a 2-stage flash skid for stripping. This simple stripper campaign in September 2010 yielded measurements that could again be reconciled with the 5deMayo thermodynamic model. Similar to the data from the 2008 campaign, the Data Fit option was put aside to avoid final results that might not represent converged flowsheets. The campaign was completed successfully, and there were 13 steady-state runs. Many measurements were unavailable for runs 4 or 10, so their analyses are not included here. Like the analysis for the 2008 campaign, necessary input values were taken directly from the pilot plant measurements for use in the Aspen Plus[®] stripper simulations. The remaining measured values were compared against the calculated values in the simulation. Again, the temperature of the liquid exiting the reboiler was used to compare against the simulation reboiler temperature. The percent deviation of the variables calculated in the simulation for each of the 11 runs is shown in Table 3.

Table 3: 2010 Concentrated PZ Pilot Plant Campaign – Simulation Deviations from Measurements

Variable	1	2	3	5	6	7	8	9	11	12	13
Lean flow	-2.1%	-1.8%	-1.6%	-3.7%	-5.5%	-3.9%	-2.7%	0.7%	8.3%	1.5%	3.0%
Lean ldg	-0.4%	-1.7%	0.5%	0.2%	-0.2%	-3.4%	-2.2%	3.2%	8.7%	2.8%	5.1%
Overhead T	4.6%	5.8%	3.4%	3.8%	6.2%	4.8%	4.0%	1.5%	0.7%	-1.0%	0.0%
CO₂ rate	7.6%	0.4%	3.7%	4.2%	-4.7%	1.7%	-0.9%	5.4%	-1.7%	6.4%	6.4%
Reb. T	-0.1%	0.3%	-0.6%	0.2%	1.0%	0.9%	0.6%	0.1%	-1.0%	-1.6%	-1.4%
Average	3.0%	2.0%	2.0%	2.4%	3.5%	2.9%	2.1%	2.2%	4.1%	2.7%	3.2%

The MAPE was determined for the five calculated variables in each run, listed in the last row of Table 4. The minimum error was 2.0%, the maximum error was 4.1%, and the average was 2.7%. Compared to the 2008 campaign which had an average error of 4.1%, the simulations of this campaign had much better agreement with the data. Moreover, the overhead CO₂ rate and lean loading (or change in loading) deviations exhibited more random behavior compared to the 2008 campaign, so the differences are more likely due to instrument precision as opposed to systematic error.

Stripping with Geothermal Heat

If a coal-fired power plant with CO₂ capture is situated over a viable source for geothermal heat, it may be desirable to use this heat source in the stripper. Stripping with geothermal heat should be optimized differently than with steam heat. Hot brine would be extracted from the ground and sensible heat would be removed before injecting it back into the ground. Therefore, geothermal heat is provided at a variable temperature, unlike steam or boilers that release latent heat at a constant temperature. Typical reboilers would operate inefficiently with geothermal heat due to an excessive approach temperature on the hot side. The flowsheet in Figure 4 had been previously suggested as an option to use geothermal heat effectively.

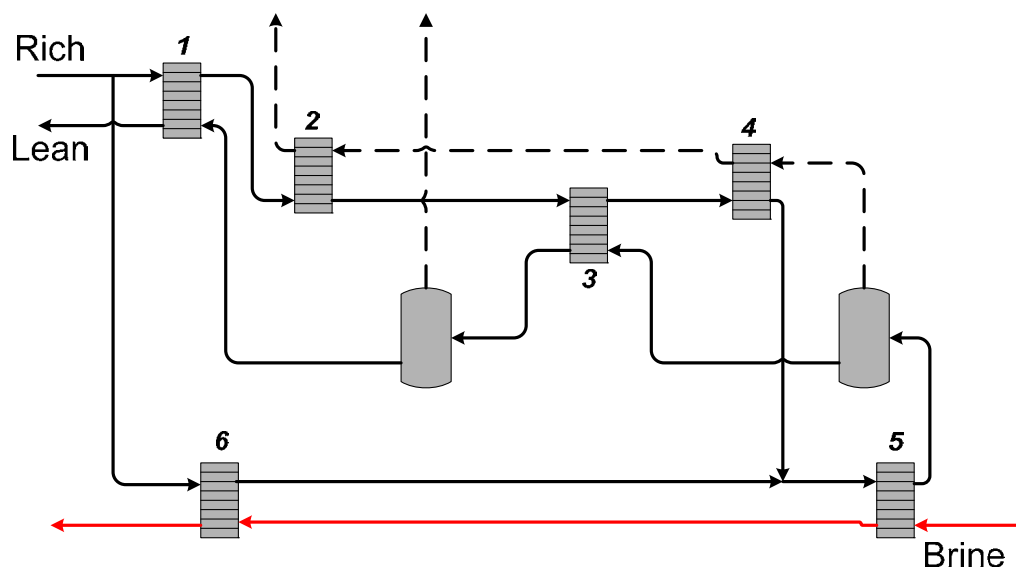


Figure 4: Advanced 2-Stage Flash for Geothermal Heating.

The flowsheet was essentially a modified form of the 2-stage flash; it used a more complex heat exchange method to heat the solvent from the absorber temperature to an adequate stripping temperature. The new heat exchange configuration applied the variable temperature heat to a countercurrent solvent stream to attain a more constant temperature driving force across the heat exchanger. An issue with this flowsheet was the extremely high approach temperature on the cold side of exchanger 6. The rich solvent entered at the temperature of the bottom of the absorber, which was assumed to be 50 °C for this analysis. The brine exited at 100 °C in the design case, so the cold side approach temperature of heat exchanger 6 was necessarily 50 °C. In an effort to balance the approach temperatures, the flowsheet in Figure 5 was proposed.

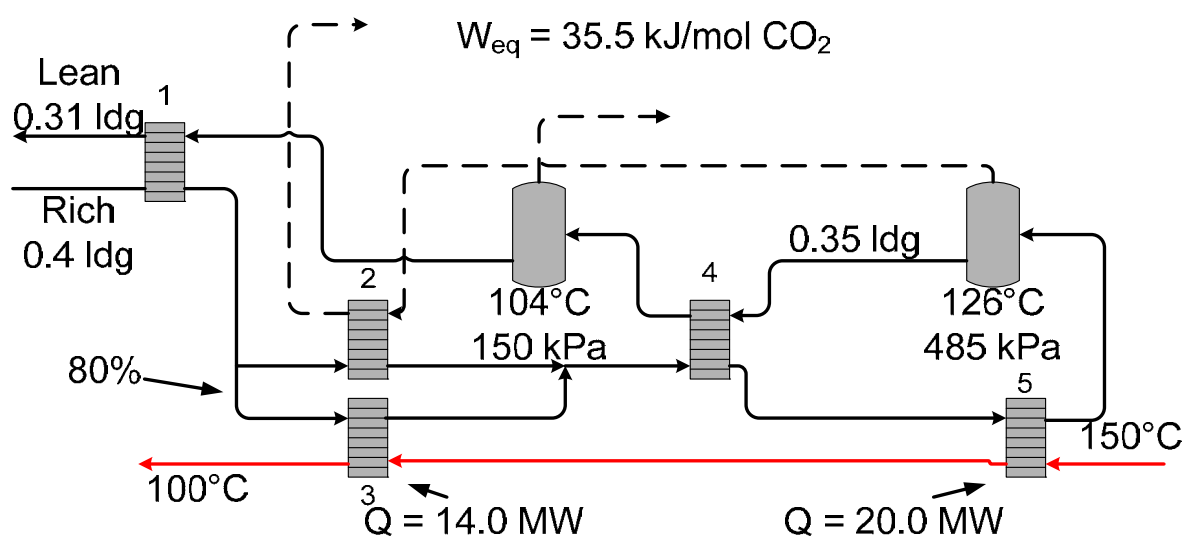


Figure 5: Revised Advanced 2-Stage Flash for Geothermal Heating. Conditions listed for design case with desired brine extraction temperature of 150 °C.

This revised flowsheet utilized a typical main cross exchanger (exchanger 1) between the rich and lean streams. Therefore, the rich solvent had a closer approach with the cooled brine. A 5 °C LMTD was maintained on all five exchangers, but a minimum approach on each side of the exchangers was specified to be 1 °C. Occasionally the heat capacity flows of opposing streams were sufficiently imbalanced to create a pinch on one side of the relevant exchanger. The total moles of vapor produced in each flash vessel were specified to be equal by varying the temperature of the low-pressure flash. Given a brine inlet of 150 °C, the brine outlet temperature of 100 °C was achieved by varying the temperature of the high-pressure flash. The final pressure of the multi-stage compressor was 150 bar, and its work requirement was calculated by Equation 3, which was a correlation derived in previous work.

$$W_{comp} \left(\frac{\text{kJ}}{\text{mol CO}_2} \right) = \begin{cases} 4.572 \ln(150/P_{in}) - 4.096, & P_{in} \leq 4.56 \text{ bar} \\ 4.023 \ln(150/P_{in}) - 2.181, & P_{in} > 4.56 \text{ bar} \end{cases} \quad (3)$$

Figure 5 shows the conditions for a selected operating point with the expected brine extraction temperature of 150 °C. The brine temperature can be expected to decrease over time as cool brine is injected back into the formation. Geologic models have suggested that the extraction temperature would stay steady at 150 °C for approximately 25 years, and by the 30-year mark the temperature would be about 148 °C. Table 4 details the change in performance and brine requirement as the extraction temperature falls below 150 °C. The change in temperature of the brine from extraction to injection was approximately held constant at 50 °C. The brine flow rate was estimated for a 50 MW coal-fired power plant with an expected CO₂ production rate of 993 tons/day.

Table 4: Advanced 2-Stage Flash Performance with Varying Brine Temperature. 8 m PZ, 0.4 rich loading, compression to 150 bar.

T_{in}	T_{out}	Lean Loading	Equivalent Work	Brine Rate	Heat Duty
$^{\circ}\text{C}$	$^{\circ}\text{C}$		kJ/mol	ton/d	kJ/mol
150.0	99.5	0.312	35.5	13702	130.1
148.0	98.1	0.311	35.6	14025	131.6
145.0	94.3	0.310	36.2	14207	135.1

This evaluation demonstrated that the proposed flowsheet would be capable of stripping to a constant lean loading with a varying brine inlet temperature. The consequence of a reduced brine temperature is an increase in the required brine flow rate. When reduced from 150 °C to 145 °C, the required brine flow rate increased by 4%.

Optimization of Interheated Column

In prior work, the interheated column configuration demonstrated its capability of significantly reducing the energy requirement of the stripper. It was the most efficient configuration evaluated for both 9 m MEA and 8 m PZ (Van Wagener et al., 2010b). In collaborative work with students from Hamburg University of Technology, an optimum operating point is being determined for two scenarios: a pre-existing coal-fired power plant with a retrofitted carbon capture system, and a newly built coal-fired power plant with carbon capture. The Hamburg

students have a rigorous model for the steam cycle of a coal-fired power plant. Their calculations require the heating, cooling, and electricity demands of the carbon capture unit to determine an optimum operating point.

This work considered the use of 8 m PZ with an intercooled absorber and an interheated stripper. With the goal of being as comprehensive as possible, an absorber model by Plaza (Rochelle et al., 2011) was used to generate estimates of the blower duty and rich/lean loadings for varying values of L/G in the absorber. Figure 6 shows the lean loading required to achieve 90% removal in the absorber as the L/G increased. The calculated rich loading is also shown on this graph. The rich loading was relatively constant around 0.4, but it had slight fluctuations.

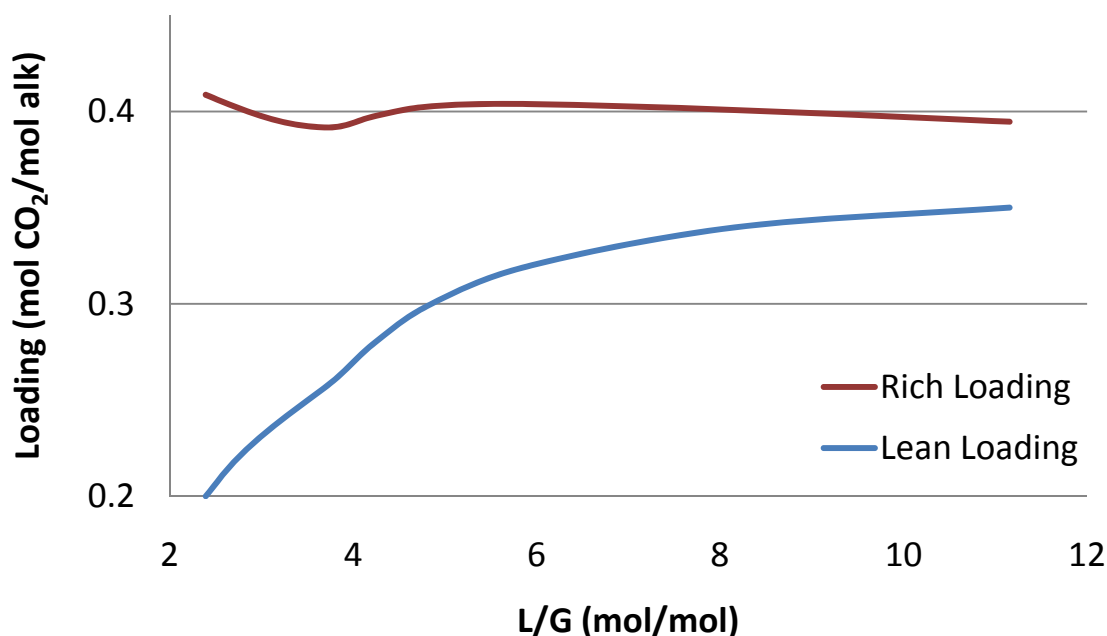


Figure 6: Performance of Intercooled Absorber with 15 m of Mellapak 2X packing.

Using rich solvent loading, temperature, and flow rate data, the interheated column was simulated with similar specifications to previous work. A 5 °C cold side approach was specified on the main cross exchanger, and a 5 °C LMTD approach was specified for the interheated exchanger and the reboiler. The lean pump constantly discharged at 275 kPa, and the rich pump was specified to achieve 300 kPa greater than the stripper pressure to overcome pressure drop and head. The stripping column had 5 m of IMTP #40 packing; this packed height was sufficient to reach equilibrium between the liquid and vapor phases at the top of the column. Reboiler temperatures of 100–150 °C in 10° increments were simulated. Figures 7–10 detail the data required for the calculations by the Hamburg students. The heat duty is used to calculate the amount of steam that must be bypassed to the capture unit. The cooling duty and electric work factor into the amount of electricity that would be consumed by the capture unit. The cooling duty included cooling for absorber intercooling and stripper overhead precooling. The electric work included contributions from the blower, rich and lean pumps, and the intercooler and interheater pumps. The pressure of the stripper factors into the electricity required for the multi-stage compressor, which can also be calculated by the Hamburg students.

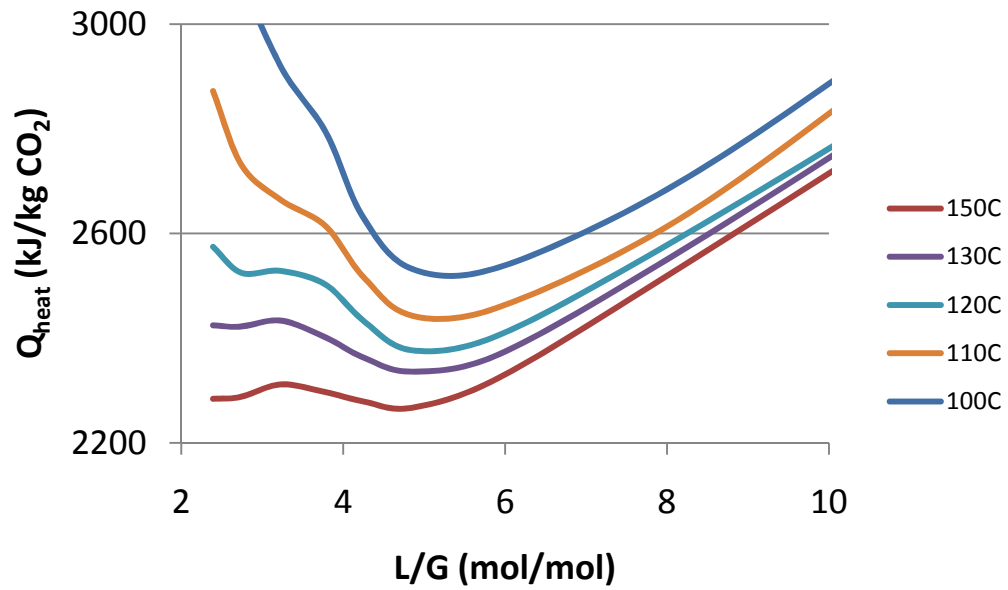


Figure 7: Interheated Column Heat Duty Requirement

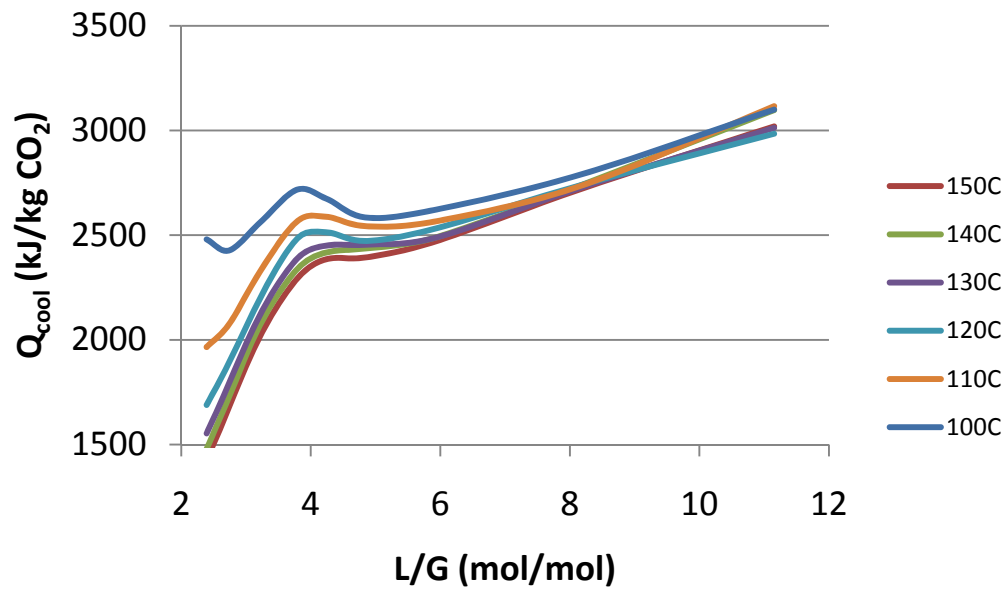


Figure 8: Interheated Column Cooling Duty Requirement

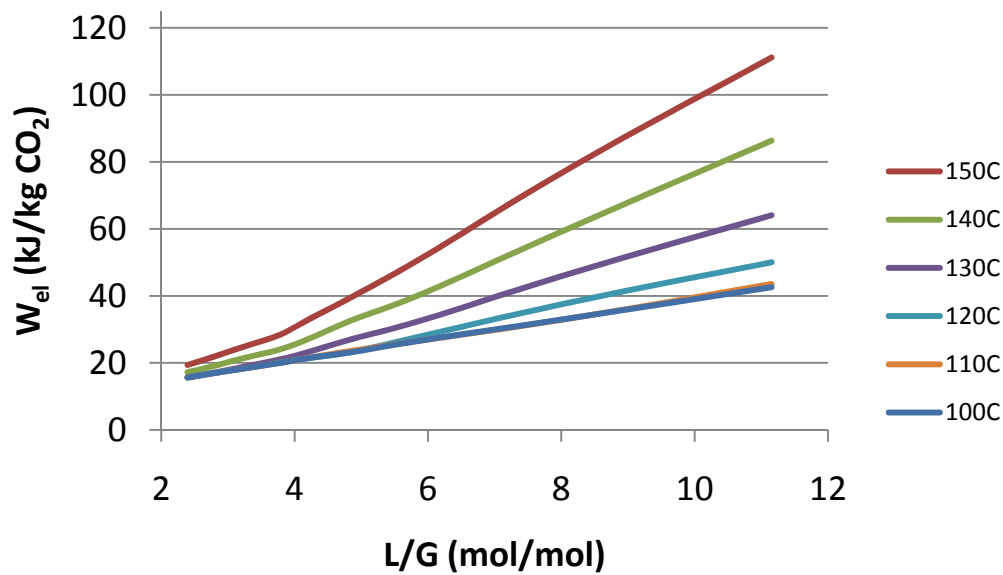


Figure 9: Interheated Column Electric Work Requirement

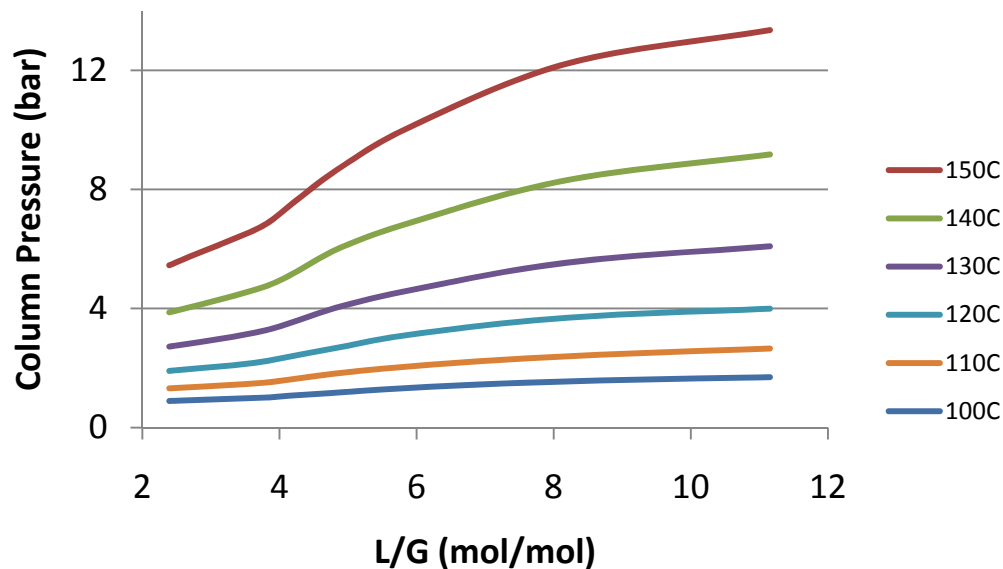


Figure 10: Interheated Column Pressure

The typical equivalent work expression in Equation 1 was used to further evaluate the performance of this configuration at the varying reboiler temperatures. The multi-pressure work correlation (Equation 3) was used to calculate the compressor work for the column pressure of each individual simulation. The trends in equivalent work are displayed in Figure 11. As expected, the configuration performed best at a reboiler temperature of 150 °C. The effect of stripping at high temperature became disadvantageous at high L/G when the lean loading was high. The higher solvent circulation rate resulted in a very high rich pump work to achieve the

high column pressure. This effect increased exponentially with increasing temperature due to the similar trend of column pressure with temperature.

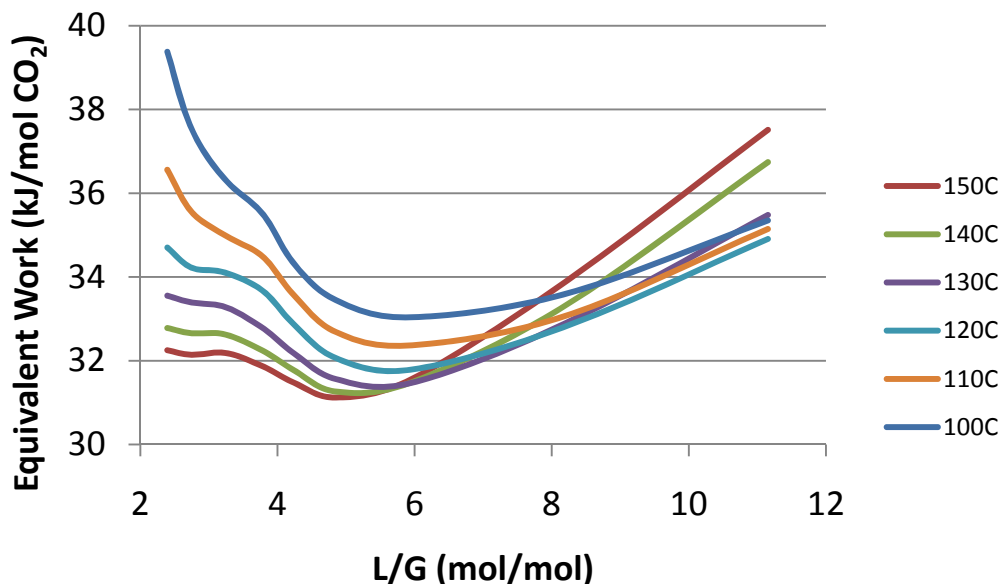


Figure 11: Interheated Column Equivalent Work Requirement

This analysis demonstrated that though the global optimum used a reboiler temperature of 150 °C, the total work requirement was more stable with variations in L/G when stripping at lower temperature. This conclusion suggests that if variability in operating conditions could be an issue in an actual plant, a lower stripping temperature may be beneficial.

Improving 2-Stage Flash Skid Performance

The pilot plant campaign in December 2010 with 8 m PZ used a newly constructed 2-stage flash skid to strip CO₂ from the solvent. The operation of this skid experienced a significant disruption during its operation; more PZ was volatilized from the 2-stage flash than the previous simple stripper campaigns, and the amine precipitated and produced clogs down the line. A proposition to eliminate this issue entailed installing small sections of packing (6-24 inches) in one or both flash tanks and splitting a small portion of the rich solvent to contact the vapor rising from the flash vessel through the packing. This configuration also begins to look like previous split feed configurations, like the double matrix. For this reason, it was anticipated that this improvement might also reduce the heating and total work requirements. A PFD of this new configuration with packing and rich solvent bypasses to both the low-pressure and high-pressure flash tanks is shown in Figure 12.

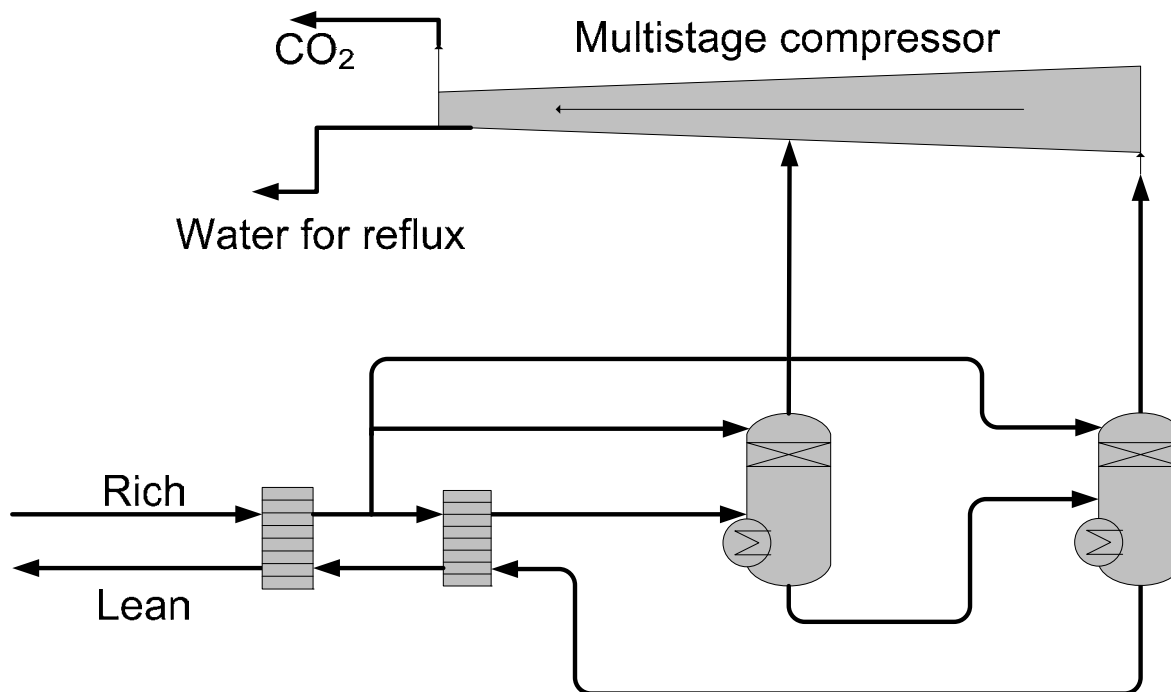


Figure 12: 2-Stage Flash with Warm Rich Bypass to Low-Pressure and High-Pressure Flash Injection

Since concentrated PZ can operate at higher temperatures than MEA, a high-pressure heat exchanger was acquired for the pilot plant in addition to the existing exchanger to facilitate the large heat duty required to accomplish the temperature swing between 40 °C and 150 °C. The split of rich solvent was simulated to occur between the two heat exchangers so that a moderate approach temperature could be maintained in the installed packing. If the rich solvent split occurred before the first heat exchanger, the solvent would be approximately 40 °C, and very little liquid could be bypassed before a temperature pinch occurred at the top of the packing. A complex heat exchanger model had not been developed, but assumptions were imposed on each heat exchanger to maintain constant performance. A constant LMTD of 5 °C was specified for the low-pressure heat exchanger. A constant average U was specified for the high-pressure heat exchanger. The total area of the high-pressure heat exchanger was 219.6 ft². The following fundamental equation for heat exchangers was used for this analysis:

$$Q = U A \Delta T \quad (4)$$

where Q is the heat duty exchanged, U is the overall heat transfer coefficient, A is the heat exchanger area, and ΔT is the temperature difference between the hot and cold streams. Unless considering ideal cases, both the overall heat transfer coefficient and the temperature difference change throughout the exchanger area. Therefore, the expression must either be integrated along the exchanger area or approximated by calculating in pieces. The latter approach was used by utilizing a base case simulation of the 2-stage flash. The following calculations are for a 2-stage flash simulation with a 5 °C LMTD on the low-pressure exchanger, a rich loading of 0.4, and a lean loading of 0.26. The temperature profile in the high-pressure exchanger was calculated by

splitting the heat duty into 5 segments. The profile is shown in Figure 13, and the conditions in the exchanger are detailed in Table 5.

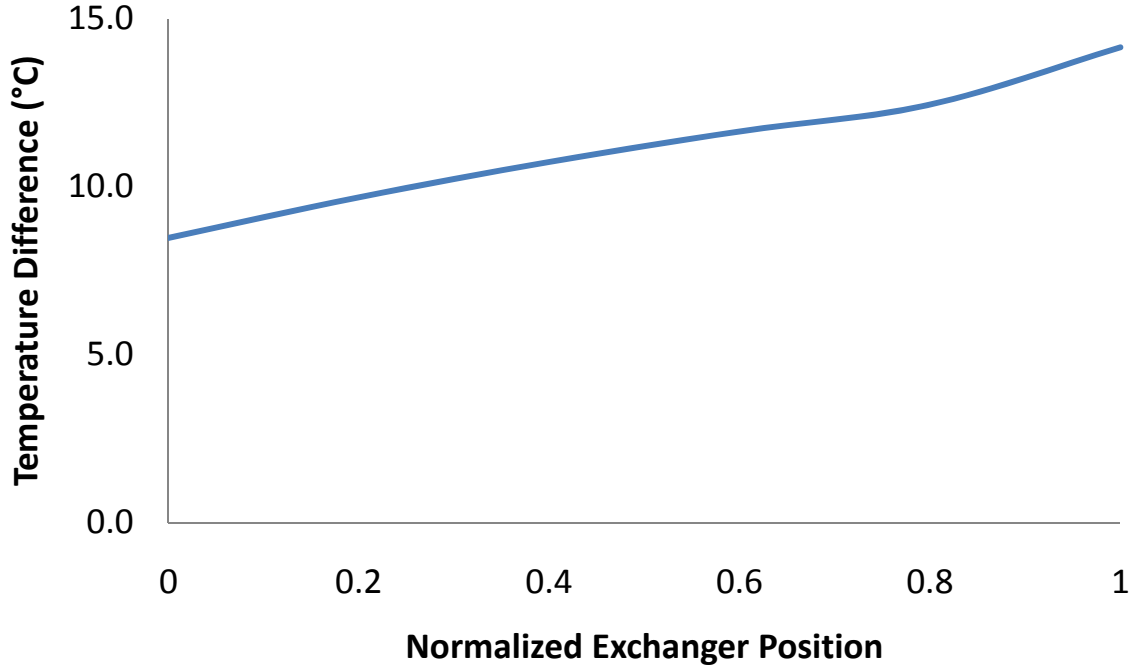


Figure 13: Profile of Temperature Difference between hot and cold streams in High-Pressure Heat Exchanger of 2-Stage Flash. 0 = cold side, 1 = hot side. 0.4 rich loading, 0.26 lean loading, 5 °C LMTD on low-pressure heat exchanger.

Table 5: High-Pressure Exchanger Conditions for 2-Stage Flash Base Case

Segment	Exchanger Position	Cold T °C	Hot T °C	Q kW	dT °C	UA kW/°C
0	0	90.0	98.5	36.0	8.5	3.96
1	0.2	99.2	108.9	36.0	9.7	3.52
2	0.4	108.5	119.3	36.0	10.7	3.22
3	0.6	117.9	129.6	36.0	11.6	2.99
4	0.8	127.4	139.8	36.0	12.4	2.71
5	1	135.9	150.0		14.2	

The total heat duty in the high-pressure heat exchanger was 179.9 kW, so each of the five segments exchanged 36.0 kW. The temperature difference for each segment was assumed to be the average of the segment's hot side and cold side values of ΔT . Therefore, the UA for each segment could be calculated as follows:

$$UA_i = \frac{Q_i}{(\Delta T_i + \Delta T_{i+1})/2} \quad (5)$$

where i is the segment. The sum of all UA_i values gave an overall UA and was divided by the exchanger area (219.6 ft^2) to give a calculated average U . This calculation gave an average U of 0.804 kW/m-K .

For all following calculations, the same average U was specified for the high-pressure heat exchanger. Several beneficial effects were observed by splitting the rich solvent and contacting the high temperature vapor in either stream with the cold liquid, detailed in Table 6. Unless otherwise specified, each bypass was 5% of the total rich solvent, and the packed section was 12 in of Mellapak 500Y. Two new alterations were considered: bypassing rich solvent to only the low-pressure flash (2SF-LP Inj), and bypassing rich solvent to both the low-pressure and high-pressure flashes (2SF-LP/HP Inj). It was found that most of the benefit came from the rich solvent injection to the low-pressure flash, and there was little more benefit by also injecting rich solvent into the high-pressure flash. The low-pressure flash had a higher PZ and water concentration than the high-pressure flash since its loading was lower, so cooling and condensing its vapor had a greater effect than for the high-pressure flash.

Table 6: Improvement with Rich Solvent Injection for Two-Stage Flash. Includes compression to 150 bar.

Rich loading mol/mol	Lean loading mol/mol	Configuration	Total heat duty kJ/mol CO_2	Total PZ in vapor mol/hour	Equivalent work kJ/mol CO_2
0.4	0.26	SS	106.1	3.7	33.2
0.4	0.26	2SF	130.1	27.0	38.7
0.4	0.26	2SF-LP Inj	113.7	12.5	35.5
0.4	0.26	2SF-LP/HP Inj	107.4	11.3	34.2
0.4	0.3	SS	101.0	2.3	32.5
0.4	0.3	2SF	108.7	8.8	36.4
0.4	0.3	2SF-LP Inj	96.0	3.2	34.0

Most importantly, the amount of volatilized PZ was reduced drastically, especially at low lean loading values like 0.26. A typical optimum lean loading for 8 m PZ would be about 0.3, where the total PZ molar flow of the combined vapor streams decreased from 8.8 mol/hour to 3.2 mol/hour. A simple stripper under similar conditions would still have a lower PZ flow rate (2.3 mol/hour), but the impact of switching from a simple stripper to the modified 2-stage flash was less drastic. Another benefit was the reduced equivalent work. Although the 2-stage flash has a smaller capital investment than a simple stripper, the downside of using the flash configuration with PZ was that the equivalent work requirement would be higher. Comparatively, MEA simulations demonstrated a reduction in the total work by switching from a simple stripper to the 2-stage flash (Van Wagener et al., 2010a). In the current simulations, the increased complexity of the rich solvent injection improved the reversibility of the flash process by reducing the amount of water vapor released, so the equivalent work decreased. Unfortunately, the equivalent work was still higher compared to a simple stripper. On the other hand, the normalized heat duty for the rich injection configurations was less than simple stripper configurations with similar conditions. Again, the reduced water vapor released decreased the total amount of heat required. Lastly, a benefit of bypassing rich solvent was a more constant approach temperature across the

high-pressure heat exchanger. Figure 14 shows the temperature profile of the 2-stage flash with injection to both the low-pressure and high-pressure flash vessels.

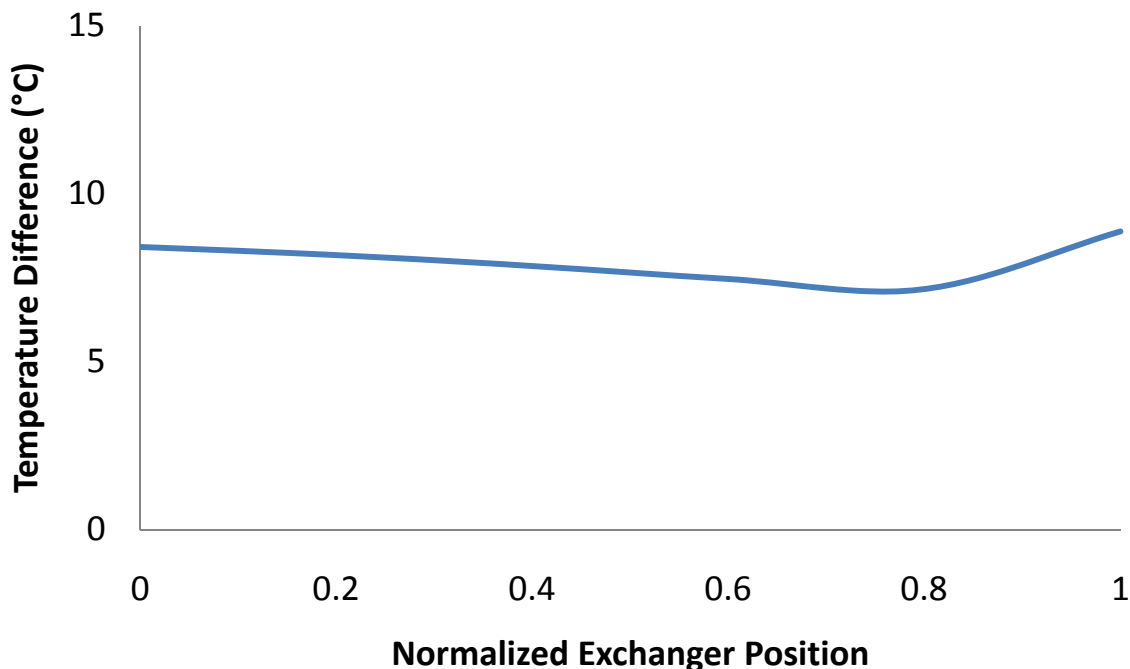


Figure 14: Profile of Temperature Difference between hot and cold streams in High-Pressure Heat Exchanger of 2-Stage Flash with 5% rich solvent injection to low-pressure and high-pressure flash vessels. 0 = cold side, 1 = hot side. 0.4 rich loading, 0.26 lean loading, 5 °C LMTD on low-pressure heat exchanger.

This configuration bypassed a total of 10% of the rich solvent around the high-pressure heat exchanger, which evened out the heat capacity flows of the hot and cold streams. In comparison to the temperature profile of the 2-stage flash base case in Figure 5, the temperature difference across the exchanger was more constant when by passing a portion of the rich solvent.

Conclusions

1. The 2008 and 2010 PZ pilot plant campaigns with simple strippers were simulated. The overall MAPE for the campaigns were 4.5% and 2.7%, respectively. The most significant deviation was in the overhead CO₂ rate, which was concluded to be due to systematic error in the pilot plant measurements.
2. The proposed advanced 2-stage flash flowsheet stripped CO₂ at typical rich and lean loadings of 0.4 and 0.31 with an equivalent work requirement of 35.5 kJ/mol CO₂. A decrease in the temperature of the extracted brine from 150 °C to 145 °C would increase the equivalent work to 36.2 kJ/mol CO₂, and the brine flow rate would increase by 4%.
3. The optimum performance of an interheated column was evaluated considering a rigorous calculation of absorber performance. The equivalent work was calculated to be 31.1 kJ/mol CO₂ was, which included the reboiler heat duty, rich pump work, lean pump

work, intercooler pump work, interheater pump work, blower work, and multi-stage compression work.

4. PZ volatility would be reduced by using a 5% cool rich bypass to 12 inches of packing in the top of the low-pressure flash tank in a 2-stage flash configuration. At a typical optimum lean loading of 0.3, the total volatilized PZ for the pilot-scale model was reduced by 64% from 8.8 mol/hour to 3.2 mol/hour.
5. The energy performance of the 2-stage flash benefited from a 5% cool rich bypass to 12 inches of packing in the top of the low-pressure flash tank. At a typical optimum lean loading of 0.3, the equivalent work decreased from 36.4 kJ/mol CO₂ to 34.0 kJ/mol CO₂.

Future Work

Sensitivity of the rich bypass 2-stage flash configuration to bypass percentage and packing height will be evaluated to determine the optimum point of performance. The energy requirement of the advanced 2-stage flash configuration for geothermal heating will be analyzed in conjunction with the cost of drilling and operating geothermal wells, calculated by a geologic model. Lastly, global optimum operating points for the interheated column will be determined considering the steam cycle performance of either pre-existing or newly built coal-fired power plants. Different operating points will optimize the net energy production for the two power plant cases.

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Modeling CO₂ Absorption Using Aqueous Amines

Quarterly Report for January 1 – March 31, 2011

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Supported by the Luminant Carbon Management Program

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The University of Texas at Austin

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Abstract

Work was conducted to assess the discrepancies found between the laminar jet and the wetted wall column model for MEA. Previous results showed large differences between the extracted kinetics from both models. Analysis showed issues with diffusivities of CO₂ and amine species, and activity coefficients of CO₂ and MEA. The diffusion coefficient was modified by user FORTRAN subroutines to match diffusion behavior reported by Aboudheir (2002). The activity coefficient of CO₂ was initially corrected with the correlations used by Dugas (2009). However, the MEA activity coefficient values and behavior largely deviated from the data reported by Dugas. It is not possible to correct the MEA activity coefficient without re-regressing the thermodynamic framework. Initially, the CO₂ activity coefficient was adjusted in an attempt to compensate the issues related to the MEA activity coefficient. This adjustment affected the fit for the equilibrium pressure of CO₂ vs. loading. The solution of this issue requires re-regression of the CO₂-MEA-H₂O parameters.

Samples from the September 2010 PZ campaign have been analyzed for loading and compared to the values obtained at the pilot plant. Results show a consistently higher measurement for the midpoint and rich data for the titrations at the pilot plant.

MEA absorption models: Laminar Jet and WWC

Previous work (Rochelle et al., 2011) showed large discrepancies between the kinetic constants obtained using the laminar jet model with Aboudheir (2002) data, and the wetted wall column model along with data by Dugas (2009). The diffusion coefficients for CO₂ and amine species were revised and a new FORTRAN subroutine was implemented. The subroutine uses correlations presented by Versteeg et al. (1988) for CO₂ in water:

$$D_{CO_2-water} = 2.35 * 10^{-6} e^{\frac{-2119}{T}} \quad (1)$$

where: $D_{CO_2-water}$ is the diffusivity of CO₂ in water in m²/s
T is the temperature in Kelvin.

The diffusivity coefficient in MEA solvent is then calculated using the following modified Stokes-Einstein relation:

$$D_{CO_2-sln} = D_{CO_2-water} \left(\frac{\mu_{water}}{\mu_{sln}} \right)^{0.8} \quad (2)$$

where: D_{CO_2-sln} is the diffusivity of CO₂ in the amine solution in m²/s;

μ is the viscosity in Pa-s. The subscript *sln* represents solvent properties.

Equations 1 and 2 were also used for N₂. The diffusion coefficients of MEA, MEA⁺, MEACOO⁻, and HCO₃⁻ were calculated using the equation for MEA in water proposed by Hayduk and Laudie (1974):

$$D_{MEA-water} = \frac{13.26 * 10^{-5}}{\mu_{water}^{1.4} V_{b-MEA}^{0.589}} \quad (3)$$

where: $D_{MEA-water}$ is the diffusivity of MEA in water in cm²/s;

μ_{water} is the viscosity of water in cP;

V_{b-MEA} is the molar volume of MEA at its normal boiling point in cm³/gmol.

The diffusivity of the amine species in the solvent is calculated by the following:

$$D_{MEA-sln} = D_{MEA-water} \left(\frac{\mu_{water}}{\mu_{sln}} \right)^{0.6} \quad (4)$$

where: $D_{MEA-sln}$ is the diffusivity of MEA in the solution;

μ_{sln} is the viscosity of the solution.

The WWC and the laminar jet models, with the modified diffusivity coefficients, were used to obtain the kinetic constants for the MEA model. The discrepancies between the two models continued with a strong dependency in loading for the kinetic constants especially for the WWC results.

Further review of the activity coefficient of MEA showed a strong dependence on loading that dramatically increases with amine concentration. MEA activity coefficients calculated by Dugas (2009) are lower than those generated by the Aspen Plus[®] model, have a lower dependence on loading, and have an inverse dependence on temperature as shown in Figures 1 and 2.

Since the reaction rates in the Aspen Plus[®] model are defined using the activities of MEA and CO₂, it is expected that the behavior of the activity coefficient of MEA will have an effect on the rate constant. As a solution to this issue, the activity coefficient of CO₂ was adjusted to match the behavior of the product of the activity coefficients of MEA and CO₂ using the values from Dugas (2009):

$$(\gamma_{MEA}^2 \gamma_{CO_2})_{Dugas} = (\gamma_{MEA}^2 \gamma_{CO_2})_{Aspen} \quad (5)$$

Where γ is the activity coefficient. The sub index *Dugas* and *Aspen* refer to the methods used to calculate the activity coefficient. *Dugas* uses the correlations presented in Dugas (2009) and *Aspen* the values in the model. The activity coefficient of MEA is squared since the rate of carbamate formation is assumed to be dependent on the square of the MEA activity. The activity coefficient of CO₂ for the model is fitted to the value obtained by solving Equation 5 for the activity coefficient of CO₂ in Aspen Plus[®] as follows:

$$(\gamma_{CO_2})_{Aspen} = \frac{(\gamma_{MEA}^2 \gamma_{CO_2})_{Dugas}}{(\gamma_{MEA}^2)_{Aspen}} \quad (6)$$

The MEA activity coefficient in Equation 6 is extracted from the Aspen Plus[®] model. Figure 3 shows the γ_{CO_2} to be fitted for 7 m MEA. The fitting in the model is done using the e-NRTL parameters related to CO₂ ($\tau_{CO_2-MEA+MEACOO^-}$, $\tau_{MEA+MEACOO^-CO_2}$, $\tau_{CO_2-MEA+HCO_3^-}$, $\tau_{MEA+HCO_3^-}$

CO₂). However, as the new values for the CO₂ activity coefficient were fitted, the VLE in the model was affected and the fit of equilibrium pressure of CO₂ with respect to loading was no longer adequate.

Figure 1: MEA activity coefficient for 7 m MEA. Dashed lines are generated using correlations found in Dugas (2009). Continuous lines are generated from the Aspen Plus[®] model.

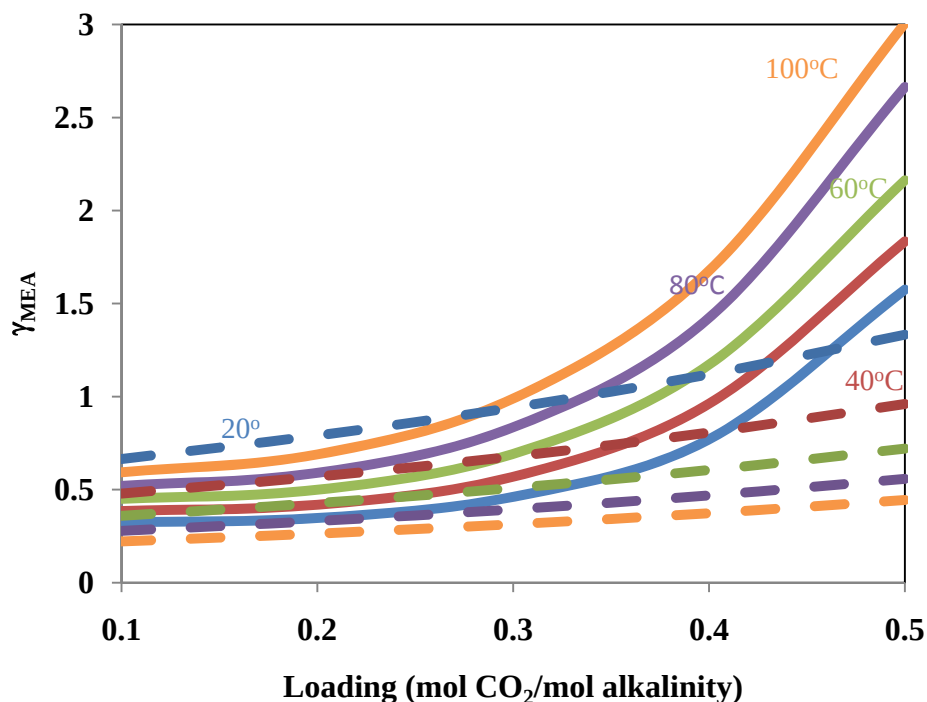


Figure 2: MEA activity coefficient for 12 m MEA. Dashed lines generated using correlations found in Dugas (2009). Continuous lines are generated from the Aspen Plus[®] model.

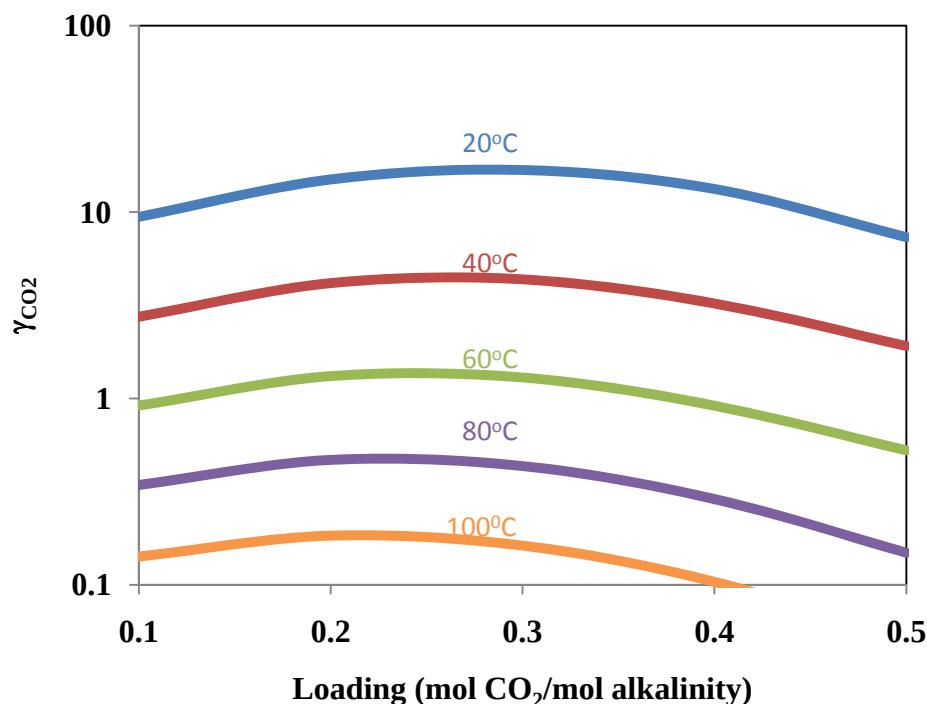


Figure 3: Adjusted CO₂ activity coefficient for 7 m MEA.

Pilot plant loading measurements

Solvent samples from the September 2010 piperazine (PZ) pilot plant campaign were analyzed in the labs on the main campus to compare results to the analysis done at the Pickle Research Center during the campaign. Freeman (Rochelle et al., 2008; Rochelle et al., 2009) reported discrepancies in the loadings measured by total inorganic carbon (TIC) used on campus and the methanol-potassium hydroxide titration conducted at the Pickle Research Center for the November 2008 campaign. The generated parity plot (Figure 4) for the analyzed samples show higher values for the midpoint and rich loading samples for the pilot plant analysis.

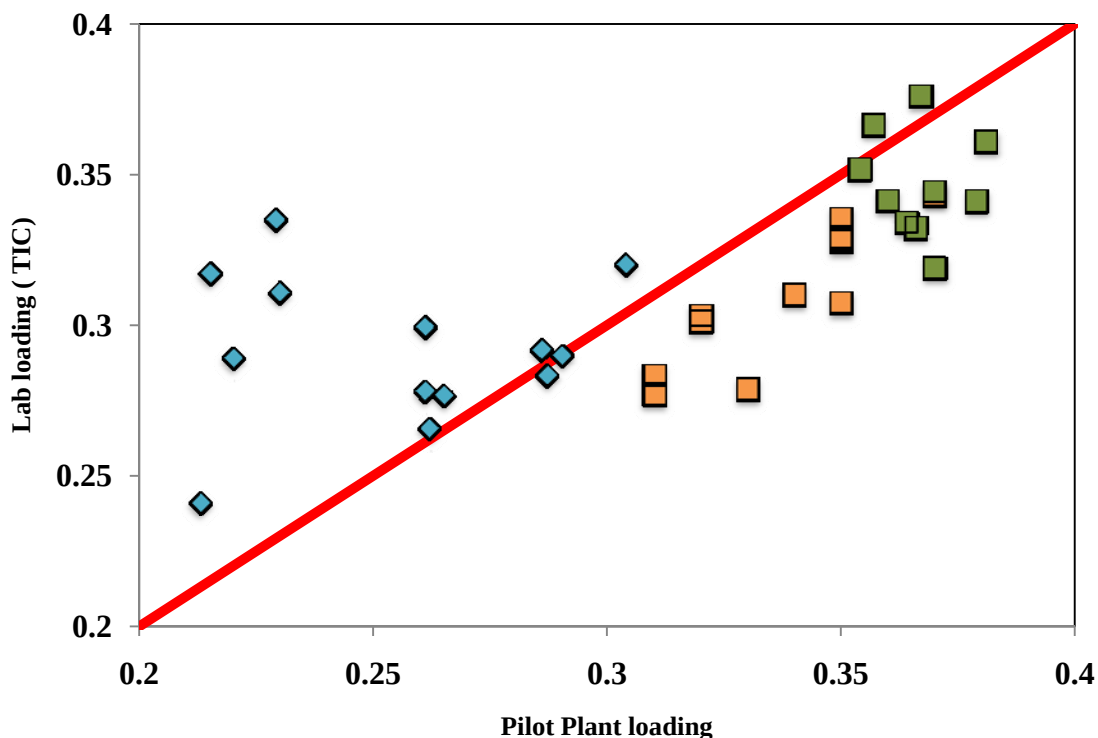


Figure 4: Loading parity plot for the November 2010 PZ campaign. Sample from ♦ (blue diamonds) lean side, (green squares) rich side, and (orange squares) middle of the absorber.

Conclusions

- Analysis of the MEA thermodynamic framework revealed that the MEA activity coefficient displays a considerable dependence on loading and an inverse dependence on temperature from the expected values based on the work by Dugas (2009). Attempts to compensate this behavior by modifying the activity coefficient of CO₂ proved inadequate, affecting the model VLE fit. Re-regression of the CO₂-MEA-H₂O model parameters is required to assess this issue and to improve the kinetic framework.
- The pilot plant methanol-potassium hydroxide titration method used to determine loadings for the samples from the September 2010 campaign shows differences with the data obtained by the TIC method used in the lab on campus. The rich and midpoint loading samples are consistently lower for the lab than for the pilot plant. This might be due to a loss of CO₂ in the richer loading samples from the time of sampling in the pilot plant to the testing in the lab. The lean side samples show consistently higher loadings for the lab when compared to the pilot plant. This requires further analysis to determine if there is experimental error in the lab analysis.

Future Work

The MEA thermodynamic framework will be re-regressed to obtain CO₂-MEA-H₂O parameters. The goal is to improve the MEA activity coefficient behavior and the MEA volatility.

The developed thermodynamic framework will be used to build laminar jet and WWC models to extract MEA kinetics. Results will be compared to assess congruency between models.

The completed model with newly extracted kinetics will then be used to build an absorber model to reconcile data from the 2008 and 2010 pilot plant campaigns.

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Measurement of Packing Effective Area and Mass Transfer Coefficients

Quarterly Report for January 1 – March 31, 2011

by Chao Wang

Supported by the Luminant Carbon Management Program,
and the Process Science and Technology Center

Department of Chemical Engineering

The University of Texas at Austin

April 30, 2011

Abstract

Packing is widely used in distillation, stripping, and scrubbing processes because of its relatively low pressure drop, good mass transfer efficiency, and ease of installation. Packing is being investigated for post-combustion carbon capture for these reasons. Research continues to focus on development of high performance packing, especially on minimizing pressure drop, maximizing mass transfer efficiency, and minimizing costs. The design of packed absorbers for carbon dioxide capture will require the reliable measurement and accurate prediction of the effective area a_e , gas and liquid film mass transfer coefficient k_G and k_L . My research is focused on the measurement of these important fundamental parameters for packings and construction of a mechanistic design model.

In this quarter, new gas film mass transfer coefficient measurements have been completed for 1-inch plastic pall rings. A second low range SO_2 analyzer has been installed to allow measurements of ppb level SO_2 concentrations. Therefore, a 10 ft bed of packing can be used which helps to minimize any end effects and provides a deeper bed for formation of natural flow distribution within the packing. The k_G measurements show performance and dependence similar to that observed with previous packings such as no dependence on liquid rate and a dependence on gas rate to 0.93 power.

The Rocha-Bravo-Fair (RBF) mass transfer model (1996) has been evaluated in this quarter. The RBF model is based on distillation systems with organic solutions and very low surface tensions. As a result, the RBF mass transfer model depends on its corresponding area model. Thus one would expect trouble with the mass transfer coefficient prediction when used with the Tsai area model. It makes more sense to use RBF $k_{G/L}$ model multiplied by RBF area model to predict $k_{G/L}a$ data instead of using RBF $k_{G/L}$ model alone. In this quarter, both RBF $k_{G/L}$ -RBF area model and RBF $k_{G/L}$ -Tsai area model are used to predict experimental ka numbers. Results show that RBF $k_{G/L}$ -RBF area model is much closer to the experimental data, which means we should use RBF k model and RBF area model together to predict ka numbers in the future.

Another dimensionless k_L model is proposed in this quarterly report. This model is based on Brunazzi (1997). Results show that this k_L model fits well with our experimental data; the average deviation is 24%.

Experimental work

Gas film mass transfer coefficient measurement for 1-inch plastic pall ring

In the last quarterly report, pressure drop, liquid hold-up, effective mass transfer area, and liquid film mass transfer coefficient for 1-inch plastic pall rings was measured. However, for the gas film mass transfer coefficient, the reaction is an instantaneous one so the outlet SO_2 concentration could be as low as 1 ppb if 10 ft of packing is used. If only one analyzer is used to measure both the inlet and outlet SO_2 concentration, only 4 ft of packing can be used. To correct this problem, another SO_2 analyzer calibrated to 0.1 ppb was installed to allow accurate SO_2 outlet measurements with 10 ft of packing. The k_{GA} result for 1-inch plastic pall rings is shown in Figure 1.

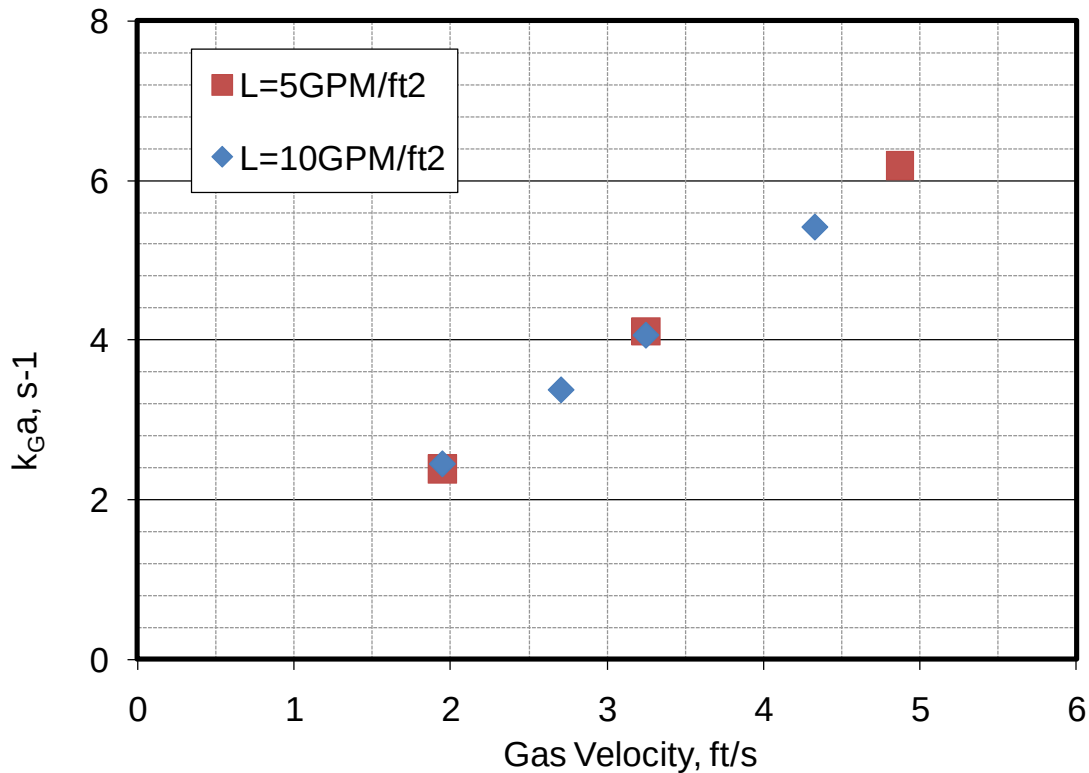


Figure 1: k_{GA} measurement for 1-inch plastic pall rings

From this figure we can see that k_G functionality is quite similar to previous packings. k_G depends on the gas flow rate and is independent of liquid flow rate. The gas film mass transfer coefficient can be determined from the directly measured volumetric gas film mass transfer coefficient (k_G) and the previously measured contact area determined from the equivalent flow conditions. The k_G results for 1-inch plastic pall rings are shown in Figure 2. Two other packings are compared with pall rings in Figure 2: the metal random packing, Raschig Super Ring (RSR) #0.5, and the Flexipac (FP) 1.6 Y High Capacity (HC). The liquid flow rate for these two packings is 10 gpm/sq.ft. From this figure, we can see that at the same condition, the k_G for the 1-inch pall ring random packing is somewhat higher than FP 1.6Y HC structured packing. k_G for 1-inch plastic pall ring is close to RSR#0.5 at the same condition. The dashed line is the Rocha-Bravo-Fair k_G model. The deviation of 1-inch plastic pall ring k_G to Rocha-Bravo-Fair model is about 20%.

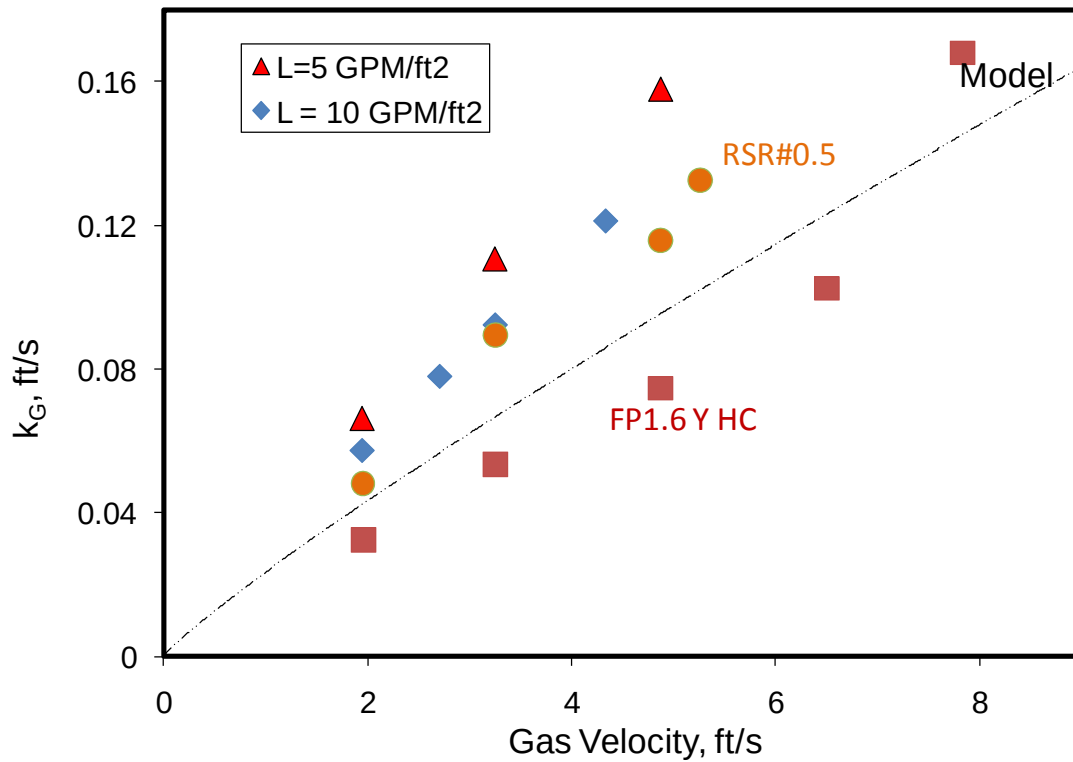


Figure 2: k_G result for 1-inch plastic pall ring

Modeling work

Rocha-Bravo-Fair (RBF)

Since the RBF model (1996) is based on data measured in the distillation column with organic solutions, there will be a large deviation when using the RBF k or area model alone to predict k or area values in water systems. Therefore it may be advantageous to use the RBF k model multiplied by its corresponding area model to predict ka numbers. In this quarter, RBF k model-RBF area model and RBF k model-Tsai area model are used to predict ka numbers.

$$\text{RBF } k_G \text{ model: } k_G = \frac{0.054 D_G}{S} \left(\frac{(u_{GE} + u_{LE}) \rho_G S}{\mu_G} \right)^{0.8} \left(\frac{\mu_G}{D_G \rho_G} \right)^{0.33} \quad (1)$$

$$\text{RBF area model: } \frac{a_e}{a_p} = F_{SE} \frac{29.12(We_L Fr_L)^{0.15} S^{0.359}}{Re_L^{0.2} \varepsilon^{0.6} (1 - 0.93 \cos \gamma)(\sin \theta)^{0.3}} \quad (2)$$

$$\text{where } Re_L = \frac{u_L S \rho_L}{\mu_L}, Fr_L = \frac{u_L^2}{Sg}, We_L = \frac{u_L^2 \rho_L S}{\sigma g_c}, \text{ in water, } \sigma = 0.072 \text{ N/m}, \cos \gamma = 0.32$$

$$\text{Tsai area model: } \frac{a_e}{a_p} = 1.34 \left[\left(\frac{\rho_L}{\sigma} \right) g^{1/3} \left(\frac{Q}{A} * \frac{Bh}{4S} \right)^{4/3} \right]^{0.116} \quad (3)$$

All the fluid physical properties are listed in Table 1. Packing properties are listed in Table 2. Comparison results are shown in Figure 3.

Table 1: Fluid physical properties

	ρ_G	ρ_L	D_G	D_L	μ_G	μ_L
unit	kg/m ³	kg/m ³	m ² /s	m ² /s	kg/(m*s)	kg/(m*s)
number	1.204	998	1.31E-05	8.6E-10	1.98E-05	0.001

Table 2: Packing properties

Packing	RSP 250	FP 1.6 Y HC	MP2X
Surface area (m ² /m ³)	250	295	205
Corrugation angle	45	45	60
Channel side, S (m)	0.014	0.017	0.02
Void fraction ε	0.92	0.95	0.99
F_{SE}	2.077	1.949	2.186

In Figure 3, all the black points are RBF predicted k_G values multiplied by RBF predicted area model, and all the red points are RBF k_G multiplied by Tsai area model. From Figure 3 we can see that the black points are closer to the $y = x$ line, which is k_{Ga} model equals k_{Ga} experimental data line than red points. Results show that the RBF k_G -RBF area model has a lower deviation; the average deviation is 24.9%.

Similar to k_G model, RBF k_L model multiplied by RBF area model, RBF k_L model multiplied by the Tsai area model is compared with experimental results shown in Figure 4.

$$\text{RBF } k_L \text{ model: } k_L = 2 \left(\frac{D_L C_E U_{LE}}{\pi S} \right)^{0.5} \quad (4)$$

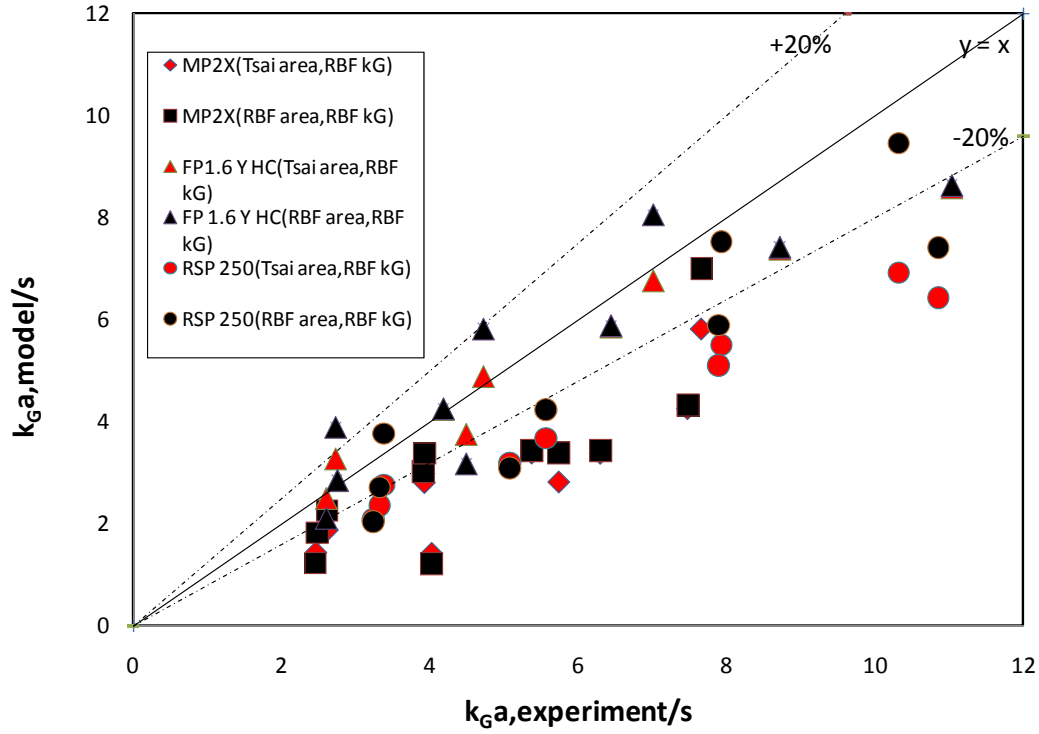


Figure 3: RBF k_G -RBF area and RBF k_G -Tsai area model compared with experimental k_{Ga}

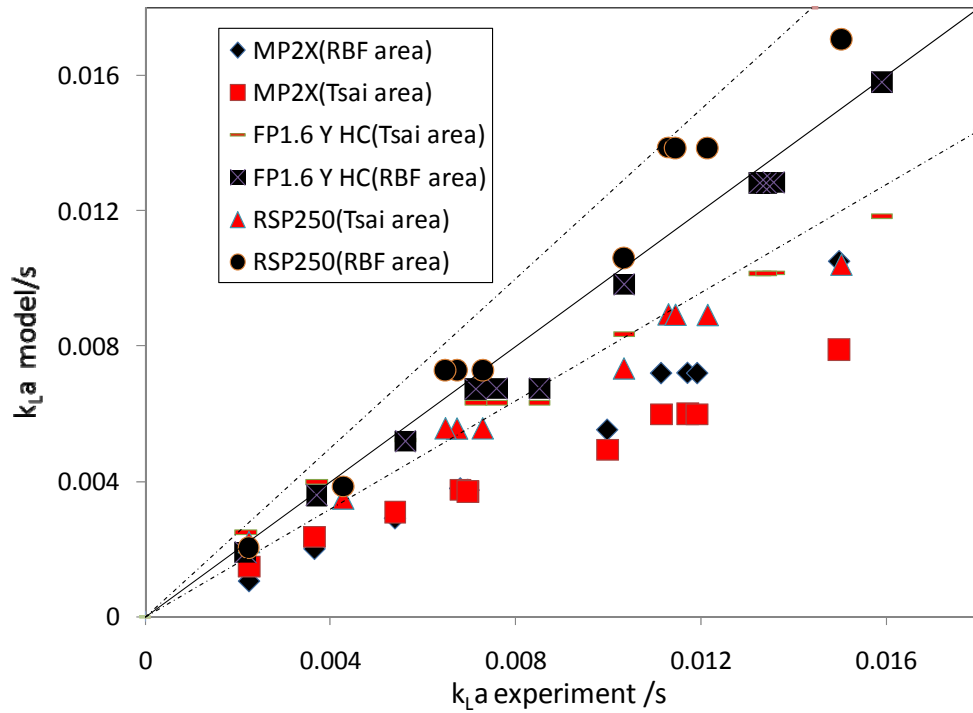


Figure 4:- RBF k_L -RBF area and RBF k_L -Tsai area model compared with experimental k_{La}

Similar to k_G model, in Figure 4 all the black points are RBF k_L multiplied by RBF area model, and all the red points are RBF k_L multiplied by Tsai area model. From Figure 4, we can see that RBF k_L *RBF area is closer to $y = x$ line with an average deviation of 20.6%.

Brunazzi's Dimensionless k_L model

Since the RBF k_L model is not dimensionless and does not consider non-laminar flow and packing geometry, we are looking for a more sophisticated k_L model. Brunazzi proposed a dimensionless k_L model for structured packing in his paper (Brunazzi, 1997). The packings analyzed in that paper are from the Sulzer structured packing family.

The dimensionless k_L model is: $Sh_L = A \frac{Gz^B}{Ka^C}$ (5);

Where: $Ka = \frac{\sigma^3 \rho_L}{\mu_L^4 g}$ (6);

$Gz = Re_L Sc_L \frac{\delta \sin \theta}{H_{el}}$ (7);

$Re_L = \frac{\rho_L S u_{LE}}{\mu_L}$ (8);

$Sc_L = \frac{\mu_L}{\rho_L D_L}$ (9);

$\delta = \left(\frac{3\mu_L}{\rho_L g \sin \theta} \frac{u_{LS}}{L \sin \theta} \right)^{0.5}$ (10).

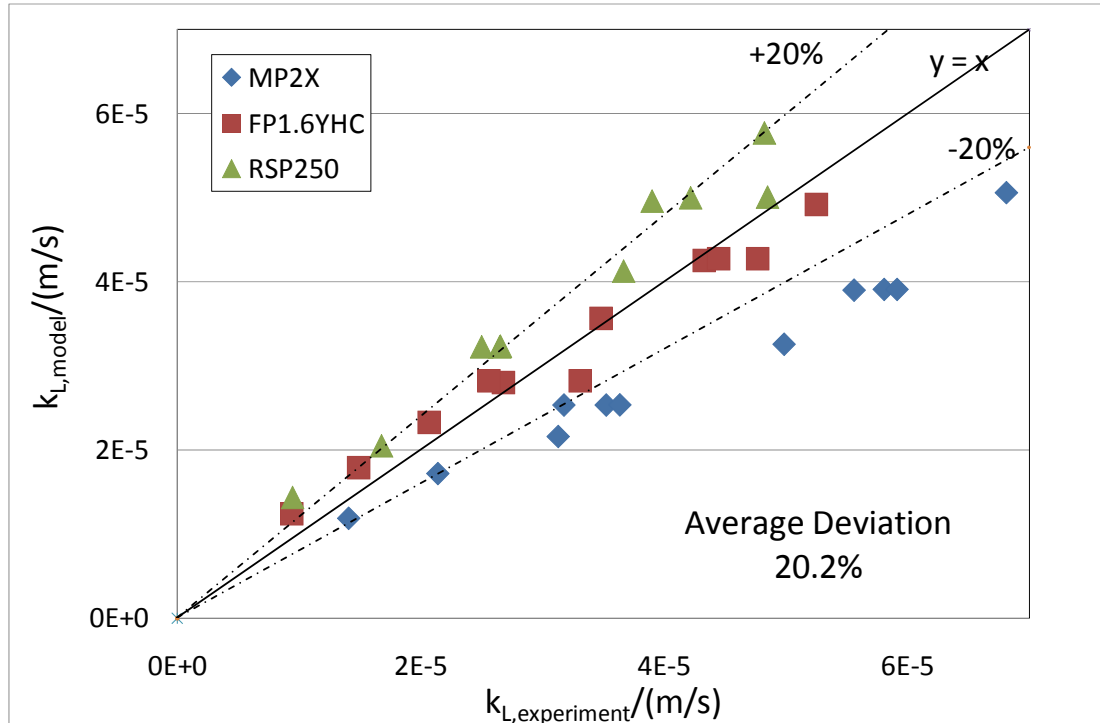


Figure 5: Brunazzi's k_L model compared with experimental results

After regressing with our experimental data, the experimental constant A and exponents B and C can be calculated. $A = 409.54$, $B = 0.5$, $C = 0.09$. Figure 5 shows Brunazzi's k_L model compared with experiment results. From Figure 5, we can see that k_L predicted by this

dimensionless model is close to the experimental results. Almost all the points are within the 20% deviation line. The average deviation is 20.2%.

Conclusions

This is the first time we have used two SO₂ analyzers for the gas phase film mass transfer coefficient measurement. k_G results for 1-inch plastic pall ring show a similar tendency to previous packings, where k_G increases with gas flow rate, but does not change much with liquid flow rate. The exponent of k_G over u_G is 0.93 for 1-inch plastic pall ring. k_G is 0.028 m/s at $u_G = 1$ m/s and $u_L = 0.0067$ m/s for this packing.

The Rocha-Bravo-Fair $k_{G/L}$ model multiplied with Rocha-Bravo-Fair area model has a better prediction over Rocha-Bravo-Fair $k_{G/L}$ model with Tsai area model. The average deviation for RBF k_G -RBF area model is 24.9%; for RBF k_L -RBF area model it is 20.6%. It is suggested that the RBF k model be used together with the RBF area model instead of using RBF k model alone for water systems.

Brunazzi's dimensionless k_L model is: $Sh_L = A \frac{Gz^B}{Ka^C}$, average deviation is 20.2%.

Future Work

Next quarter, we will measure a 75-degree corrugation angle packing-GTC 350Z. After that, we will measure Raschig Super Ring #0.7, another metal random packing. Mass transfer models will also be developed.

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Dynamics and Control of MEA Plant in Response to Foaming in the Absorber

Quarterly Report for January 1 – March 31, 2011

by Sepideh Ziaei Fashami

Supported by the Luminant Carbon Management Program

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April 30, 2011

Abstract

This work presents results on dynamic effects of absorber foaming on MEA absorption/stripping, explores possible control strategies, and identifies effective strategies for safe and stable plant operation.

To simulate foaming on the absorber packing bed, the liquid hold-up time in the absorber packing was increased with a +10% step change in a linear factor affecting the liquid hold-up equation used in the model.

Open loop analysis indicated a sharp overshoot in the stripper pressure, which mainly resulted from the initial rise and drop in the rich loading. This dynamic behavior necessitates pressure control on the stripper to protect the stripper column and multi-stage compressor. Controlling stripper pressure by either steam valve or pressure valve is not an effective strategy especially if these valves are wide open normally and become saturated during abnormal conditions.

Rich solution flow rate was found to be the best manipulated variable, as it can decrease the magnitude of overshoot and keep the pressure close to the set point. This variable dampens the influence of the rich loading on the stripper pressure by decreasing the CO₂ desorption.

According to the dynamic results, level ratio control on lean and rich tank by lean solution flow rate is necessary to keep the liquid levels in balance and prevent the pumps from running dry. If this control loop acts with a delay time equal to the liquid hold-up time in the equipment between tanks (reboiler and stripper), it gives the best dynamic response for stripper pressure and other process variables.

Introduction

Dynamic modeling of a process is a helpful tool that is commonly used for analyzing the dynamic behavior and designing control strategies in a process in response to possible disturbances. This application has been previously employed for dynamic analysis and operation optimization of CO₂ absorption process with aqueous amines (Kvamsdal et al., 2009; Ziaei et al., 2010; Lawal et al., 2010).

No previous studies examined the dynamic behavior of capture in response to foaming in the packed columns which is an abnormal condition that happens frequently. This work focuses on studying the dynamic effects of the absorber foaming on the whole system, explores possible control strategies, and identifies the most effective ones for controlling key process variables in capture.

Analytical Methods

As explained in previous quarterly reports, a fully integrated model of the MEA system was created in an Aspen Custom Modeler® flow sheet. It consists of the dynamic model of the absorber and stripper, dynamic model of completely mixed rich and lean storage tanks, steady state models of the heat exchangers, steady state performance curves of the multi-stage compressor, and a first order-approximated model of a three-stage steam turbine.

In this study, the dynamic responses of the plant are investigated in response to the +10% step change in the liquid hold-up on the packing bed of the absorber. The goal is to find the best control strategy that keeps the operation of the plant stable and safe during this abnormal condition. In order to get knowledge on how this disturbance influences the stability and safety of the plant, the system is run with fixed opening position control valves (no closed control loop) (Figure 1). Then, based on loop analyses, some control options are explored, simulated, and the results are compared.

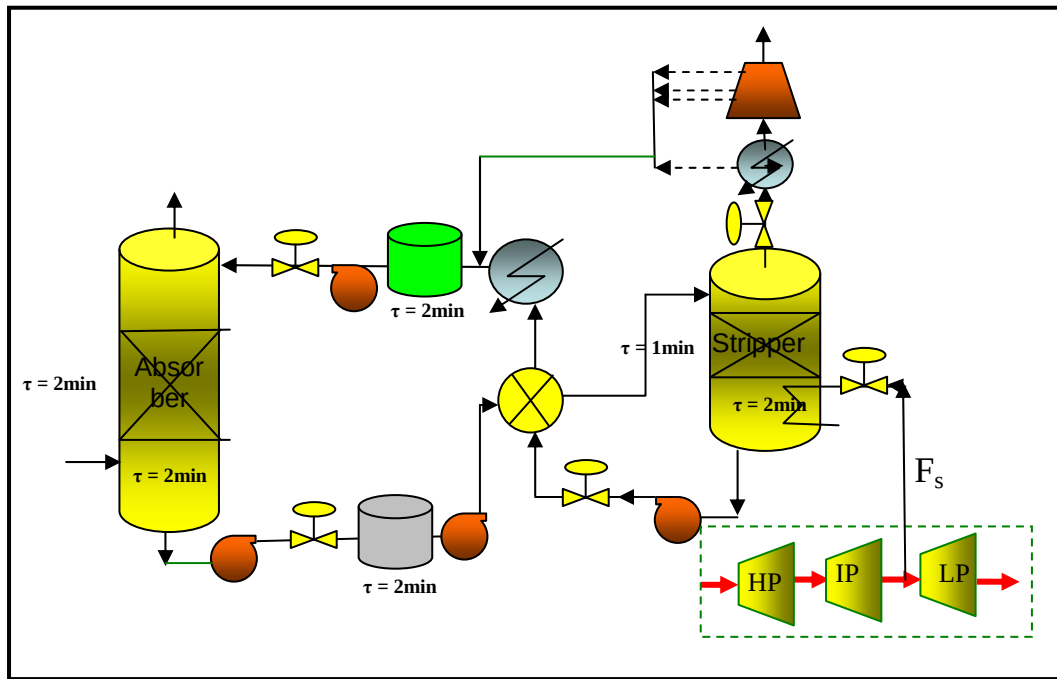


Figure 1: Flow sheet of MEA plant with control valves and with no control loops

In the simulation, the liquid hold-up time on the absorber packing is increased suddenly by making a +10% step change in a linear factor in the liquid hold-up equation used in the model.

Figure 1 shows the initial liquid hold-up time of all inventories in this case study. We assumed that initial hold-up time of the sumps and tanks is 2 min, while initial liquid hold-up time of the

beds in the columns is calculated by the model as a function of liquid and gas rates, properties, and packing properties at initial conditions.

Results and discussion

Safe and stable operation of the plant is the primary goal during abnormal conditions such as foaming. For this purpose, we have looked at dynamic responses of key process variables, which have limitations to change during the transition time to protect the upstream or downstream equipment.

Open loop analysis

When foaming happens in the absorber, the liquid hold-up rises on the packing bed and liquid rate coming out of the absorber decreases initially and then comes back to its initial value (Figure 2). Consequently, the response of loading in the rich solution coming out of the absorber shows an initial peak, however this overshoot is damped by the rich tank placed downstream of the absorber (Figure 3).

The initial rise in the rich loading leads to more desorption of CO_2 in the stripper and an apparent initial increase in the stripper top pressure. As the rich loading in the rich tank comes back to near its initial value, the pressure in the stripper drops and reaches steady state within the same time as the loading in the rich tank (Figure 4).

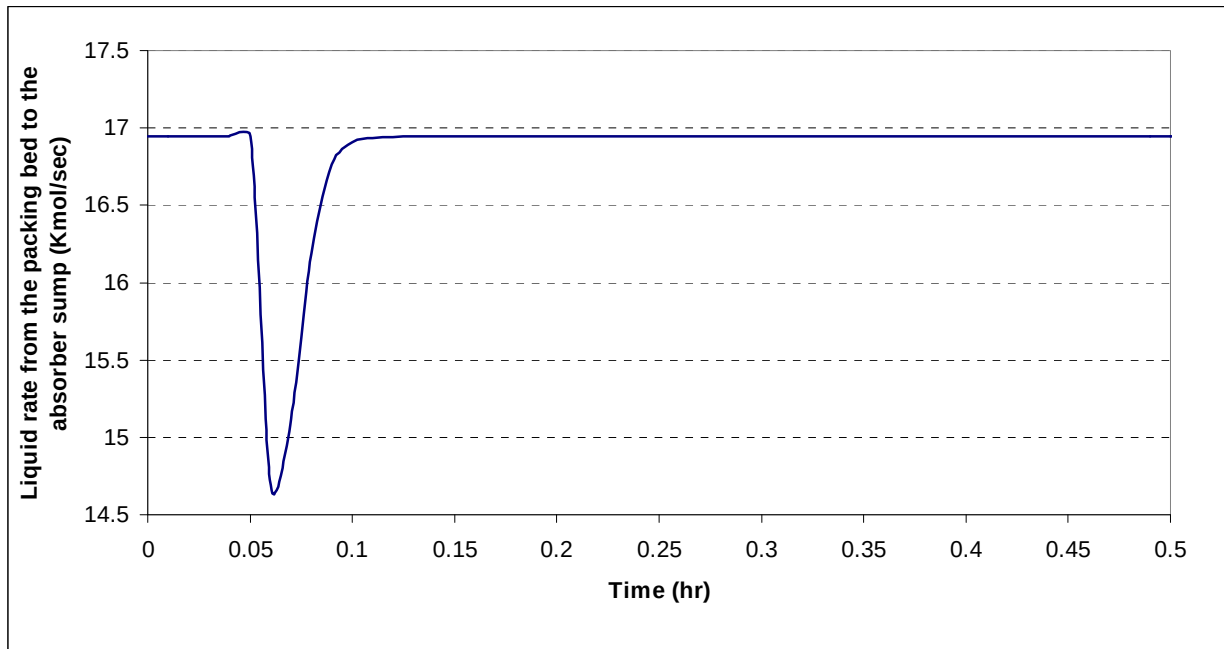


Figure 2: Open loop dynamic response to +10% step change in liquid hold-up on the absorber packing bed at 0.05 hr, plant designed removal = 90% and lean loading = 0.225, $H_{\text{abs}} = 15\text{m}$, $H_{\text{strip}} = 10\text{m}$, cross heat exchanger $\Delta T_{\text{design}} = 5^\circ\text{C}$, reboiler $\Delta T_{\text{design}} = 10^\circ\text{C}$, reboiler $T_{\text{design}} = 120^\circ\text{C}$, $\tau_{\text{sumps}} = 2\text{ min}$, $\tau_{\text{tanks}} = 2\text{ min}$.

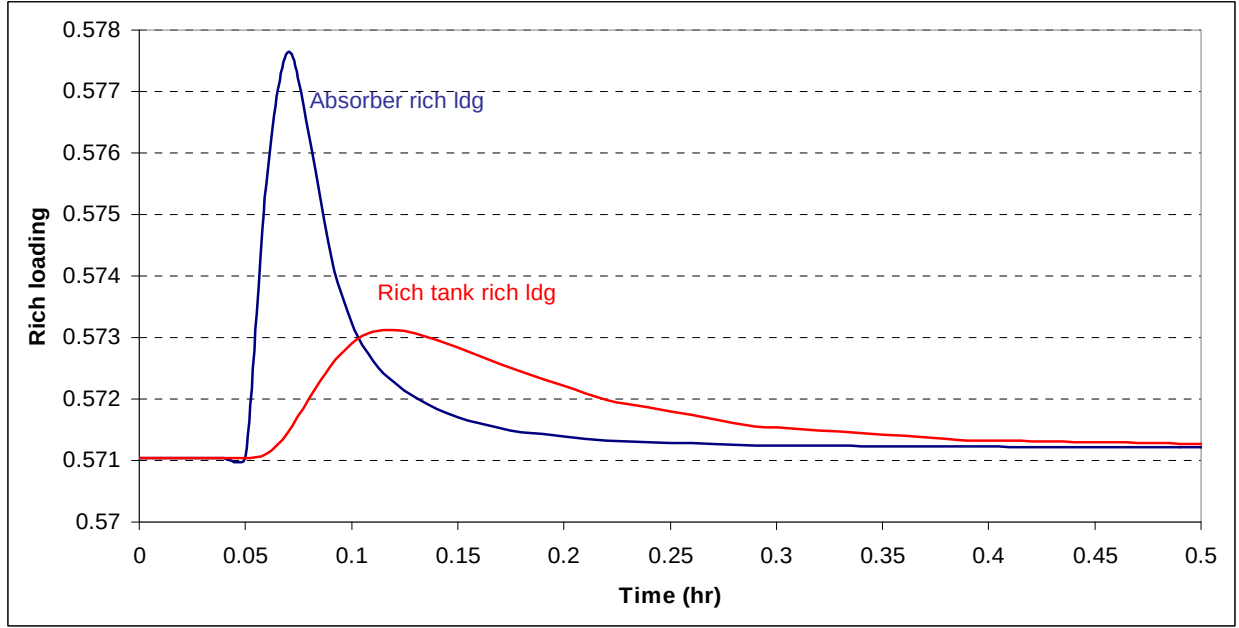


Figure 3: Open loop dynamic response to +10% step change in liquid hold-up on the absorber packing bed at 0.05 hr, plant designed removal = 90% and lean loading = 0.225, $H_{abs} = 15\text{m}$, $H_{strip} = 10\text{m}$, cross heat exchanger $\Delta T_{design} = 5^\circ\text{C}$, reboiler $\Delta T_{design} = 10^\circ\text{C}$, reboiler $T_{design} = 120^\circ\text{C}$, $\tau_{sumps} = 2\text{ min}$, $\tau_{tanks} = 2\text{ min}$.

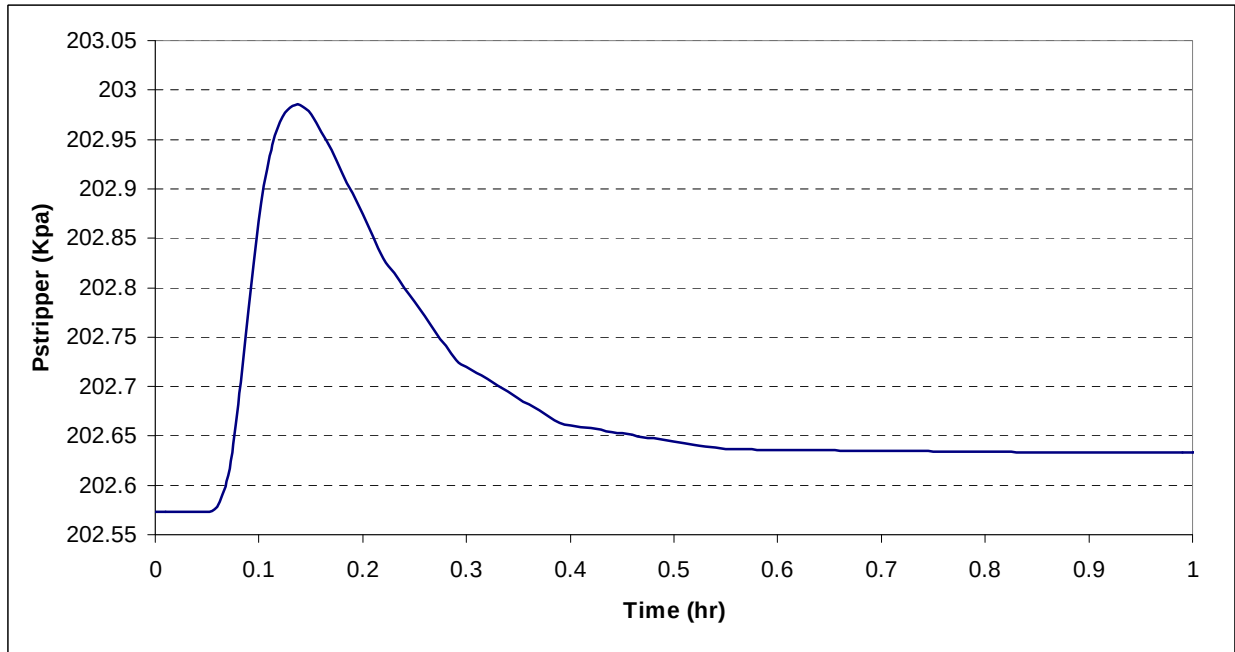


Figure 4: Open loop dynamic response to +10% step change in liquid hold-up on the absorber packing bed at 0.05 hr, plant designed removal = 90% and lean loading = 0.225, $H_{abs} = 15\text{m}$, $H_{strip} = 10\text{m}$, cross heat exchanger $\Delta T_{design} = 5^\circ\text{C}$, reboiler $\Delta T_{design} = 10^\circ\text{C}$, reboiler $T_{design} = 120^\circ\text{C}$, $\tau_{sumps} = 2\text{ min}$, $\tau_{tanks} = 2\text{ min}$.

Therefore, when the plant is exposed to a disturbance such as foaming in the absorber, stripper top pressure is one of the key variables that should be controlled and kept below its allowable

value to prevent the column from being overpressurized and the multi-stage compressor being damaged.

The other auxiliary equipment in the flow sheet that should be protected during abnormal conditions is the pumps placed downstream of the sumps and tanks. If a vessel runs out of liquid or even the level becomes less than the minimum allowable level, the downstream pump is likely to be damaged.

When the levels are free to change in the absence of control, the liquid level in the absorber sumps drops immediately and stays at a lower level as liquid hold-up on the bed of the absorber increases. The level in the rich tank increases because the outlet solvent rate decreases initially due to the initial increase in the stripper pressure. In the reboiler the initial drop of the level results from two factors: initial increasing of stripper pressure that leads to an increase of outlet liquid rate and initial reduction of inlet liquid flow rate. The level in the lean tank also increases initially because the inlet flow rate goes up while the outlet rate does not change significantly (Figure 5).

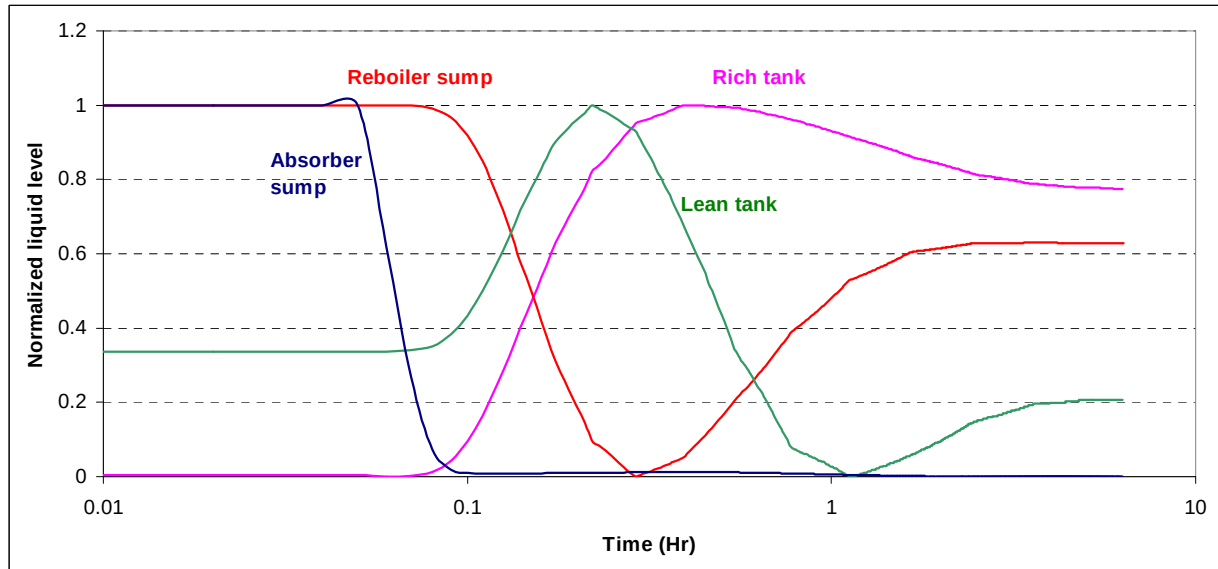


Figure 5: Open loop dynamic response normalized liquid level to +10% step change in liquid hold-up on the absorber packing bed at 0.05 hr, plant designed removal = 90% and lean loading = 0.225, $H_{abs} = 15\text{m}$, $H_{strip} = 10\text{m}$, cross heat exchanger $\Delta T_{design} = 5^\circ\text{C}$, reboiler $\Delta T_{design} = 10^\circ\text{C}$, reboiler $T_{design} = 120^\circ\text{C}$, $\tau_{sumps} = 2\text{ min}$, $\tau_{tanks} = 2\text{ min}$,

$$\text{normalized liquid level} = \left\{ \frac{L - L_{min}}{L_{max} - L_{min}} \right\}$$

When the levels are not controlled, the absorber sump, reboiler sump, and lean tank will be in the danger of running out of liquid, and the rich tank could be flooded if either initial hold-up of the vessels is small or the magnitude of foaming (accumulating liquid) is large. Protecting the pumps from running dry and being damaged necessitates level control.

Pressure control in the stripper

As discussed in the open loop analysis section, the stripper pressure should be controlled for safe operation of the stripper column and CO_2 compressor. The liquid levels should also be

controlled for protecting pumps and balancing the liquid hold-up in all inventories. In this section, different strategies for stripper pressure control are discussed.

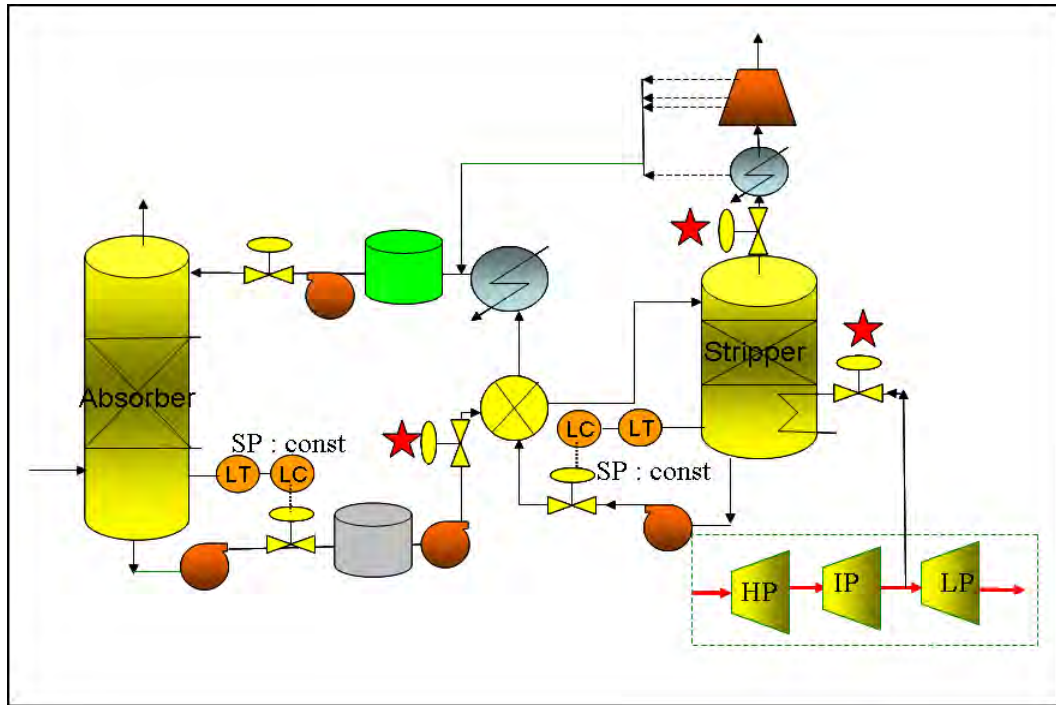


Figure 6: Flow sheet of MEA plant with sump levels controllers and available control valves for controlling the stripper pressure (labeled by red stars)

As shown in Figure 6, the flow through three control valves can influence the pressure in the stripper: pressure valve at top of the stripper, reboiler inlet steam valve and liquid valve placed downstream of the rich tank.

In this work, we do not implement an advanced multi-variable control method; a multi-SISO control system is used. Under this method only one valve should be picked to control the pressure in the stripper.

The dynamic behavior of the closed pressure control loop with each control valve is investigated to see which one offers the best dynamic responses. It is energy saving if the valves on the vapor streams such as stripper pressure valve and steam valve remain wide open during normal operation.

Figure 7 compares the closed loop dynamic responses of the stripper top pressure with the above-mentioned control valves. Both saturated and non-saturated conditions are included for manipulating steam valve and pressure valve.

As shown in this figure, applying saturation to valves amplifies the magnitude of overshoot and gives worse dynamic response relative to an unsaturated valve. A rich solution valve offers the best control performance by reducing the magnitude of initial overshoot and keeping the pressure close to the control loop set point.

. The rich solution flow rate is found to be the most effective variable for pressure control among outlet vapor rate and steam rate. It is able to reject the effect of rich loading on the stripper pressure directly along with saving energy by avoiding manipulation of valves on vapor streams. The mechanism of control is when the rich loading rises, the solution flow rate reduces to reduce the CO₂ desorption rate and consequently the stripper pressure.

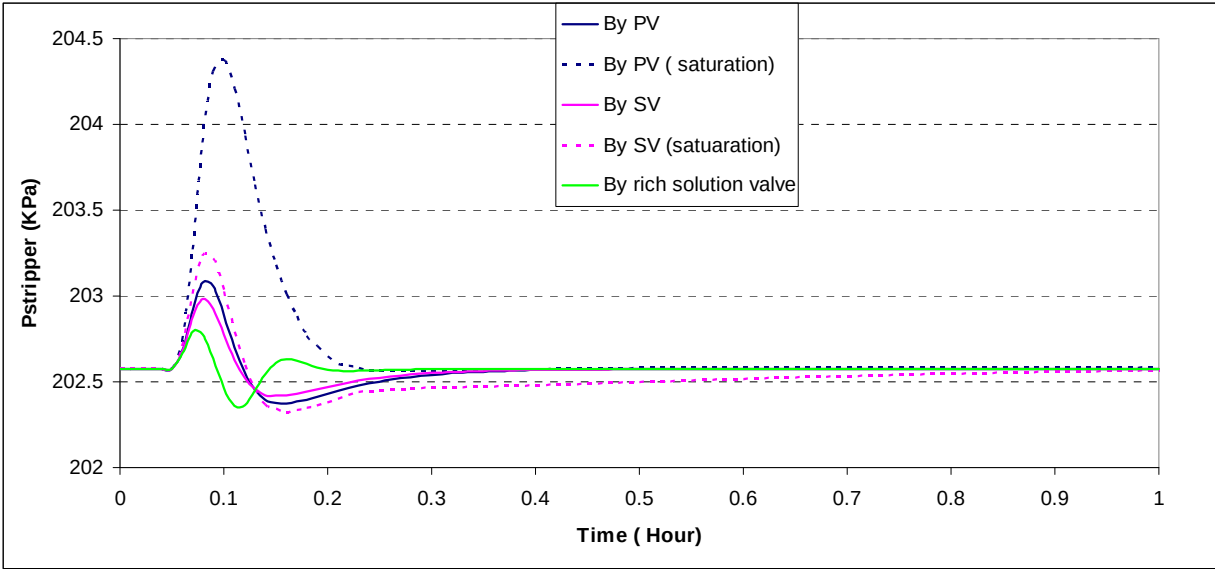


Figure 7: Closed loop dynamic response of stripper top pressure to +10% step change in liquid hold-up on the absorber packing bed at 0.05 hr, plant designed removal = 90% and lean loading = 0.225, H_{abs} = 15m, H_{strip} = 10m, cross heat exchanger ΔT_{design} = 5 °C, reboiler ΔT_{design} = 10 °C, reboiler T_{design} = 120 °C, τ_{sumps} = 2 min, τ_{tanks} = 2 min

Level ratio control

In this section, a level ratio controller is added to the flow sheet to control the liquid transfer between tanks in response to the foaming in the absorber by adjusting the lean solution flow rate. The levels in sumps are controlled tightly and the stripper top pressure is controlled by rich solution rate via a PI controller (Figure 8).

Figures 9 and 10 illustrate why this ratio level control should be considered. When the liquid level in tanks is not under control, as the hold-up on the packing bed of absorber increases, the liquid in the rich tank accumulates and the level in the lean tank reduces gradually and none of the levels reach steady state. Adding level ratio control stabilizes and balances hold-up in both tanks. In analysis, sump levels and stripper top pressure are controlled tightly (via PI controllers), while the ratio of levels in the tanks is controlled by a proportional (P) controller.

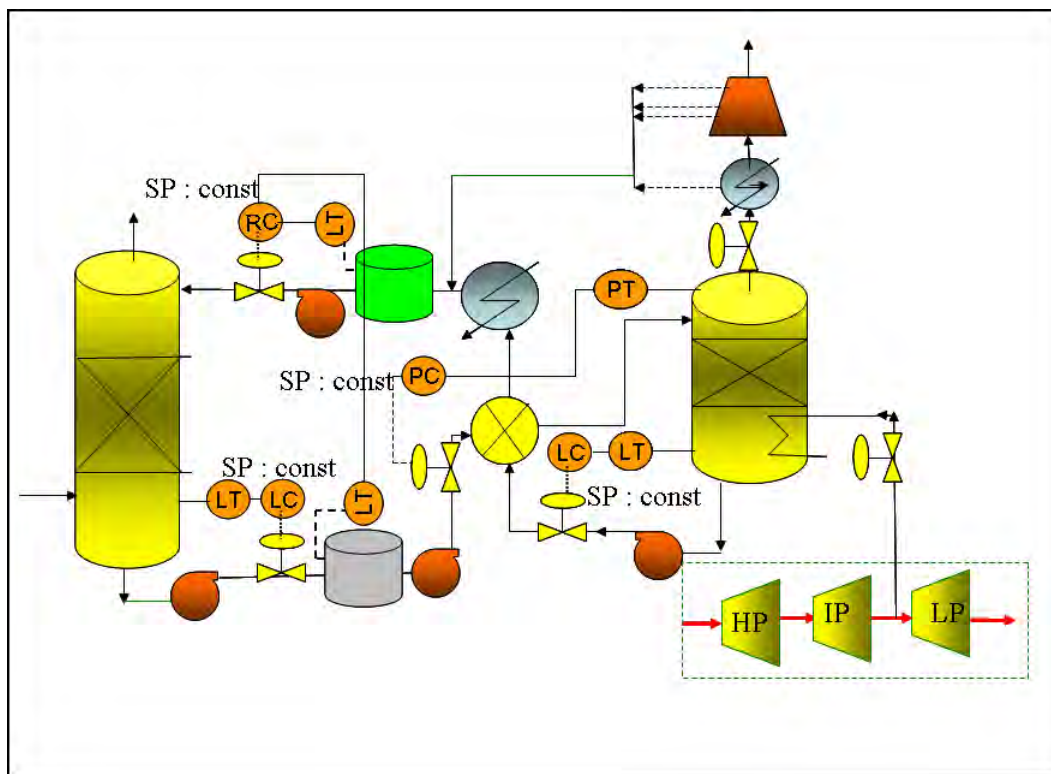


Figure 8: Flow sheet of MEA plant with sump levels, stripper pressure and tank levels ratio on control

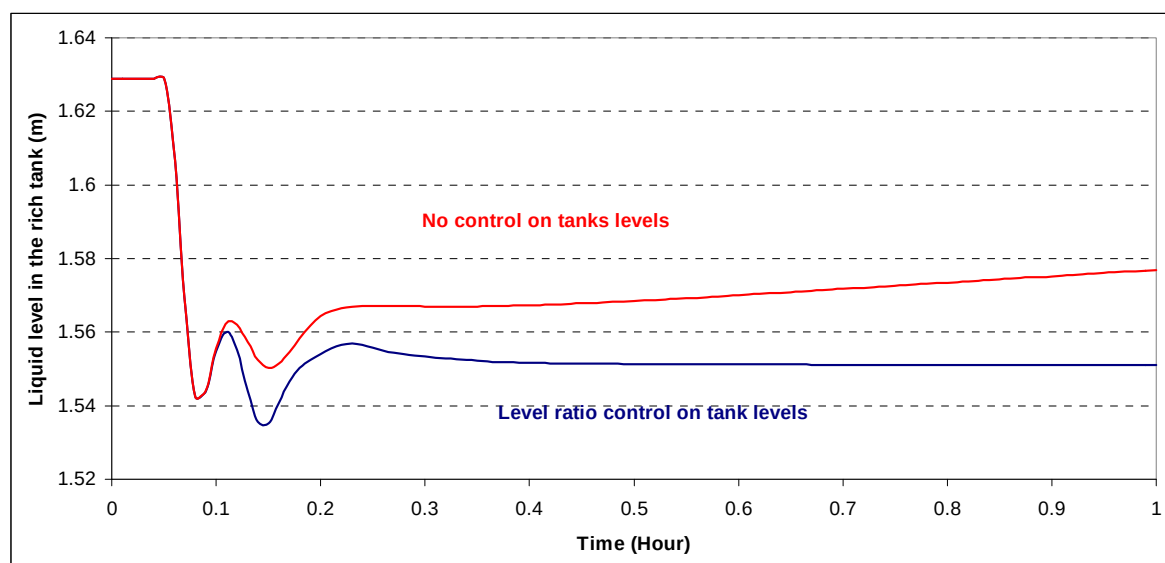


Figure 9: Rich tank level responses to +10% step change in liquid hold-up on the absorber packing bed at 0.05 hr, plant designed removal = 90% and lean loading = 0.225, $H_{\text{abs}} = 15\text{m}$, $H_{\text{strip}} = 10\text{m}$, cross heat exchanger $\Delta T_{\text{design}} = 5^\circ\text{C}$, reboiler $\Delta T_{\text{design}} = 10^\circ\text{C}$, reboiler $T_{\text{design}} = 120^\circ\text{C}$, $\tau_{\text{sumps}} = 2\text{ min}$, $\tau_{\text{tanks}} = 2\text{ min}$

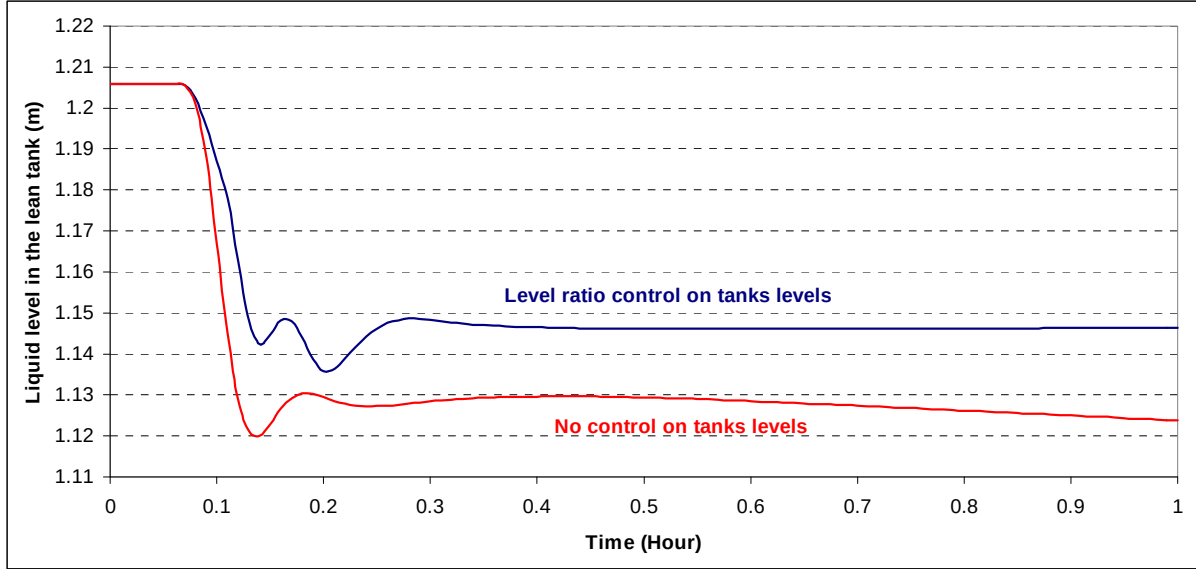


Figure 10: Lean tank level responses to +10% step change in liquid hold-up on the absorber packing bed at 0.05 hr, plant designed removal = 90% and lean loading = 0.225, $H_{\text{abs}} = 15\text{m}$, $H_{\text{strip}} = 10\text{m}$, cross heat exchanger $\Delta T_{\text{design}} = 5^\circ\text{C}$, reboiler $\Delta T_{\text{design}} = 10^\circ\text{C}$, reboiler $T_{\text{design}} = 120^\circ\text{C}$, $\tau_{\text{sumps}} = 2\text{ min}$, $\tau_{\text{tanks}} = 2\text{ min}$

When the level ratio control acts right after changing the liquid level in the rich tank and before the lean tank level is influenced by the disturbance, the dynamic responses may be oscillatory. It is expected that applying delay time in level ratio control can improve the dynamic response of the system. Figure 11 proves this by comparing the effect of the delay time (ranging from 0 to 5 min) on the stripper pressure response. It shows that there is an optimum delay time (3 min) that minimizes the amplitude of the oscillations and provides the best behavior for stripper pressure. This optimum delay time is equal to total initial liquid hold-up time in the stripper and reboiler. In other words, it is equivalent to the lag between lean tank and rich tank.

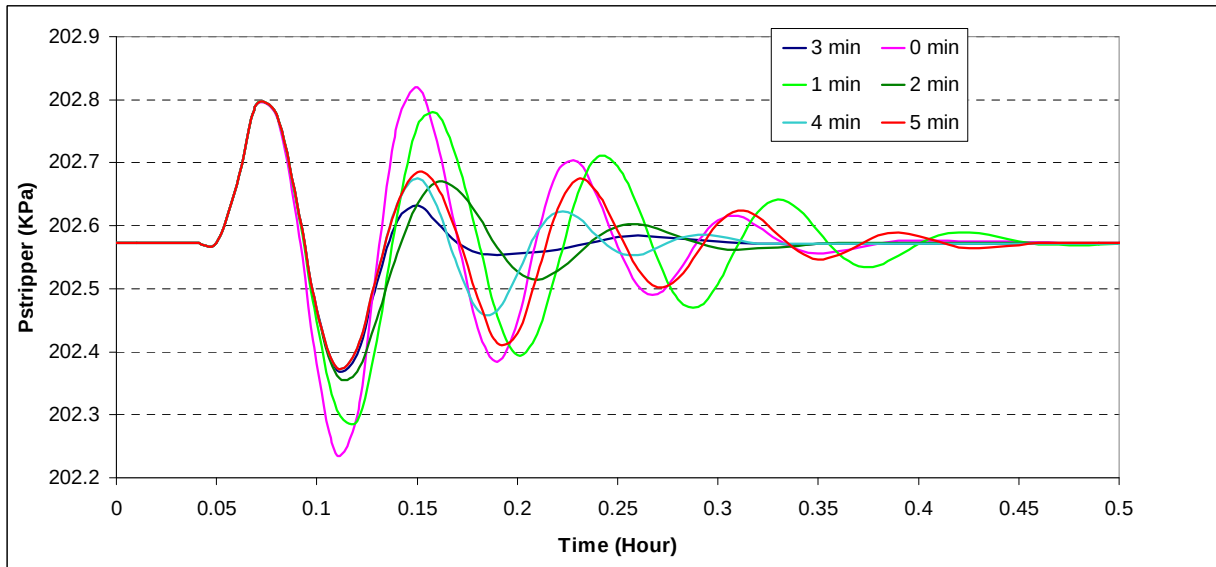


Figure 12: The effects of level ratio control delay time on stripper pressure behavior in response to +10% step change in liquid hold-up on the absorber packing bed at 0.05 hr,

plant designed removal = 90% and lean loading = 0.225, $H_{abs} = 15\text{m}$, $H_{strip} = 10\text{m}$, cross heat exchanger $\Delta T_{design} = 5\text{ }^{\circ}\text{C}$, reboiler $\Delta T_{design} = 10\text{ }^{\circ}\text{C}$, reboiler $T_{design} = 120\text{ }^{\circ}\text{C}$, $\tau_{sumps} = 2\text{ min}$, $\tau_{tanks} = 2\text{ min}$

Figure 12 indicates that 3 min delayed level ratio control does not influence the dynamic response of controlled stripper pressure very much relative to the case with uncontrolled tank levels. It means that the control loop interaction between pressure and level ratio control loops is minimized when the ratio control is delayed by a time period equal to the lag between tanks.

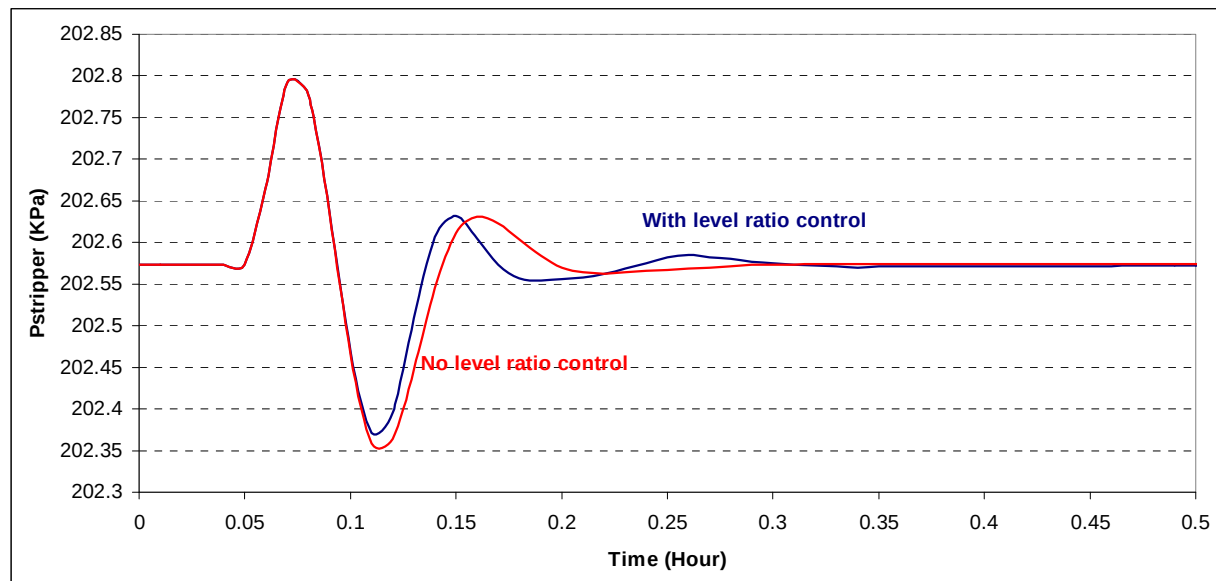


Figure 12: Stripper top pressure responses to +10% step change in liquid hold-up on the absorber packing bed at 0.05 hr, plant designed removal = 90% and lean loading = 0.225, $H_{abs} = 15\text{m}$, $H_{strip} = 10\text{m}$, cross heat exchanger $\Delta T_{design} = 5\text{ }^{\circ}\text{C}$, reboiler $\Delta T_{design} = 10\text{ }^{\circ}\text{C}$, reboiler $T_{design} = 120\text{ }^{\circ}\text{C}$, $\tau_{sumps} = 2\text{ min}$, $\tau_{tanks} = 2\text{ min}$

Conclusions

This work has investigated the dynamic behavior of MEA absorption/stripping process in response to the absorber foaming in the absence of any control. There follows a summary of conclusions from the open loop study:

1. A sharp initial overshoot appears in the stripper pressure, which is mainly the result of the initial rise and drop in the rich loading.
2. In order to operate the stripper and multi-stage compressor safely, the stripper pressure should be controlled.
3. The rich solution storage tank damps this overshoot and provides better rich loading response to the stripper.
4. The liquid in the absorber sump, lean tank, and reboiler sump gets to a lower level relative to the initial value while the liquid accumulates in the rich tank.
5. The levels should be controlled within an allowable range to prevent the pumps from running dry.

Closed control loop analysis has been done to establish how to control the stripper pressure and tanks levels effectively. The conclusions on control are summarized below:

6. Controlling stripper pressure by either steam valve or pressure valve is not an effective pressure control strategy specially if these valves are wide open in an energy saving normal operation and become saturated under abnormal conditions.
7. Controlling stripper pressure by rich solution flow rate was found to be the best strategy as it decreases the magnitude of overshoot response and keeps the pressure close to the set point. This variable can be easily adjusted to decrease the CO₂ desorption in the stripper and prevent the stripper from being overpressurized when the rich loading rises.
8. Level ratio control on tanks keeps the liquid levels in balance and prevents the pumps from running dry. If this control loop acts with a delay time equal to the liquid hold-up time in the equipment between rich and lean tanks (reboiler and stripper), it gives the best dynamic response (minimum number of oscillations with minimum magnitudes) for stripper pressure and other process variables.

Future Work

For the next quarterly report, we plan to investigate the effects of foaming in the stripper on dynamic performance of the system and explore applicable and effective control strategies to operate the whole plant safely during these abnormal conditions.

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Modeling CO₂ Recovery for Optimal Dynamic Operations

Quarterly Report for January 1 – March 30, 2011

by Ricardo Dunia

Supported by the Luminant Carbon Management Program

Department of Chemical Engineering

The University of Texas at Austin

April 30, 2011

Abstract

This report presents the use of the Subspace Identification Method with Principal Component Analysis (SIMPCA), a subspace system identification technique used to develop a dynamic empirical model for a Linear Quadratic Gaussian (LQG) controller with integral action. Such a controller is made to attain optimal operating conditions for a CO₂ capture pilot plant. Reference signals are used in conjunction with the controller integral action to bring few process outputs towards their set-points.

Introduction

There is a diversity of predictive multi-variable controllers in the literature. However, not all of them have been successfully implemented in industrial applications. This is because model maintenance and operator training play an important role in the durability of an advanced controller. Linear quadratic regulators (LQR) with Kalman filters and integral action have been recently implemented in the control of solid oxide fuel cell gas turbine in hybrid power plant systems. The results show that the LQR ensures better maintenance of the fuel cell stack voltage and temperature that improves fuel cell system durability. LQR has been also used in the control of rotor speed of wind turbines to reduce the drive-train fatigue damage and improve power regulation. In this research work we use the LQR with a state estimator (LQG) and integral action to control a recovery process.

LQG with Integral Action

Process engineers dictate requirements for a set of process outputs to follow a list of reference variables. Such a condition introduces a list of integrators or additional states:

$$x_I(k+1) = x_I(k) + r(k) - I_r y(k)$$

The incorporation of these integrators determines the following steady state feasible condition,

$$r = I_r y^*$$

where the superscripts * denote “steady state”.

The model identified in the last quarter is used to develop a Linear Quadratic Gaussian controller (LQG) with integral action. The integral action is achieved by augmenting the state vector with integrators and providing the respective reference profiles for the controlled variables, CVs. Therefore, the controller will try to maintain zero offset for the chosen CVs even in the presence

of process-model mismatch. The CO₂ concentration at the top of the absorber (y_8) and the rich CO₂ gas flow at the top of the stripper (y_{39}) were chosen as CVs. All inputs, with the exception of the flue gas flow disturbance, are adjusted by the controller to achieve optimal operating responses. The cost weight matrix R has been designed based on the different manipulated variables costs. In a similar manner, state deviations from nominal conditions are also penalized based on the following state-output weight conversion,

$$Q = C^T Q_y C$$

where Q_y is the weight cost matrix for the output deviation vector.

Results

Figure 1 illustrates the closed loop time response to $r^* = [-1 \ 1]^T$. The CVs reach their respective reference values within 1500 s (100 samples), while the MVs show a smooth trajectory towards their desirable steady states. It is important to emphasize that the controller internal model considered in these responses is identical to the actual system.

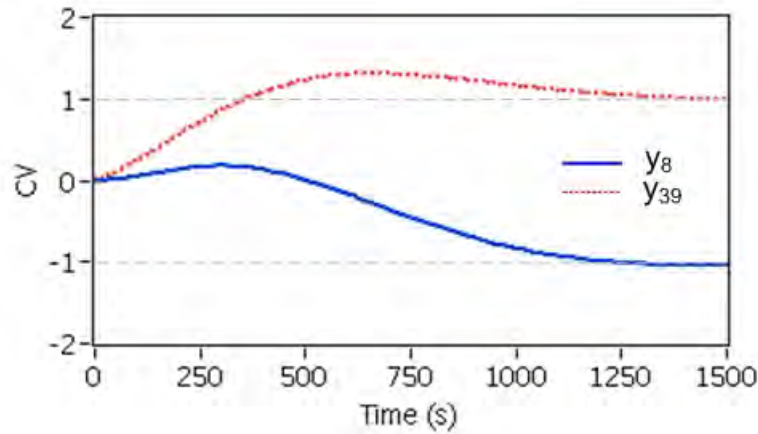


Figure 1a: CVs are the CO₂ concentration at the top of the absorber y_8 and the rich CO₂ gas flow at the top of the stripper y_{39} .

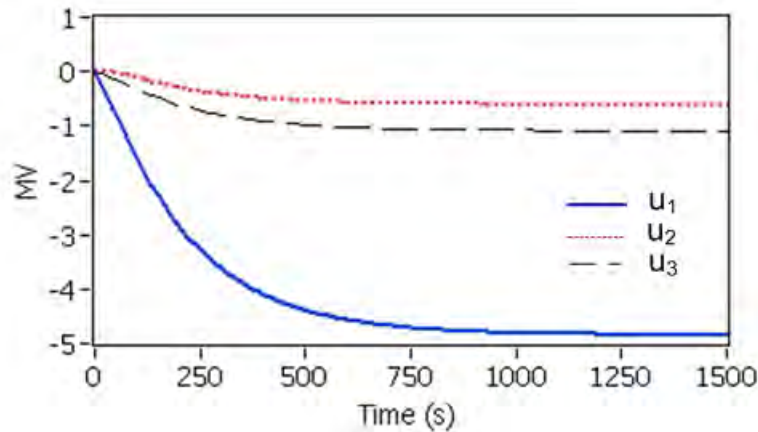


Figure 1b: MVs are the solvent flow (u_1), reboiler steam flow (u_2) and stripper pressure (u_3).

CVs are the CO₂ concentration at the top of the absorber (y_8) and the rich CO₂ gas flow at the top of the stripper (y_{39}). The MVs are the solvent flow (u_1), reboiler steam flow (u_2) and stripper pressure (u_3).

Process-model mismatch is detrimental to the closed loop performance of this LQR with integral action, to the point that closed loop responses can become unstable when this mismatch is significant. To illustrate the effect of process-model mismatch, the system matrix A of the process, denoted by A_{sys} , is modified based on the following expression:

$$A_{sys} = A + \alpha \Delta A$$

where ΔA represents the mismatch matrix and $0 < \alpha < 1$ determines the magnitude of the mismatch. Figure 2 illustrates the effect of the mismatch in the phase diagram defined by the CVs. For $\alpha = 1$ the response becomes oscillatory and unstable. In such a case the integral action intends to bring the system towards the $[-1 \ 1]$ target point but the process-model discrepancy prevents the controller from providing a stable closed loop response.

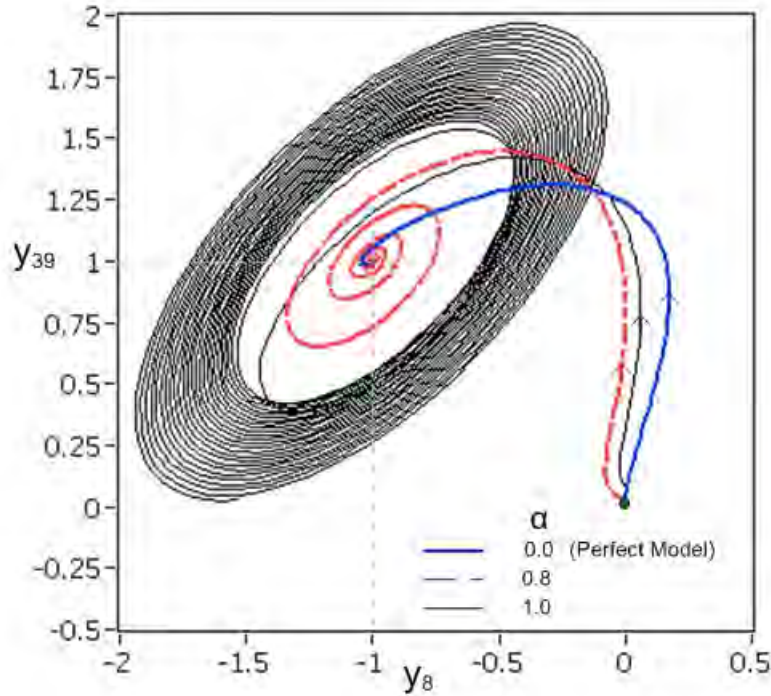


Figure 2: Effect of process-model mismatch in the CVs phase diagram.

Conclusions

The Subspace Identification Method with Principal Component Analysis (SIMPCA) is successfully used to develop a dynamic empirical model for the CO₂ recovery pilot plant at the PRC in Austin, Texas. This model predicts the dynamic response of more than sixty outputs with only six dynamic states. Four main decision variables are used to bring the plant from one operating condition to another. A multi-variable LQG controller is here developed based on the SIMPCA model in order to assist the operators in stabilizing the plant in an optimal manner around desirable operating conditions. The results show that LQG is well capable of bringing the plant to optimal steady state conditions in cases where the controller model provides a

reliable prediction of the system outputs. In future work, process constraints will be incorporated in the controller structure to account for potential limitations during significant power consumption swinging.

Electric Grid-Level Implications of Flexible CO₂ Capture Operation

Quarterly Report for January 1 – March 31, 2011

by Stuart Cohen

Supported by the EPA STAR Fellowship Program and the

Luminant Carbon Management Program

Department of Chemical Engineering

The University of Texas at Austin

April 30, 2011

Abstract

Flexible post-combustion absorption/stripping that vents carbon dioxide (CO₂) or stores rich solvent at partial or zero load was investigated using a previously developed model that maximizes annual profits for a coal-fired facility using 7 m monoethanolamine (MEA) for CO₂ capture. The model uses electricity prices as input and chooses base plant and CO₂ capture operating points in each 15-minute interval, subject to constraints on base plant and CO₂ capture system operation. In this quarter, the model was used to compare operating profits, net present value, and CO₂ emissions of a facility with and without flexible and inflexible CO₂ capture for three disparate 20-year CO₂ price paths.

Major conclusions were:

- Flexible CO₂ capture in response to volatile electricity prices is most valuable if future CO₂ prices hover near a range of \$40–50/tCO₂.
- Sustained CO₂ prices above \$100/tCO₂ are required to make CO₂ capture retrofit preferable to continued operation of a facility without CO₂ capture, but the benefit of flexibility could be limited in this CO₂ price regime.
- Flexible and inflexible CO₂ capture reduces CO₂ emissions substantially over a broad range of CO₂ price scenarios.

Introduction to Flexible CO₂ Capture

Flexible operation of a post-combustion amine absorption and stripping system entails varying the liquid and vapor flow rates in the stripping and/or absorption systems in order to choose the most economical carbon dioxide (CO₂) capture operating point for current electricity market conditions. During partial- or zero-load CO₂ capture, some or all of the steam being used for solvent regeneration is redirected back to the low pressure turbine in the power cycle to increase electrical output. The resulting decrease in CO₂ flow exiting the stripper also reduces energy requirements for CO₂ compression. Solvent flow to the absorber and stripper and flue gas flow to the absorber could also be modulated for efficient system operation.

Flexible CO₂ capture could allow the plant operator to increase power output when electricity prices are high if additional electricity sales offset any increase in CO₂ emissions costs under a CO₂ regulatory framework (Ziaii et al., 2008). In addition, operating CO₂ capture at zero load during annual peak electricity demand can eliminate the need to spend billions of dollars to replace generation capacity lost when CO₂ capture operates at full load (Cohen et al., 2010b).

There are two basic concepts for flexible CO₂ capture using amine scrubbing. One reduces the energy requirements of solvent stripping and CO₂ compression while allowing CO₂ removal rate to fall. Figure 1 displays one way to implement such a configuration, where steam and rich solvent flow rates to the stripper are reduced equally and simultaneously during partial- or zero-load operation (Ziaii et al., 2008). At partial load, rich solvent diverted from the stripper is recycled to the absorber, so CO₂ removal rates in the absorber will decrease as solvent becomes saturated with CO₂. Zero load could involve recirculating all solvent through the absorber, or the CO₂ capture system could be bypassed completely. Assuming a retrofit application where the low pressure turbine and generator has been sized to operate without CO₂ capture, this design has negligible capital cost, but its primary disadvantage is any cost and environmental impacts of increased CO₂ emissions.

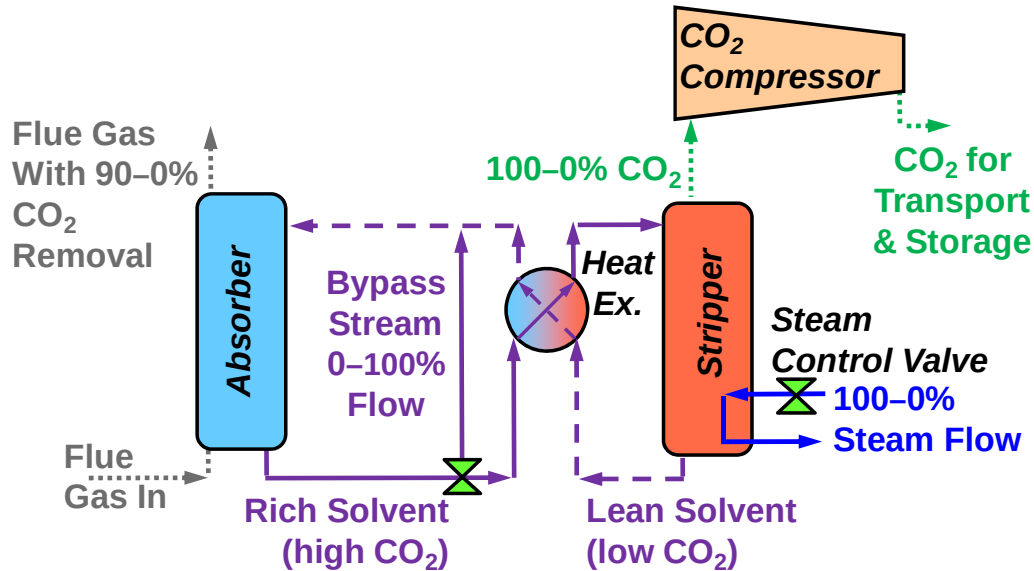


Figure 1: Simultaneously reducing steam and rich solvent flow to the stripper allows increased output, but at the expense of additional CO₂ emissions.

Another flexible CO₂ capture concept uses auxiliary solvent storage tanks to maintain high CO₂ removal when stripping and compression systems operate at partial or zero load (Figure 2) (Chalmers and Gibbins, 2007; Rochelle et al., 2009). When electricity prices are high, the plant can reduce stripper and compressor load while maintaining full-load CO₂ absorption by feeding the absorber from a lean solvent storage tank and depositing rich solvent into another tank. When electricity prices are low, stripping and compression systems return to a higher load to treat the current process stream and the stored rich solvent. To treat both the current stream and stored solvent, stripping and compression systems must be larger and require more total energy than a CO₂ capture system without solvent storage. Maintaining high CO₂ removal keeps operating costs down while storing rich solvent, but any operating profit improvement must be weighed against the capital cost of solvent inventory, storage tanks, and larger stripping and

compression equipment. A facility with solvent storage would likely also maintain the ability to vent CO₂ when economically desirable or necessary for maintenance.

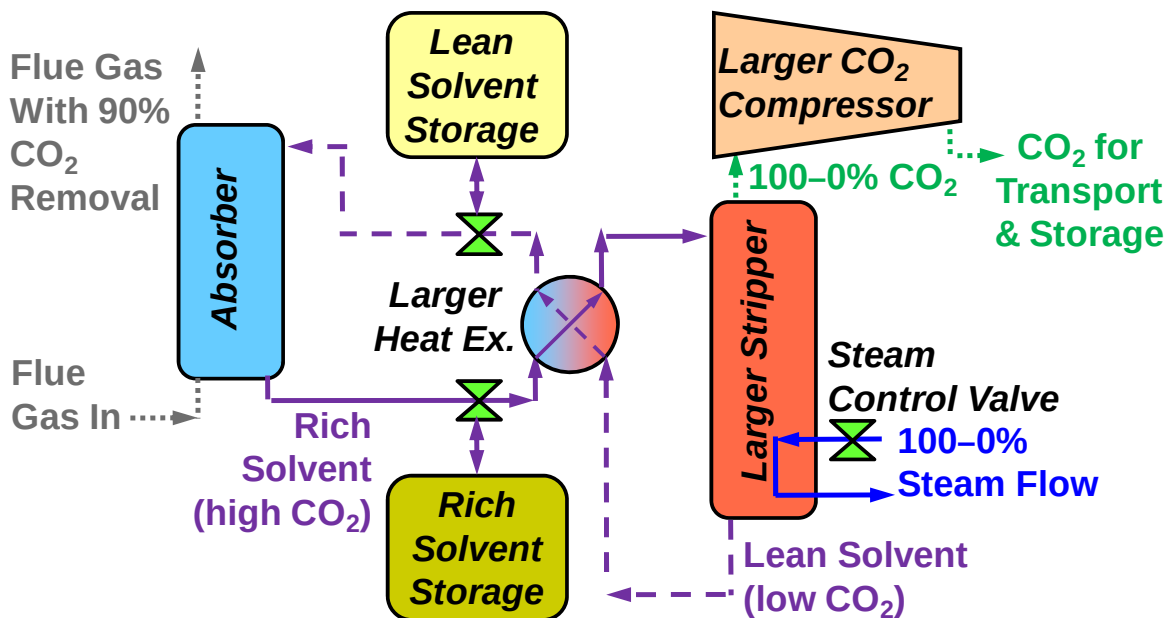


Figure 2: Including solvent storage incurs significant capital costs but allows continued high CO₂ removal at partial and zero load.

Methodology

This quarter I used the model described in previous work to analyze the impact of CO₂ price path over an investment lifetime on the economic and environmental performance of a coal-fired facility with and without flexible and inflexible CO₂ capture (Rochelle et al., 2010a; Rochelle et al., 2010b; Cohen et al., 2010a). A brief description of the model formulation is included below.

The model imports electricity prices in 15-minute intervals over a specified time period and maximizes profits for a single facility by choosing the base plant and CO₂ capture operating point in each interval. The versatile modeling framework allows for investigation of CO₂ capture operation in response to volatile electricity prices. The model can compare a facility with flexible CO₂ capture of the types shown in Figures 1 and 2 to a facility with inflexible capture or no CO₂ capture. Current analyses assume post-combustion CO₂ capture using 7 m monoethanolamine (MEA) at a coal-fired facility, but model parameters could be adjusted to study gas-fired facilities or other chemical solvents.

Input electricity prices used in all studies described below are 2008 market clearing electricity prices in the Electric Reliability Council of Texas (ERCOT). To approximate the effect of CO₂ price on electricity prices, input electricity prices are increased uniformly by the average CO₂ emissions cost of natural gas-fired facilities in ERCOT. This approach is reasonable for ERCOT because gas-fired facilities typically set wholesale market electricity prices even with reasonably high CO₂ prices (PE, 2009; ERCOT, 2007). Other electricity systems might require a more rigorous price adjustment procedure depending on their capacity mix. Rather than assuming perfect price foreknowledge, day-ahead price forecasting is approximated by creating pseudo-forecasted prices used to optimize plant operation and then calculating profits based on CO₂

price-adjusted historical prices. Pseudo-forecasted prices are generated by removing outliers and smoothing historical price data until the discrepancy with actual prices is close to errors typical of accurate day-ahead forecasting models (Li et al., 2005; 2007).

The model is implemented as a mixed-integer linear program with variables for the on/off status and load of the base plant, absorption, and stripping/compression systems. Base plant load is the fraction of maximum gross power plant output without CO₂ capture energy. Absorption load is the ratio of the quantity of CO₂ removed to the maximum possible quantity of CO₂ removed with the base plant at full load. Stripping and compression load is the ratio of stripping steam mass flow to the mass flow required to strip all CO₂ from an absorber at 100% load. An inflexible capture system requires absorber and stripper load to equal base plant load. A venting-only flexible capture system can reduce absorber and stripper load below base plant load to increase power output, but absorber and stripper load must always be equal. A flexible capture system with solvent storage decouples absorber and stripper load, and stripper load can exceed 100% if components are oversized.

The profit equation sums electricity sales revenue and costs over all 15-minute intervals. Costs are calculated for base plant startup, fuel, CO₂ emissions, base plant variable operation and maintenance (VOM), and CO₂ capture system VOM including solvent makeup, caustic for reclaiming, degradation product waste disposal, water for CO₂ capture and compression, CO₂ transport and storage, and ramping costs for CO₂ capture components.

The model includes constraints on minimum and maximum load and system response time for the base plant, absorber, and stripper. The solvent storage configuration also limits maximum stripper load by the size of stripping and compression equipment and the quantity of steam available for extraction. The size of solvent storage facilities is also specified by the maximum quantity of CO₂ that can be stored in rich solvent, and a flow balance uses relative absorber and stripper load to monitor the stored quantity of CO₂. The maximum quantity of CO₂ that can be stored is a function of storage tank size, solvent properties, and the design difference between rich and lean loading (CO₂ carrying capacity).

CO₂ Price Path Scenario Analysis

The net present value of each plant configuration over a 20-year economic life is calculated for three CO₂ price paths chosen from the U.S. Energy Information Administration (EIA) analysis of the proposed American Power Act of 2010 (APA2010), which proposed to create a cap-and-trade program for CO₂ and six other greenhouse gases (GHG) (USEIA, 2010). To assess facility behavior under a wide range of policy scenarios, this work uses the final 20 years of calculated CO₂ equivalent allowance price paths for the EIA-APA2010 “Basic,” “No International,” and “Limited Tech., No International” scenarios (Figure 3). “Basic” is the nominal scenario, “No International” implies more expensive GHG mitigation because international offsets cannot be used to meet GHG limitations, and “Limited Tech.” further increases mitigation costs by assuming key GHG abatement technologies do not develop quickly in response to GHG limitations (USEIA, 2010). The assumptions of the “Limited Tech.” scenario are not necessarily consistent with the use of CO₂ capture in this work, but the scenario still provides an example high CO₂ price curve.

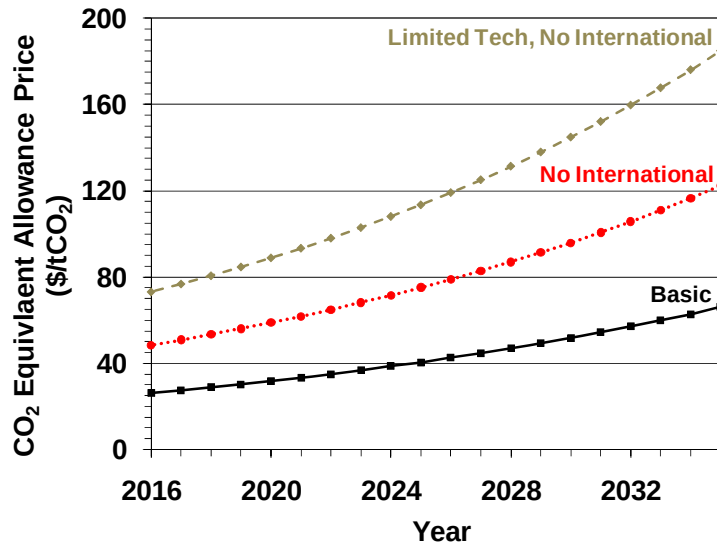


Figure 3: Three CO₂ price paths from the EIA analysis of the APA2010 proposed legislation provide scenarios to compare each CO₂ capture configuration (USEIA, 2010).

Input Parameters

Table 1 displays major input parameters used in the analysis. Base plant heat rate and CO₂ emissions rate are averages for ERCOT coal-fired facilities, and startup cost and ramp limits are estimated from literature (USEPA, 2007; Mortensen, 1998; Chen and Pang, 1976). A typical 90% CO₂ removal value is used along with a design capacity and CO₂ capture equivalent work from previous modeling results (Ziaii et al., 2008; Oyeneke, 2006). Of the total energy requirement for CO₂ capture derived from modeling results, 11% is attributed to absorption and the rest to stripping and compression based on a report suggesting that 1/9 of the efficiency penalty at full-load CO₂ capture is attributed to absorption systems (Ziaii et al., 2008; Chalmers et al., 2010). Default capture system ramp limits are set slightly faster than those of the base plant, and absorber and stripper ramp limits are assumed equal and the same in either direction. The default solvent storage system size is chosen based on the maximum value solvent storage system identified in previous work (Cohen et al., 2010a). Electricity prices from 2008 are used as input, so the coal price is the average for Texas in 2008 (ERCOT, 2008; USEIA, 2009).

Table 1: The following default parameters are used in the scenario analysis.

Parameter	Units	Value
<i>Base Plant (coal-fired)</i>		
Maximum output	MW	500
Minimum output	MW	150
CO ₂ emissions rate (without CO ₂ capture)	tCO ₂ /MWh	1.03
Heat rate (without CO ₂ capture)	MMBTU/MWh	10.8
Ramp limit	MW/min	20
Startup cost	\$/startup	10,000
<i>CO₂ Capture System (7 m MEA solvent)</i>		
CO ₂ removal	Fractional	0.9
Energy requirement (equivalent work)	MWh/tCO ₂	0.269
Minimum absorber/stripper load	Fractional	0.3
Absorber/stripper ramp limit	% load change/min	5
Design capacity (rich minus lean loading)	molCO ₂ /molMEA	0.12
Solvent storage system size (if applicable)	Maximum hours with full absorption and no stripping	0.5
<i>Electricity Market</i>		
Coal price	\$/MMBTU	1.54

MMBTU = million British thermal units. All monetary quantities are assumed to be 2006 USD.

Results

Producing model results at each of the 60 CO₂ prices is unnecessary because many CO₂ prices are similar. Instead, results were generated for a subset of CO₂ prices in the range \$0–200/tCO₂, and desired quantities at each CO₂ price on a path were found by linearly interpolating between those quantities at the nearest analyzed CO₂ prices.

Figure 4 displays the outcome of this procedure for before-tax operating profits over all 20 years for a facility without capture, with inflexible capture, and with flexible capture and solvent storage under the Basic and No International CO₂ price paths. CO₂ emissions for the venting-only flexible capture configuration are almost identical to those with solvent storage, with emissions being slightly greater because solvent storage allows greater utilization of CO₂ absorption during partial-load stripping and compression. Without CO₂ capture, emissions decrease over time because operating costs increase faster than electricity prices as CO₂ prices increase, causing reduced plant utilization. The increase in cost or price with CO₂ price depends on the emissions rate, and a facility without CO₂ capture has a much higher emissions rate than natural gas-based facilities assumed to set electricity prices. Emissions costs at an inflexible CO₂ capture facility increase slower than electricity prices as CO₂ prices rise, so increasing plant utilization over time causes CO₂ emissions increase slightly.

The solvent storage configuration has the biggest qualitative difference in results with the two CO₂ price paths. The Basic scenario has relatively low initial CO₂ prices, so CO₂ emissions with flexible capture are initially high when operation is usually more economical with capture

systems at zero load. Any emissions above the inflexible configuration indicate CO₂ venting; although solvent storage is available, CO₂ venting is still economical, albeit in lower quantities than with venting-only flexible capture. Zero-load CO₂ capture then becomes less desirable over time until annual emissions approach those with inflexible capture. Under higher CO₂ prices in the No International case, CO₂ venting is rarely economical even in 2016, and emissions quickly approach levels with inflexible capture. Solvent storage systems are still utilized by operating stripping and compression systems flexibly, but partial-load absorption is rarely economical once CO₂ prices exceed \$70/tCO₂. CO₂ emissions trends in the Limited Tech., No International scenario have similar behavior to the No International scenario, but emissions without CO₂ capture actually fall below those with CO₂ capture after 2028 when plant capacity factor without CO₂ capture has fallen below 10%.

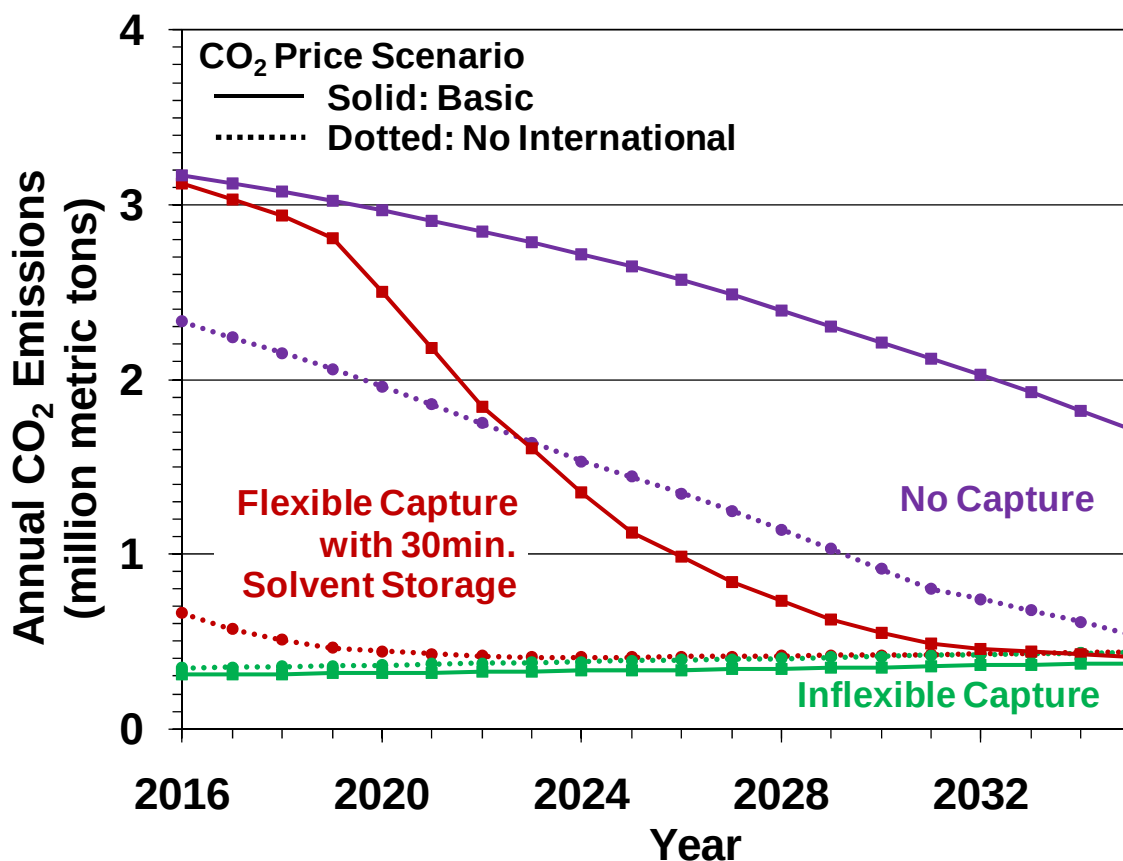


Figure 4: CO₂ emissions decrease over time due to increased CO₂ capture utilization and decreased operation without CO₂ capture.

Cumulative CO₂ emissions over time are the most important statistic from an environmental standpoint. Figure 5 displays cumulative 20-year CO₂ emissions for each configuration and CO₂ price path. Under the more lenient Basic scenario, CO₂ emissions are very high without CO₂ capture. Though flexible capture is not utilized in early years, cumulative CO₂ is 43% less than without CO₂ capture. Inflexible CO₂ capture is lower still, with an 87% reduction from emissions without CO₂ capture. In scenarios with higher CO₂ prices, cumulative emissions are similar between flexible and inflexible CO₂ capture systems, reflecting lower utilization of flexibility. Decreased CO₂ emissions from the facility without CO₂ capture due to decreased

plant utilization also reduces the net benefit of using CO₂ capture at this facility, but CO₂ capture still achieves a reduction of at least 36% after dispatch behavior is taken into account.

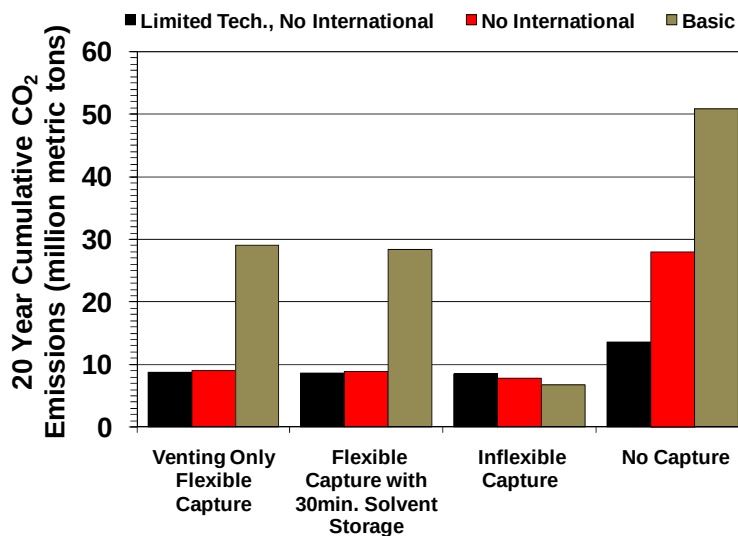


Figure 5: CO₂ capture reduces cumulative 20-year CO₂ emissions by at least 36% for the analyzed CO₂ price paths.

Economic results are displayed in Figure 6, which shows annual before-tax operating profits for the configurations and CO₂ price paths appearing in Figure 4. Despite increasing electricity prices, profits fall over time without CO₂ capture in both CO₂ price scenarios due to decreased utilization and increased emissions costs, but profits are higher than those with inflexible CO₂ capture at lower CO₂ prices experienced earlier in the Basic scenario. In the Basic scenario, profits with inflexible CO₂ capture do not exceed those without CO₂ capture until 2027, when the CO₂ price is about \$45/tCO₂. However, profits with flexible CO₂ capture and solvent storage follow the upper envelope of the No Capture and Inflexible curves, with profits exceeding both after 2021. The benefits of flexibility decrease as CO₂ prices increase, but advantages would be significant over plant lifetime if CO₂ prices instead hovered around \$40–50/tCO₂. Profits in the venting-only flexible capture configuration are similar to but slightly below those with solvent storage, with solvent storage allowing some additional revenue without increasing CO₂ emissions costs.

The No International scenario has much higher CO₂ prices in each year, so profits without CO₂ capture are much lower, and there is a more limited benefit of CO₂ capture flexibility. CO₂ capture is critical to maintaining operating profits under these CO₂ price conditions, and while the benefit from flexibility is small, it is maintained throughout the time horizon. The temporal trends in the No International scenario are exaggerated in the Limited Tech., No International scenario, with a much larger discrepancy between profits with and without CO₂ capture.

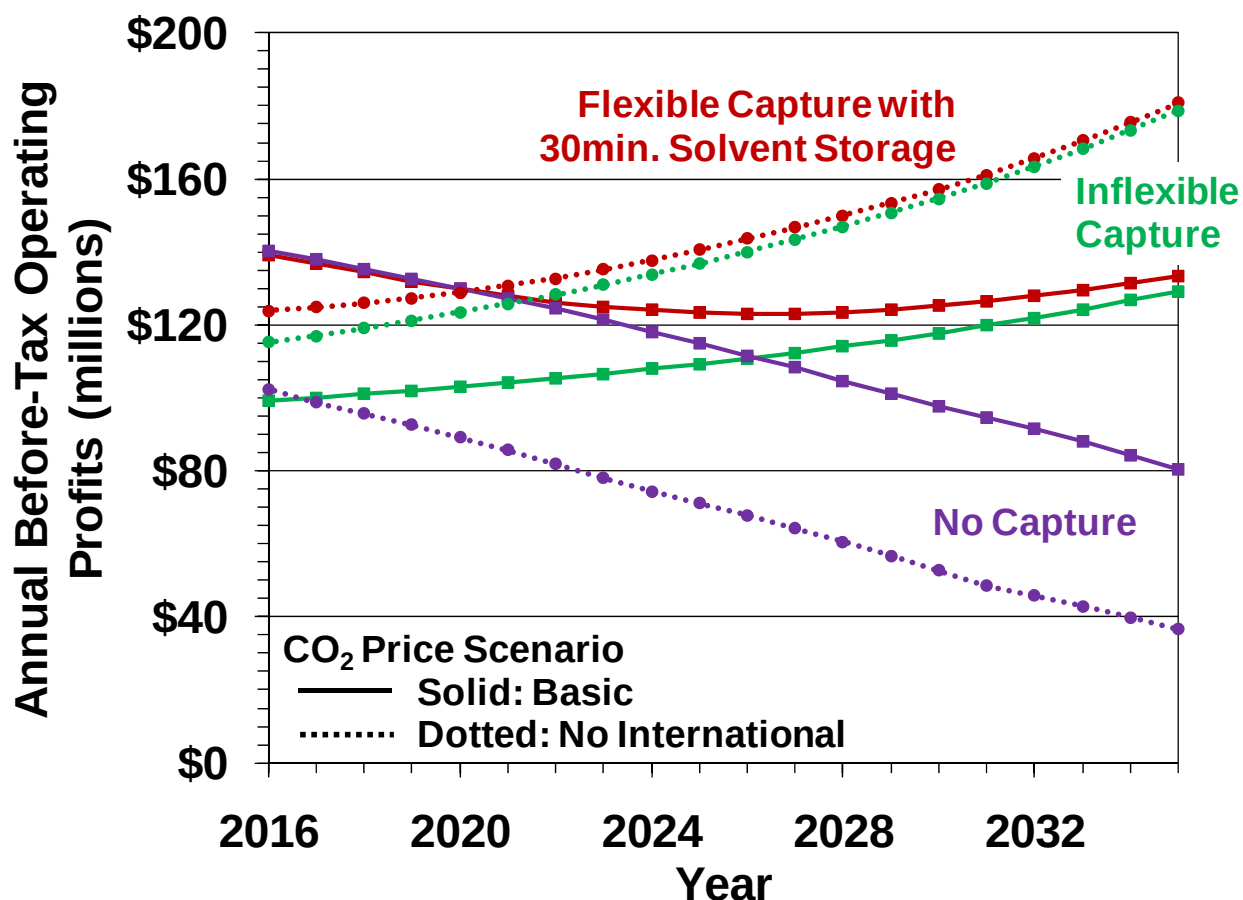


Figure 6: CO₂ capture flexibility allows greatest operating profits, especially at intermediate CO₂ prices from 2025–2029 in the Basic scenario.

Before-tax operating profits were then reduced by a tax rate of 38%, discounted at 10.3% per year, and added to any CO₂ capture capital costs to compare the net present value (NPV) of each configuration under each CO₂ price path (NETL, 2005). Tax and discount rates are recommended values from U.S. National Energy Technology Lab (NETL) carbon capture and sequestration (CCS) systems analysis guidelines (NETL, 2005). All CO₂ capture configurations are assumed to be retrofits, so there are no capital costs without CO₂ capture, CO₂ capture systems are assumed to be \$907.7/kW, and the 30-min. solvent storage system adds \$22.5/kW (Rubin et al., 2007). The capital cost for the base CO₂ capture system is taken from literature, and the capital cost for solvent storage is the total cost of solvent inventory, storage tanks, and larger stripping and compression equipment calculated in previous work (Cohen et al., 2010a).

The resulting NPV is displayed in Figure 7. The difference in NPV with and without CO₂ capture is highly dependent on the assumed capital cost for CO₂ capture systems. With \$907.7/kW, NPV is greater with CO₂ capture only for the Limited Tech., No International scenario, which has very high CO₂ prices. However, differences in NPV within CO₂ capture scenarios are independent of base CO₂ capture system capital costs, assuming there is negligible capital expense for venting-only flexible capture. Flexible configurations have greater NPV than inflexible for all scenarios studied, especially under the Basic scenario where CO₂ prices are often in the region where flexibility is most valuable. However, though solvent storage always

provides an operating profit benefit, NPV with solvent storage is slightly less than with venting-only flexible capture for all CO₂ price paths. Though 30 min. of solvent storage is optimal for 20 years with constant CO₂ prices at \$50/tCO₂, cumulative discounted benefits in this analysis do not offset the incremental capital cost of solvent storage. Nevertheless, a CO₂ capture process better optimized for solvent storage could yield different results, especially under different economic assumptions. A detailed study of solvent storage system design will be performed in the future.

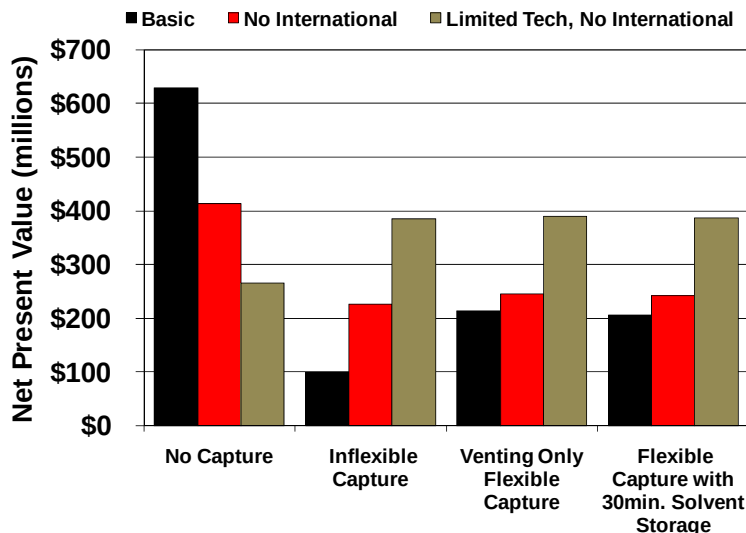


Figure 7: High CO₂ prices are required for NPV to be greatest with CO₂ capture, but flexibility always provides at least some benefit relative to an inflexible CO₂ capture configuration.

Additional Research Activities

A collaborative work with Hannah Chalmers and Jon Gibbins of the University of Edinburgh (formerly of Imperial College London) entitled “Comparing post-combustion CO₂ capture operation at retrofitted coal-fired power plants in the Texas and Great Britain electric grids” has been accepted for publication by Environmental Research Letters (ERL), an online, open access journal. The abstract of the paper is included below.

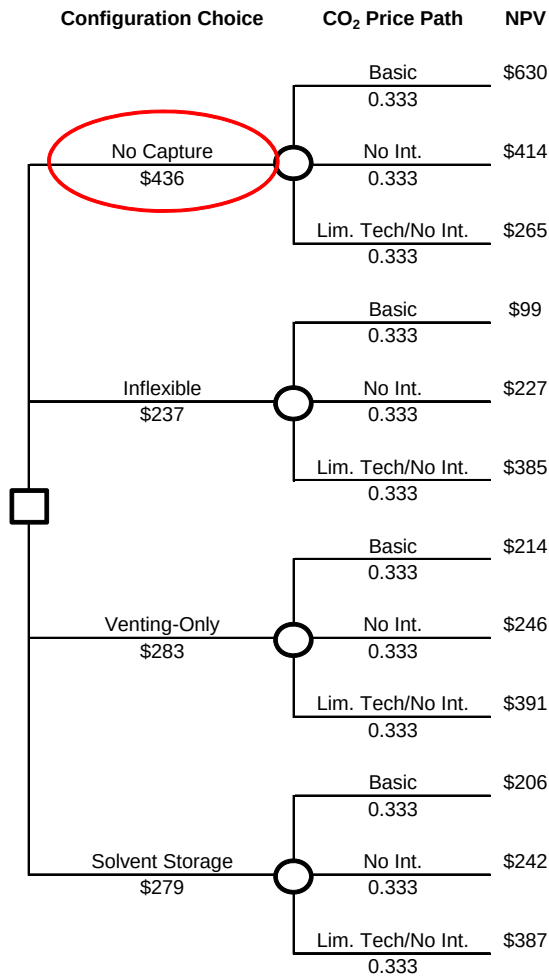
This work analyzes carbon dioxide (CO₂) capture system operation within the Electric Reliability Council of Texas (ERCOT) and Great Britain (GB) electric grids using a previously developed first-order hourly electricity dispatch and pricing model. The grids are compared in their 2006 configuration with the addition of coal-based CO₂ capture retrofits and emissions penalties from 0–100 US dollars per metric ton of CO₂ (USD/tCO₂). CO₂ capture flexibility is investigated by comparing inflexible CO₂ capture systems to flexible ones that can choose between full and zero load CO₂ capture depending on which operating mode has lower costs or higher profits. Comparing these two grids is interesting because they have similar installed capacity and peak demand, and both are isolated electricity systems with competitive wholesale electricity markets. However, differences in capacity mix, demand patterns, and fuel markets produce diverging behaviours of CO₂ capture at coal-fired power plants. Coal-fired facilities are

primarily base load in ERCOT for a large range of CO₂ prices but are comparably later in the dispatch order in GB and consequently often supply intermediate load. As a result, the ability to capture CO₂ is more important for ensuring dispatch of coal-fired facilities in GB than in ERCOT when CO₂ prices are high. In GB, higher overall coal prices mean that CO₂ prices must be slightly higher than in ERCOT before the emissions savings of CO₂ capture offset capture energy costs. However, once CO₂ capture is economical, operating CO₂ capture on half the coal fleet in each grid achieves greater emissions reductions in GB because total coal-based capacity is 6 GW greater than in ERCOT. Studied market characteristics suggest greater opportunity for flexible CO₂ capture to improve operating profits in ERCOT, but profit improvements can be offset by a flexibility cost penalty.

Significant effort this semester has been expended utilizing coursework to develop computational modeling and decision analysis skills that will become useful in the later stages of my dissertation work. A stronger foundation in computational skills will enhance my modeling capabilities, and a decision analysis framework can utilize previous economic and environmental results as possible outcomes of choices and chance events.

As an example, consider Utility A and Utility B, each faced with a decision between the four plant configurations discussed in the scenario analysis above. Utility A believes there is an equal probability that each of the three CO₂ price paths will occur, but Utility B believes there is a 10% chance of the Basic scenario, 20% chance of the No International Scenario, and a 70% chance of the Limited Tech., No International Scenario. Assuming both utilities are risk neutral (ambivalent to taking or leaving a deal to win or lose any amount), the decision trees below find that Utility A should choose not to build CO₂ capture, and Utility B should choose to build a flexible CO₂ capture system without solvent storage. Such analysis can be extended to consider multiple decisions and a large number of uncertain parameters.

Utility A



Utility B

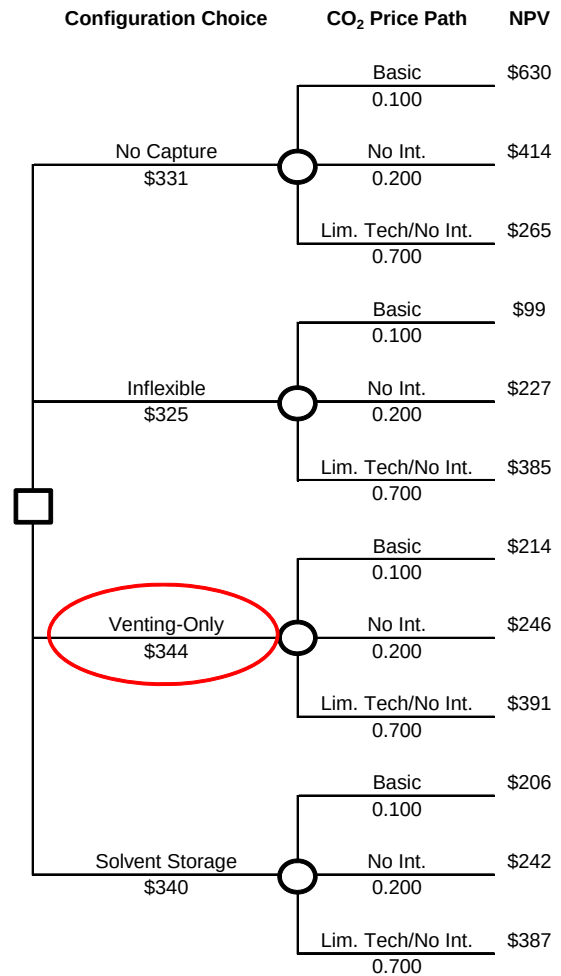


Figure 8: The best plant configuration choice depends on the belief about the probability of each CO₂ price path.

Conclusions

- Flexible CO₂ capture in response to volatile electricity prices is most valuable if future CO₂ prices hover near a range of \$40–50/tCO₂.
- Sustained CO₂ prices above \$100/tCO₂ are required to make CO₂ capture retrofit preferable to continued operation of a facility without CO₂ capture, but the benefit of flexibility could be limited in this CO₂ price regime.
- Flexible and inflexible CO₂ capture reduces CO₂ emissions substantially over a broad range of CO₂ price scenarios.

Future Work

The single plant optimization model will continue to be used to study the sensitivity of results to market conditions such as fuel and electricity prices. The model will then be used for a detailed study of the solvent storage configuration that compares solvents and design operating points to test tradeoffs among solvent price, solvent capacity, and energy performance. Sensitivity to the

capital cost of stripping and compression equipment will be explored, as well as the degree to which equipment is oversized for treating stored rich solvent.

After these studies using the single plant model, flexible CO₂ capture systems will be included in a least-cost electricity dispatch model with multiple facilities of different power plant types. This new modeling framework will be useful to investigate the ability of flexible CO₂ capture systems to provide reserve capacity and operate in response to intermittent renewable energy sources. Results from both models will be used to inform investment analysis using traditional NPV calculations and more rigorous approaches to decision making under uncertainty.

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MDEA/PZ Degradation in Cycled Solvents

Quarterly Report for January 1 – March 31, 2011

by

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and

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Abstract

When cycled and oxidatively degraded using the low-gas method, 7 m MDEA in the blend oxidatively degraded to DEA, which then oxidized to bicine. We demonstrated that when methylaminoethanol (MAE) was formed in these same experiments with 7 m MDEA and the blend, the MAE subsequently oxidized to hydroxyethylsarcosine (HES). In low gas experiments with both solvents at 55 °C, loss rates of DEA and MAE were ~ 18–20 mM/hr.

When 6 m MDEA/1 m MAE was cycled from 55 to 120 °C, the production of DEA was either suppressed or masked, and bicine production was suppressed. Indicators of amine degradation including formate, total formate, primary/secondary amine production, and parent amine (MDEA) and alkalinity loss were also suppressed, indicating that either a competition for oxygen to oxidize MAE to HES or a general suppression of overall oxidation is occurring.

HES was synthesized and identified as a single, stand alone peak using the HPLC amino acid method. The concentration of HES at the end of experiment C-21, which cycled 7 m MDEA/2 m PZ from 55 to 120 °C, was approximately 192 mM, which represented approximately 10.5% of lost carbon as MDEA and PZ loss.

When the oxidative degradation effects in 7 m DEA in low gas experiment OD-6 were isolated, it was determined that the major amine degradation product was MEA, which was rapidly formed in correlation with rapid initial loss of DEA (18.2 mM/hr). Total formate was approximately 10X formate alone, and glycolamide formed rapidly, but behaved as a reaction intermediate, decreasing in concentration after approximately 150 hours. In low gas experiment OD-7, 7 m MAE was degraded at 55 °C. Rapid loss in MAE concentration was accompanied by the production of MEA, HES, and total formate. MEA and HES both reached a steady state concentration after approximately 150 hours. As observed in OD-6, total formate was ~10X formate concentration.

Oxidative degradation mechanisms have been postulated for the degradation of MDEA and the generation of DEA, MAE, bicine, and HES in 7 m MDEA and 7 m MDEA/2 m PZ. In each

case, the pathway relies on the presence of free radicals to initiate an e^- abstraction from an α -carbon on the amine, a subsequent H^+ abstraction, and the formation of a hydroperoxide compound which will decompose to an amine/amino acid and an aldehyde.

7 m MDEA/2 m PZ did not thermally degrade over the range of 120 to 150 °C in unloaded solutions. However, lean ($\alpha = 0.1$) and rich ($\alpha = 0.25$) solutions of the solvent readily degraded both components over the temperature range of 120 to 150 °C. At 135 and 150 °C, the fraction PZ remaining was essentially zero within 50 and 15 days, respectively. Thermal degradation led to the formation of PZ derivatives including MPZ, DMPZ, AEP, and NPZ. When their concentrations are compared to those of PZ loss, only ~50% of the PZ functional group can be accounted for. DMAE did not behave as a reaction intermediate.

Introduction

During the 1st quarter 2011, seven cycling experiments (C-27 through C-33) were completed in the Integrated Solvent Degradation Apparatus (ISDA). All experiments entailed delivering a purge gas of 98% O₂/2% CO₂ at a flow rate of 100 ml/min into the oxidative reactor headspace, and maintaining this vessel at 55 °C. All stock solvents for the ISDA experiments were amended with stainless steel dissolved metal salts (0.4 mM Fe, 0.1 mM Cr, and 0.05 mM Ni). Additionally, the redesigned (reduced in size by a factor of ten) thermal reactor was utilized in all experiments. Experiments C-27, C-31, and C-32 were conducted with 6 or 7 m MDEA, C-28 and C-29 were conducted with 8 m PZ, and C-30 and C-33 were conducted with 7 m MDEA/2 m PZ. Experiments C-31 (6 m MDEA/1 m MAE) and C-32 (6 m MDEA/1 m DEA) were conducted to assist in understanding the degradation of MDEA; DEA and MAE are intermediate degradation products of MDEA, and starting with a known significant concentration of these products allowed the production of amino acids in cycled 7 m MDEA and 7 m MDEA/2 m PZ to be evaluated.

In addition to the cycling experiments with the ISDA, two low gas oxidative batch experiments at a constant temperature of 55 °C were completed. These included OD-6 with 7 m diethanolamine (DEA), and OD-7 with 7 m MAE. As with C-31 and C-32, these two experiments allowed the production of amino acids and other degradation products from known MDEA degradation intermediates to be evaluated, but in the general absence of thermally induced processes.

Thermal degradation experiment Thermal No. 16 was completed in late 4th quarter 2010, but only a partial assessment of results was made in the document Fourth Quarterly Progress Report (Rochelle, 2011). This report presents a more comprehensive review of those data.

Cycling (ISDA) Experiments Discussion

Table 1 provides a summary of the degradation rates measured for a subset of the ISDA experiments, including all of the most recent experiments completed in the quarter. Data listed in yellow are for 8 m PZ, data listed in orange are for 7 m MDEA/2 m PZ, and data listed in gray are for blends of MDEA. Comprehensive data tables for experiments C-27 through C-33 are included at the end of this report as Tables A-1 through A-14.

Two key findings made this quarter impact the assessment of all data discussed in this report. The first finding is the discovery of the near-complete overlap in DEA and MAE peaks on the cation chromatograph (~11.5 to 11.7 minutes), preventing the separation of these peaks and

accurate quantification of either compound. Because both compounds are confirmed products of MDEA degradation in cycled solvents (using GC-MS and IC-MS analytical techniques), the concentration of these compounds as a product of MDEA and blend degradation is now expressed as the combined concentration of DEA/MAE as DEA; the DEA calibration curve is used to express the actual concentration of both.

The second key finding is the presence of hydroxyethyl sarcosine (HES) as a product of 7 m MDEA and blend degradation. HES is formed in the oxidative degradation of MAE (Critchfield and Jenkins, 1998). The presence of HES in cycled samples was confirmed through synthesis of this compound, and its concentration estimated in select experiments. HES synthesis and comparison to degraded samples is discussed in detail below.

Table 1: Rates in Cycled 7 m MDEA ($\alpha = 0.1$ mols CO₂/mol alk)

Expt	Solvent	T _{th} (°C)	Other Conditions	Alk Loss (mM/hr)	MDEA Loss (mM/hr)	PZ Loss (mM/hr)	DEA Prod Rate (mM/hr)	Formate Prod (mM/hr)	Formate w/ Hydrolysis (mM/hr)	Bicine (mM/hr)	Glycine (mM)	EDA Prod (mM/hr)
C-3	7 m MDEA	55	SS metals	1.5	0.9	NA	0	0.005	0.01	0.002	0	NM
C-11	7 m MDEA	80	SS metals; bubble vessel	1.3	0.91	NA	0	0.034	0.039	0.027	0.009	NM
C-12	7 m MDEA	90	SS metals; bubble vessel	2.5	2.87	NA	1.55	0.12	0.15	0.084	0.006	NM
C-10	7 m MDEA	100	SS metals; bubble vessel	3	4.1	NA	1.64	0.18	0.31	0.22	0.007	NM
C-6	7 m MDEA	120	SS metals; bubble vessel	4.93	4.6	NA	2.56	0.28	0.34	0.34	0.007	NM
C-17	8 m PZ	90	SS metals; bubble vessel	0.067	NA	0.11	0.07	0.013	0.038	0	0.003	0.07
C-16	8 m PZ	120	SS metals; bubble vessel	0.91	NA	1.1	0	0.046	0.130	0	0.013	0.17
C-28	8 m PZ	110	SS metals; bubble vessel, new thermal reactor	1.02	NA	1.63	0	0.021	0.06	0	0.005	0
C-29	8 m PZ	125	SS metals; bubble vessel, new thermal reactor	0.89	NA	3.64	0	0.061	0.22	0	0.02	0.36
C-22	7 m MDEA/2 m PZ	90	SS metals; bubble vessel	3.2	1.6	0.79	1.23	0.2	0.41	0.22*	0	0
C-33	7 m MDEA/2 m PZ	90	SS metals; bubble vessel; new thermal reactor	0.051	0.45	0.11	0.28	0.032	0.06	0.025	0	0
C-23	7 m MDEA/2 m PZ	100	SS metals; bubble vessel	1.2	2.82	0.72	2.9	0.19	0.41	0.22		0
C-21	7 m MDEA/2 m PZ	120	SS metals; bubble vessel	2.5	2.7	1.2	1.5 (4*)	0.22	0.50	0.14	0.005	0
C-30	7 m MDEA/2 m PZ	125	SS metals; bubble vessel, new thermal reactor	4.7	5	2.19	?	0.36	0.86	0.39	0	0
C-25	7 m MDEA	120	SS metals; bubble vessel, new thermal reactor	4.4	5.1	NM	3.1	0.61	0.96	1.25	0.011	0
C-26	7 m MDEA	130	SS metals; bubble vessel, new thermal reactor	3.67	15.6	NM	2.73 (MAE)	0.31	0.28	0.95	0	0
C-27	7 m MDEA	100	SS metals; bubble vessel, new thermal reactor	1.88	3.16	NM	0	0.105	0.11	0 (0.44)	0	0
C-20	7 m MDEA+100 mM Formate	120	SS metals; bubble vessel	1.08	3.96	NA	0.18	-0.4	-0.37	0.89	0.1	0
C-24	7 m MDEA + 100 mM DEA	120	SS metals; bubble vessel	2.7	0.99	NM	3.63	0.38	0.50	1	0.008	0
C-31	6 m MDEA/1 m MAE	120	SS metals; bubble vessel, new thermal reactor	3.4	2.73	NA	0	0.28	0.55	0 (0.74)	0	0
C-32	6 m MDEA/1 m DEA	90	SS metals; bubble vessel, new thermal reactor	0.9	0.59	NA	0.155	0.016	0.04	0.17	0	0

Experiment C-27

Experiment C-27 entailed cycling 7 m MDEA at an initial loading of 0.1 mol CO₂/mol alkalinity from 55 to 100 °C in the ISDA. Note that 7 m MDEA was cycled in the ISDA from 55 °C to 100 °C in experiment C-10, which was conducted with the original (larger) thermal reactor. The data from C-27 reflect a consistently lower level of degradation with the smaller thermal reactor. For example, the formate production rate in C-27 was 0.11 mM/hr compared to 0.18 mM/hr in C-10. These results confirm that a lower residence time at the higher temperature of the thermal reactor results in less oxidative degradation.

Experiments C-28 and C-29

Experiments C-28 and C-29 were conducted with 8 m PZ to provide degradation data over a range of thermal reactor temperatures, and to provide the basis for development of an oxidative degradation model as previously developed for 7 m MDEA. C-29 was conducted with the thermal reactor set at 125 °C, and these data can be best compared to C-16 in which the larger thermal reactor was set at 120 °C. These data indicate an increase in the loss of PZ (3.64 vs. 1.1 mM/hr) and production of total formate and ethylenediamine (EDA) with the thermal reactor set at 125 °C, but no increase in alkalinity loss.

Experiments C-30 and C-33

In experiment C-30, 7 m MDEA/2 m PZ was cycled to 125 °C in the redesigned thermal reactor to obtain degradation data at this higher temperature. C-30 data can be compared to data generated by experiment C-21 where the thermal reactor was maintained at 120 °C. All degradation parameters indicate an increase in rate with an increase in the thermal reactor temperature from 120 to 125 °C.

In experiment C-33, 7 m MDEA/2 m PZ was cycled to 90 °C with the redesigned thermal reactor to match the temperature conditions of C-22 with the larger reactor. However, the rates measured in C-33 were generally a full order of magnitude less than those measured in C-22, indicating that the smaller thermal reactor had a much greater effect when the solvent was cycled to a lower temperature; the effect of a lower residence time in the smaller reactor resulted in limiting the activation of the principal degradation mechanisms.

Experiments C-31 and C-32

In experiment C-31, 6 m MDEA/1 m MAE at an initial loading of 0.12 mols CO₂/mol alkalinity was cycled from 55 to 120 °C to study the effect of having an initially large concentration of MAE present on the production of amino acids including bicine and HES. In experiment C-32, 6 m MDEA/1 m DEA at an initial loading of 0.12 mols CO₂/mol alkalinity was cycled from 55 to 90 °C to study the effect of having an initially large concentration of DEA on the production of the same amino acids. Experiment C-32 was a variation on C-24 which entailed cycling 7 m MDEA + 100 mM DEA from 55 to 120 °C.

In C-31 (Table 1), DEA production was either suppressed or masked by the presence of the MAE peak on the cation chromatograph in all samples. As discussed in the Introduction, the overlap in DEA and MAE peaks with cation chromatography prevents quantification of either compound with accuracy. However, given the starting concentration of 1 m MAE in C-31, DEA production may have been suppressed for the initial period of the experiment, and the increase in the peak size at a retention time of ~11.7 minutes was mostly due to increase in MAE concentration. The data support the conclusion that the amino acid bicine is produced in cycled 7 m MDEA through the oxidation of the secondary amine degradation intermediate product DEA. Evidence of this effect exists in C-31 degradation results where a delay in the production of bicine was observed for almost 50 hours of cycling, at which time the production of bicine occurred at a rate of ~0.75 mM/hr (Figure 1). Note that the production of formate and total formate (formate + formamide) was suppressed in this experiment when compared to the results of C-25. Finally, the combined DEA/MAE production rate was an order of magnitude less, regardless of the MAE-DEA split, suggesting that the initial presence of MAE suppresses overall oxidative degradation and production of formate, amine products (DEA or MAE), and amides.

This conclusion is supported by the MDEA loss rate (2.7 mM/hr) being cut in half when compared to the rate measured in C-25 (5.1 mM/hr).

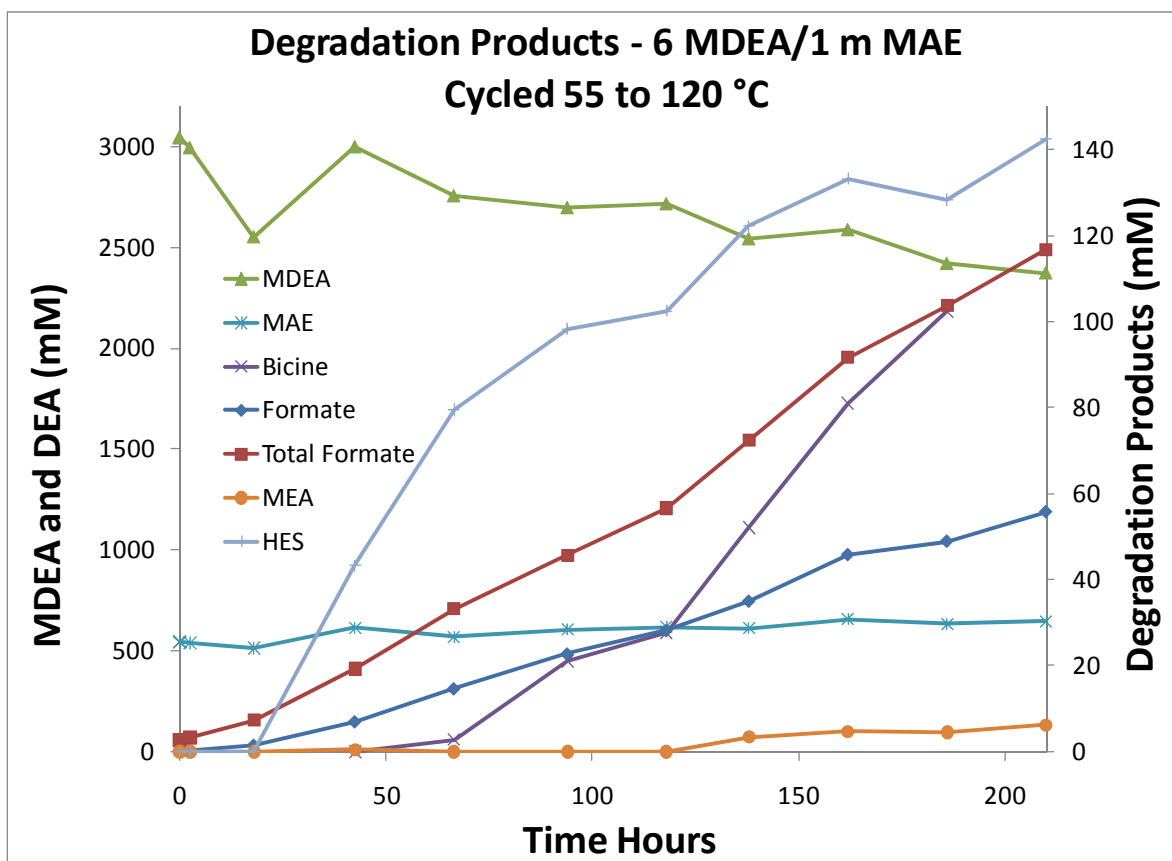


Figure 1: Degradation Products in 6 m MDEA/1 m MAE ($\alpha = 0.12$) Cycled 55 to 120 °C

In addition to the degradation products discussed above, we confirmed the presence of HES in samples from C-31 through the synthesis of this amino acid and direct comparison using the HPLC amino acid chromatography method.

HES Synthesis

HES was synthesized with a base-catalyzed (0.2 M NaOH) aqueous reaction between MAE (1 M) and monochloroacetic acid (MCAA) (0.1 M). MAE and MCAA were added to the basic solution in an open beaker and stirred for four hours at approximately 60 °C to facilitate the substitution reaction between MAE and MCAA; MAE underwent an arm substitution reaction to replace an H^+ with an acetic acid group, producing HES (Figure 2). The presence of HES was confirmed from injection and separation on the HPLC amino acid system (Dionex AAA method). A single large peak eluted at approximately 20.8 minutes which correlated with a peak repeatedly observed in degraded 7 m MDEA as well as C-31 samples. Figure 3 illustrates the peak response from the synthesized HES as well as sample injection for C-31-10. Direct injection of the end product solution on a Thermo Finnigan TSQ mass spectrometer was used to confirm the presence of HES; a compound mass of 133.1 in this solution was observed. Figure 4 presents the chromatogram from the synthesized HES injection overlaid with sample C-21-15. Experiment C-21 entailed cycling 7 m MDEA/2 m PZ from 55 to 120 °C. The HES peak aligns

in both chromatograms, indicating that HES is formed when this blend is degraded in an oxygen rich system.

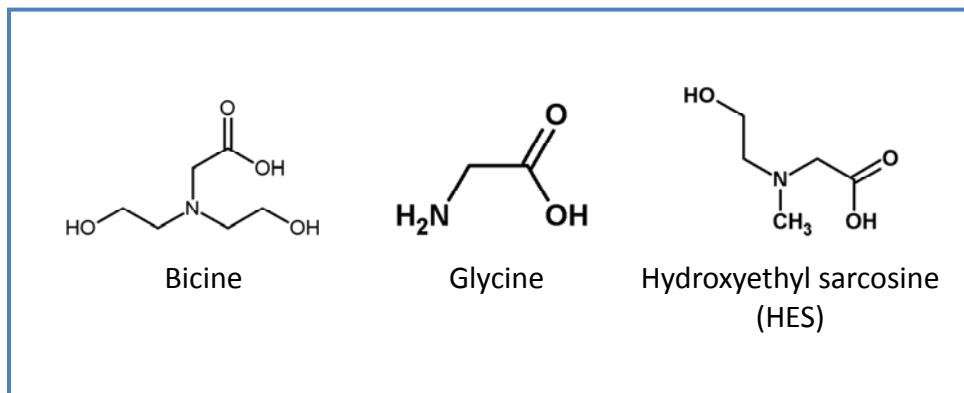


Figure 2: Amino Acid Structures

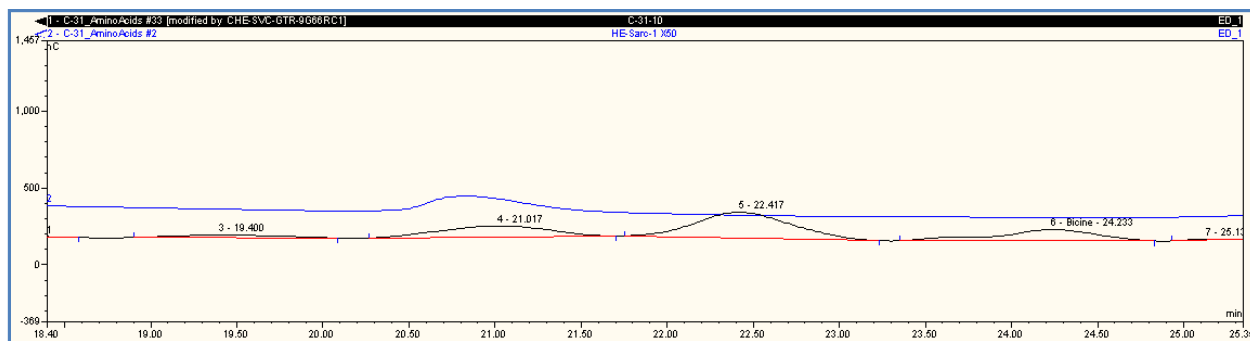


Figure 3: Amino Acid Chromatogram – HES comparison to C-31-10 Sample

Not knowing whether the HES synthesis reaction was complete, we utilized the peak size and response factor for glycine standards run on the AAA method to conservatively estimate the concentration of HES in C-31-10 as ~3 mM. The glycine peak elutes at ~20.2 minutes, which is close to HES. The concentration of HES was estimated another way assuming the reaction between MCAA and MAE went to completion (all MCAA reacted with MAE to provide a concentration of 0.1 M HES). This solution was diluted 20X, 50X, and 100X in water and analyzed by the HPLC amino acid method to provide a response curve. Using this method, the HES concentration in C-31-10 was estimated at 142 mM, which is comparable to the bicine concentration in this sample (~130 mM). Using this standard method, HES concentration in C-21-15 was ~192 mM, which accounts for approximately ~10.5 and 7.5% of carbon and nitrogen loss, respectively, and is 2.5X the concentration of bicine (~79 mM) accumulated in this sample.

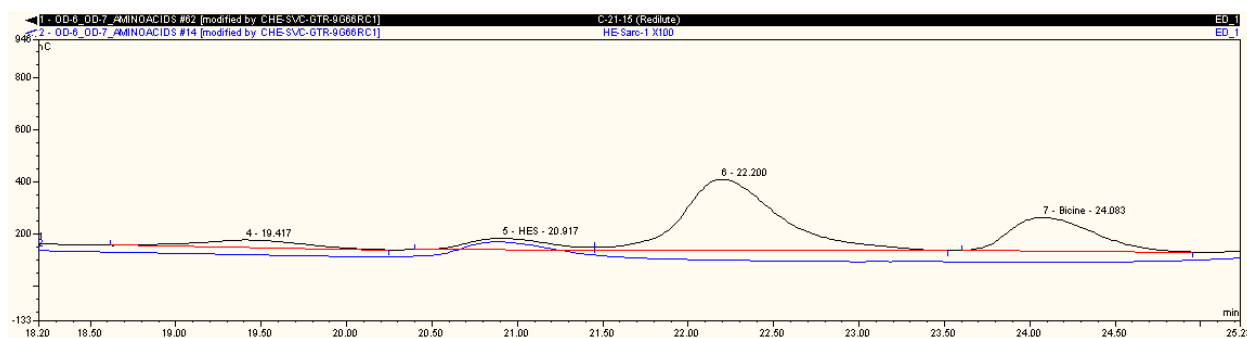


Figure 4: Amino Acid Chromatogram – HES comparison to C-21-15 Sample

The results from experiment C-32 (6 m MDEA/1 m DEA cycled from 55 to 90 °C) are best compared to the results of C-12 which entailed cycling 7 m MDEA from 55 to 90 °C, but in the absence of DEA as an initial amendment. The thermal reactor size was ten-fold in C-12, and would generally prevent as much degradation to occur in C-32 as in C-12. All key degradation parameters, with the exception of bicine production, exhibited an order of magnitude suppression in rates, including MDEA and alkalinity loss rates (0.85 and 0.59 mM/hr, respectively) when compared to the C-12 data. The bicine production rate increased from 0.08 mM/hr in C-12 to 0.17 mM/hr in C-32, supporting the conclusion that in cycled 7 m MDEA, the production of bicine comes from the degradation of the intermediate secondary amine, DEA. Unlike the results of C-31, bicine production experienced a very short lag (~25 hrs), further supporting the conclusion that bicine is produced from the oxidation of DEA. HES was not produced in C-32, indicating that when cycled to only 90 °C with significant DEA present, MDEA conversion to MAE is insufficient to allow the further oxidation of MAE to HES.

Finally, MEA was quantified in both C-31 and C-32. MEA in C-31-10 was ~6 mM, which was ten-fold that observed in C-32-8, and may be the result of cycling to a higher temperature in experiment C-32. The cycled 6 m MDEA/1 m MAE exhibited a greater propensity to produce MEA than 6 m MDEA/1 m DEA, which represents a loss of a methyl group from MAE as opposed to the loss of a hydroxyethyl group from DEA.

MEA-Amino Acid Synthesis

The presence of MEA in samples from C-32 (7 m MDEA/2 m PZ) indicated the possible presence of an amino acid similar in structure to MEA, and the need to synthesize this compound. We utilized the same base-catalyzed synthesis method used in the preparation of HES for the preparation of an amino acid of MEA. 1 m MEA and 0.1 M MCAA were added to a 0.2 M NaOH aqueous solution, and stirred at 60 °C for approximately four hours. The amino acid synthesis product was injected following the HPLC AAA method and a double peak eluted at ~22.4 minutes, which corresponded to a peak of the same retention time observed in degraded 7 m MDEA samples (C-31-10). The same synthesis product was analyzed through direct injection on the mass spectrometer, and the presence of an amino acid with a molecular weight of 119.1 was confirmed. It appears that MAE degrades to MEA when cycled, which can form an amino acid with a molecular weight of 119.1. The synthesized product produced a double peak, which prevented an accurate estimate of amino acid concentration being made.

Low Gas Experiments OD-6 and OD-7

Two low gas oxidative experiments at 55 °C were completed in the quarter. In OD-6, 7 m DEA was degraded, while in OD-7, 7 m MAE was degraded for 378 hours. Both solvents were supplemented with the metal salts as in every cycling experiment. The reactor mechanics for these low gas experiments were maintained the same as those for all previous low gas experiments conducted in Rochelle lab at 55 °C; the Teflon lined reactors (TOR) utilized by Stephanie Freeman were used for these experiments. Table 2 lists the degradation rate data for OD-6 and OD-7, and can be compared to the data from the ISDA cycling experiments.

Table 2: Rates in low gas experiments OD-6 and OD-7

Expt	Solvent	T _{th} (°C)	Alk Loss (mM/hr)	MDEA Loss (mM/hr)	PZ Loss (mM/hr)	DEA Prod Rate (mM/hr)	Formate Prod (mM/hr)	Formate w/ Hydrolysis (mM/hr)	Bicine (mM/hr)	Glycine (mM)	EDA Prod (mM/hr)	MAE Prod (mM)
OD-6	7 m DEA	55	3.9	NA	NA	-18.2	0.157	1.03	1.46	0.008	0	0
OD-7	7 m MAE	55	4.9	NA	NA	0	0.206	1.03	0 (0.11)	0	0	-20

The degradation products in OD-6 included formate, total formate (formate + amides), bicine, MEA, and glycolamides measured as recoverable glycolate after sample hydrolyzation with NaOH. Figure 5 depicts the degradation products in OD-6. The concentration of glycolamides increased for the first 100 hours of degradation, but decreased to less than 25 mM for the last 100 hours of degradation, indicating a decomposition of amides with a glycolic acid group. Formate production occurred at 0.16 mM/hr, whereas total formate (formate + amides) production occurred at 1.0 mM/hr, indicating that amides (measured as formate) were nearly ten times the formate production rate. The bicine production rate was 1.46 mM/hr, which was also an order of magnitude greater than the rate measured in C-32 where 6 m MDEA/1 m DEA was cycled to 90 °C in the thermal reactor. The initial bicine production rate was 0 mM/hr in OD-7, further isolating the mechanism for bicine production to oxidation of DEA. The major amine degradation product in this experiment was MEA, the primary amine formed when DEA loses one hydroxyethyl group. The solvent experienced a rapid loss of DEA concentration for the first 100 hours of the low-gas experiment (OD-6), accompanied by production of MEA. The DEA concentration reached a steady state concentration (~2,250 mM) after approximately 150 hours, which corresponded to the time at which the MEA concentration reached a steady state concentration (~225 mM). The rapid degradation period associated with DEA (<150 hours) also corresponded to the period of glycolamide formation; after approximately 150 hours, the glycolamide concentration declined to a steady state concentration of less than 25 mM. It is possible that the glycolamide decomposes back to DEA and glycolic acid, resulting in the DEA concentration no longer decreasing in the experiment. However, the glycolate concentrations in the non-hydrolyzed samples were 10 to 30X less than the corresponding concentrations in the hydrolyzed concentrations. Further, the glycolate (without hydrolyzation) concentration also experienced a decrease after approximately 150 hours of degradation, indicating that the reduction in total glycolate (glycolate + amides) did not correlate with an increase in glycolate alone. Thus, any decomposition in amides of glycolate was not evidenced by an increase in glycolate composition, but may have resulted in an increase in amines (DEA).

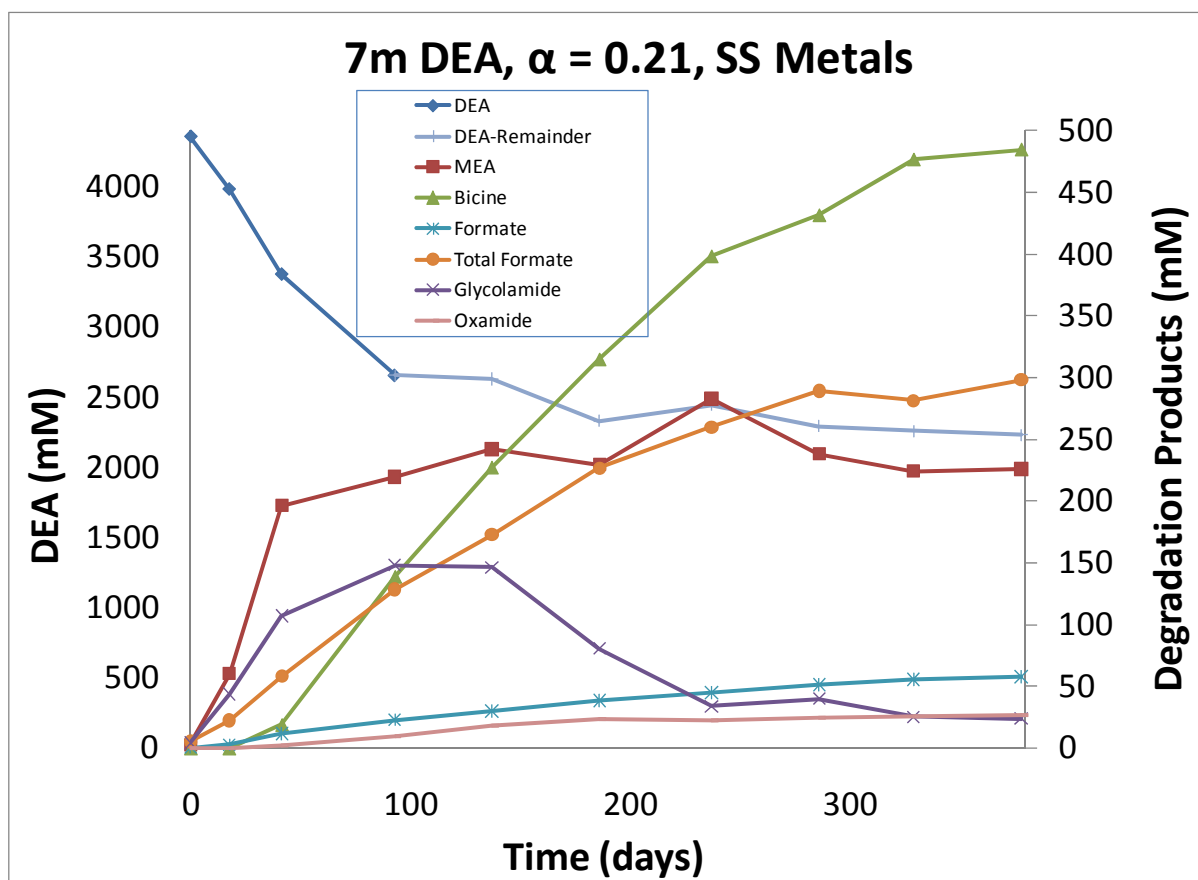


Figure 5: Degradation Products in OD-6 (7 m DEA, $\alpha = 0.12$), Oxidation at 55 °C with 98% $O_2/2\%$ CO_2

In OD-7, the MAE concentration experienced a decrease in concentration at a rate of 20 mM/hr, which is comparable to the loss rate of DEA in OD-6 (18.2 mM/hr). Total formate production in both experiments was ~ 1.0 mM/hr, whereas the formate production rate was 0.21 compared to 0.16 mM/hr in OD-6. OD-7 samples generally exhibited no bicine for the first 150 hours of degradation; after this initial lag period, bicine production occurred at a rate of 0.11 mM/hr, and accumulated to a concentration of ~ 31 mM after 378 hours of degradation at 55 °C. The lag in bicine production indicates that some DEA must be produced in oxidatively degraded MAE, but also lags for ~ 150 hours, after which the DEA is oxidized to bicine. HES production occurred at an initially rapid rate, but reached a steady state (~ 180 mM) after only 25 hours of oxidative degradation. Figure 6 presents the degradation products with time in OD-7. The data in Figure 6 illustrate that concentrations of MAE, MEA, and HES all reach steady state after approximately 100 hours of oxidative degradation in the low gas experiment. Bicine reaches a steady state after experiencing no production (lag time) for almost 150 hours.

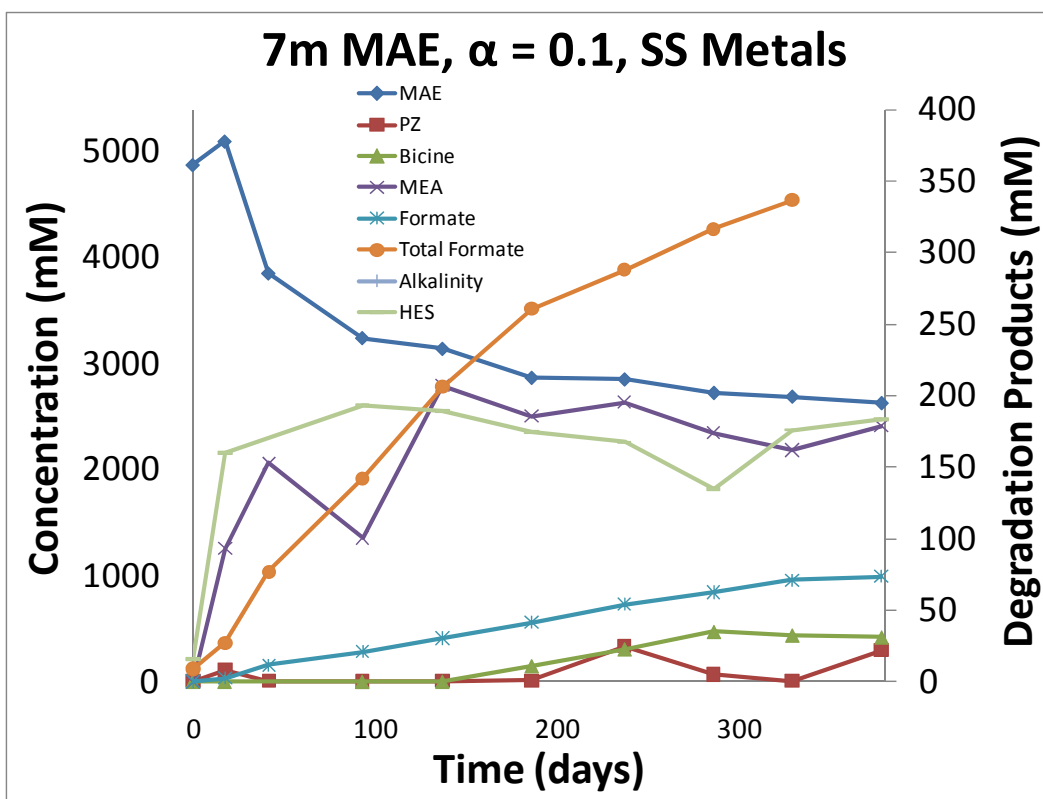


Figure 6: Degradation Products in 7 m MAE low-gas experiment OD-7, Oxidation with 98% O₂/2% CO₂ at 55 °C

Oxidative Degradation Pathways

In the previous quarterly report (Rochelle, 2011), we postulated a mechanism for the oxidative degradation of MDEA to DEA. That pathway required the presence of free radicals, which we believe are formed in the subject experiments as well as industrial applications by the presence of dissolved transition metals salts (iron, chromium, and nickel in our experiments) which initiate single electron abstraction from the alpha-carbon of amines in cycled solvents. With oxygen at its solubility limit in experimental solutions, the proton abstracted product of this initial step will quickly form a peroxide, which will then undergo decomposition in the presence of the metal salts. We have presented this step as homolytic cleavage, resulting in the propagation of free radicals in the solvent. However, the work of Blanksby et al. (2002) suggests the possibility of this step being a base-mediated decomposition, resulting in the formation of an aldehyde after proton transfer occurs. Homolytic cleavage explains the propagation of free radicals in the degraded solvent. Finally, it is expected that the alcohol formed in the presence of an abundance of amine will break apart to form the secondary amine DEA and formaldehyde. An analogous decomposition of MDEA to MAE can occur, as presented in Figure 7. It is believed that this process is occurring in cycled MDEA/PZ, which leads to the production of bicine and HES in the degraded blend.

Figure 8 presents a proposed pathway for the degradation of MAE to HES, which is analogous to the formation of bicine from DEA. We believe that the metals salts create and propagate free radical oxidation mechanisms that explain the formation of degradation intermediates and end

products. A hydrogen abstraction step in the presence of free radicals initiates the decomposition of MAE to the amino acid HES. The hydroxyacetaldehyde will react at the aldehyde functionality with MAE to form a tertiary amine with an aldehyde arm, which will readily oxidize in the presence of oxygen to form HES.

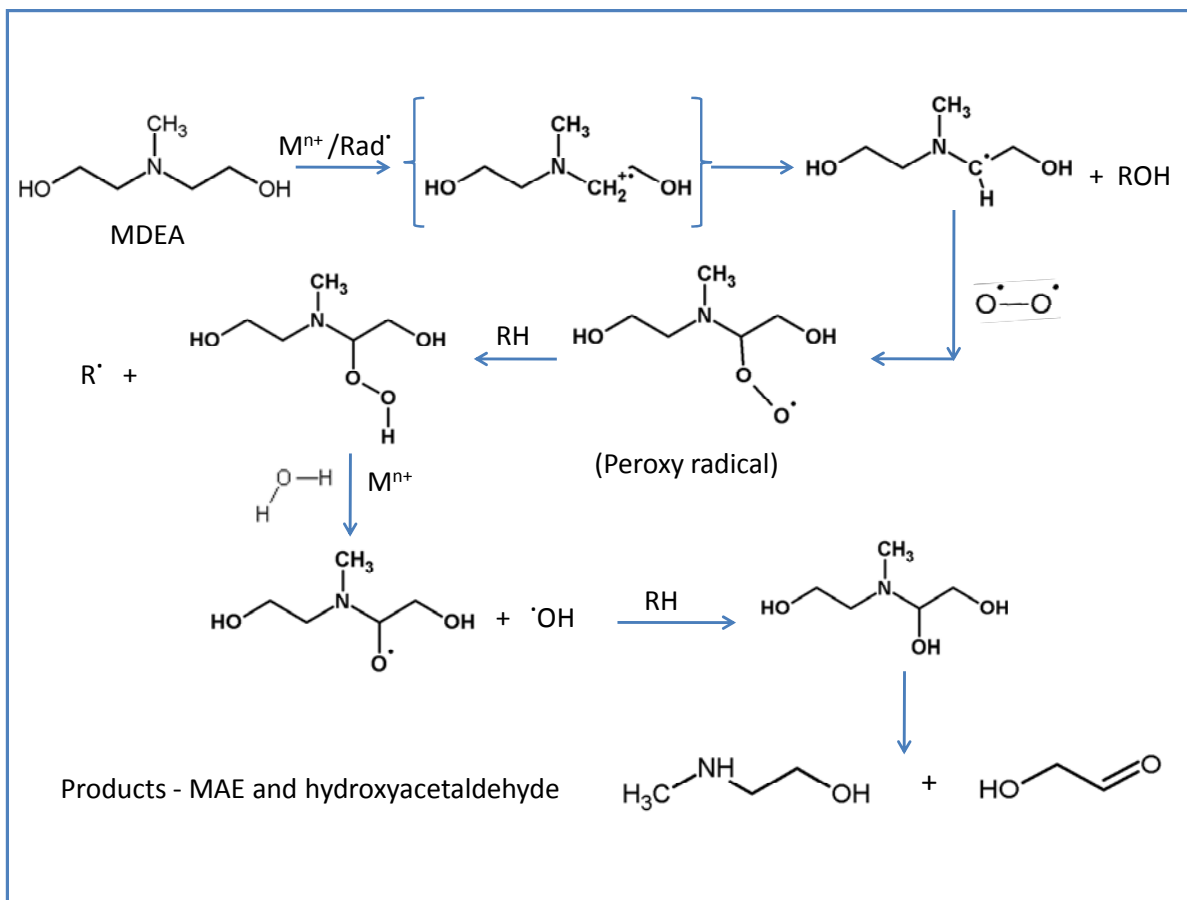


Figure 7: Proposed oxidative degradation pathway for MDEA to form MAE and hydroxyacetaldehyde

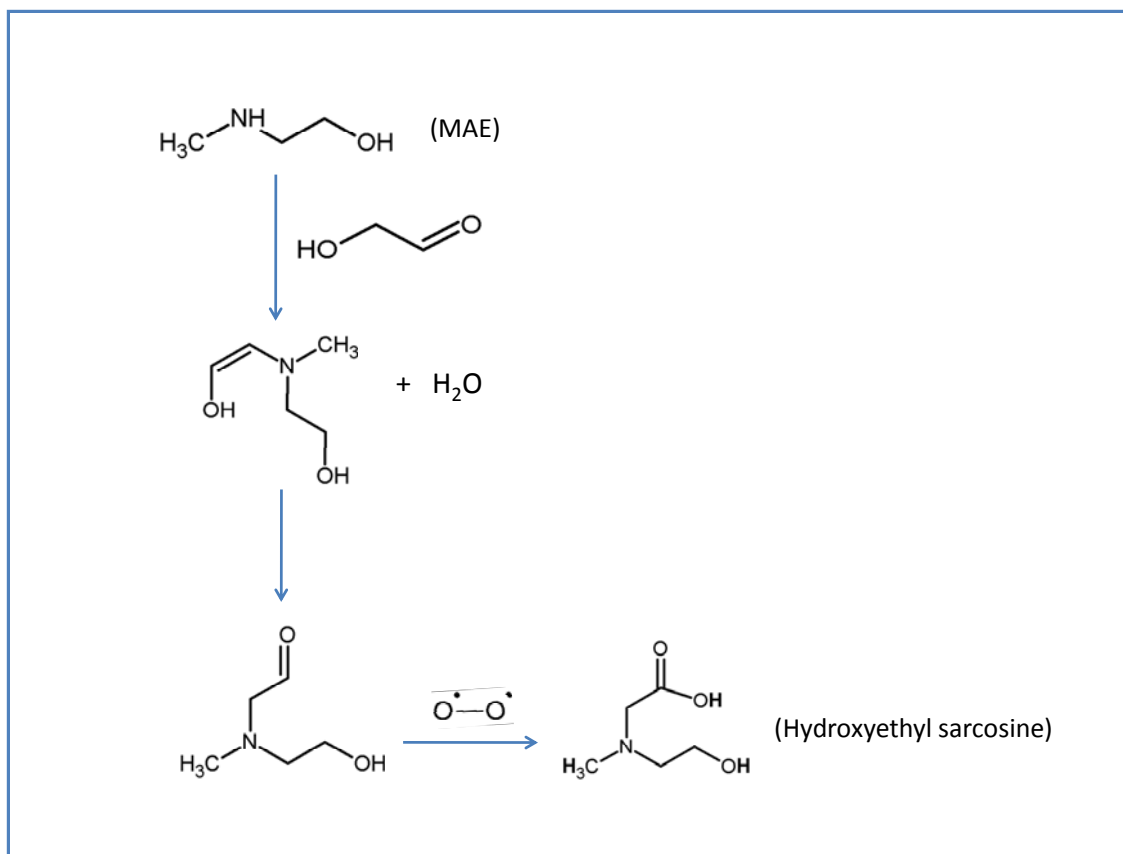


Figure 8: Oxidative degradation pathway – MAE to HES

Thermal Degradation

Thermal No. 16 entailed thermally degrading 7 m MDEA/2 m PZ ($\alpha = 0.0, 0.1$ and 0.25) at temperatures of $120, 135,$ and $150\text{ }^{\circ}\text{C}$ for several weeks using Swagelok[®] sample cylinders. Figures 9 through 11 present the MDEA and PZ concentrations plotted for each temperature series. At each temperature up to $150\text{ }^{\circ}\text{C}$, the concentrations of both MDEA and PZ are generally stable in unloaded solvents. However, at a lean loading of $0.1\text{ mols CO}_2/\text{mol}$ alkalinity, near complete loss of PZ is experienced within 75 days at $135\text{ }^{\circ}\text{C}$. At $150\text{ }^{\circ}\text{C}$, PZ is completely degraded within 20 days.

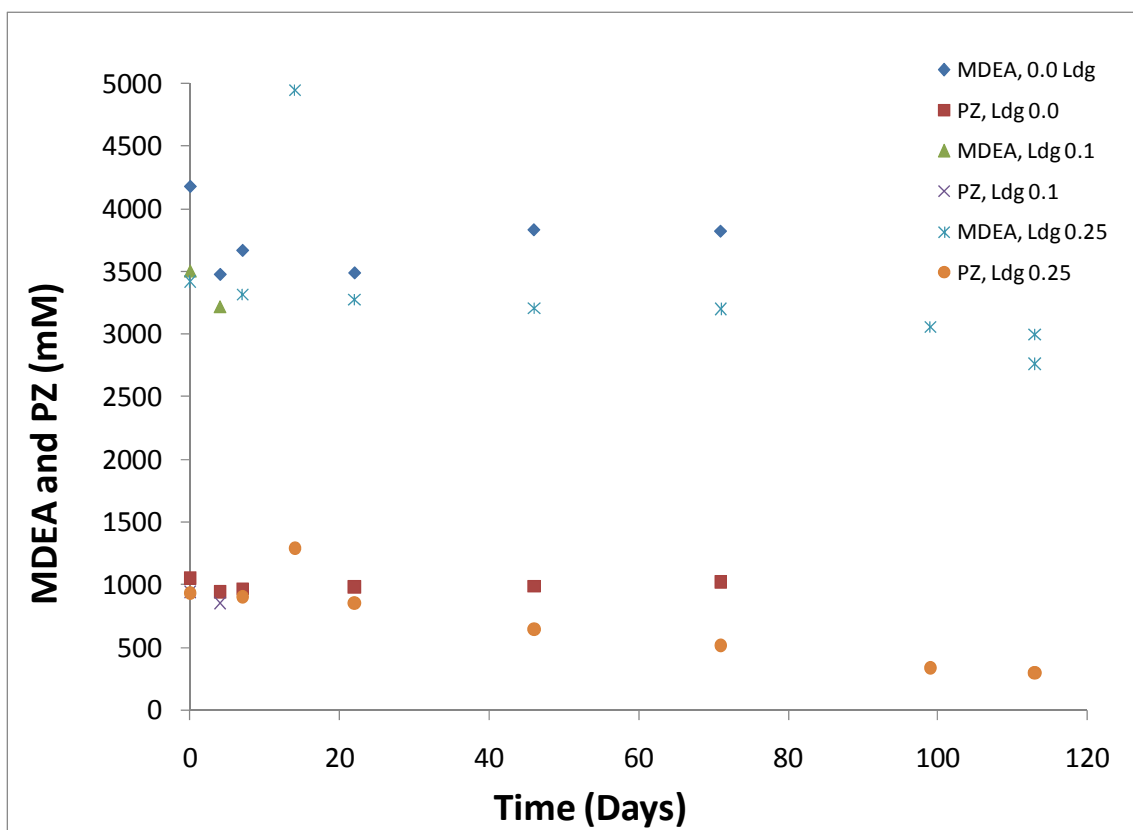


Figure 9: Thermal degradation of 7 m MDEA/2 m PZ at 120 °C

The degradation product and parent amine concentrations in the sample series initially loaded to 0.25 mols CO₂/mol alkalinity and degraded at 150 °C are plotted in Figure 12. Major degradation products included DEA, MPZ, dimethyl PZ (DMPZ), aminoethyl PZ (AEP), and N-formyl PZ (NPZ). The concentration of DEA, MPZ, and NPZ all increased rapidly at the higher temperatures (135 and 150 °C), but then experienced a decrease over the last several weeks of degradation, indicating probable degradation of these products at these temperatures. Of the major degradation products identified in the thermally degraded blend, only the DMPZ maintained its concentration or increased through the end of the experiment. This latter observation suggests that arm switching of methyl groups from MDEA to PZ continues as MPZ reacts with MDEA to acquire an additional methyl group to form DMPZ. Because of this continued arm switching, loss of MDEA continues, accompanied by DMPZ formation. It is also probable that DMPZ is being formed as MPZ is being subsequently converted to DMPZ. MPZ can thus be regarded as a degradation intermediate in the blend.

Of note, the compound dimethylaminoethanol (DMAE) was only detected in the rich loaded blend (0.25 mols CO₂/mol alkalinity), and only when degraded at 150 °C for more than 70 days. This observation is in limited agreement with the findings of Chakma and Meisen (1997) who reported the presence of DMAE, but reported it is the first degradation product to be observed when CO₂ loaded solutions of MDEA were thermally degraded. In our study (Thermal No. 16), DMAE is only observed after DEA and PZ derivatives are consistently observed over the early times. Chakma and Meisen also report that DMAE and triethanolamine (TEA) behave as degradation intermediates, whereas in Thermal No. 16, DMAE does not appear to be a precursor

to other amine degradation products. DMAE appearance late in the experiment suggests that degradation processes including methyl group arm switching occur much more readily when PZ is present, which is supported by the fact that PZ is a much stronger nucleophile in the solvent blend than MDEA.

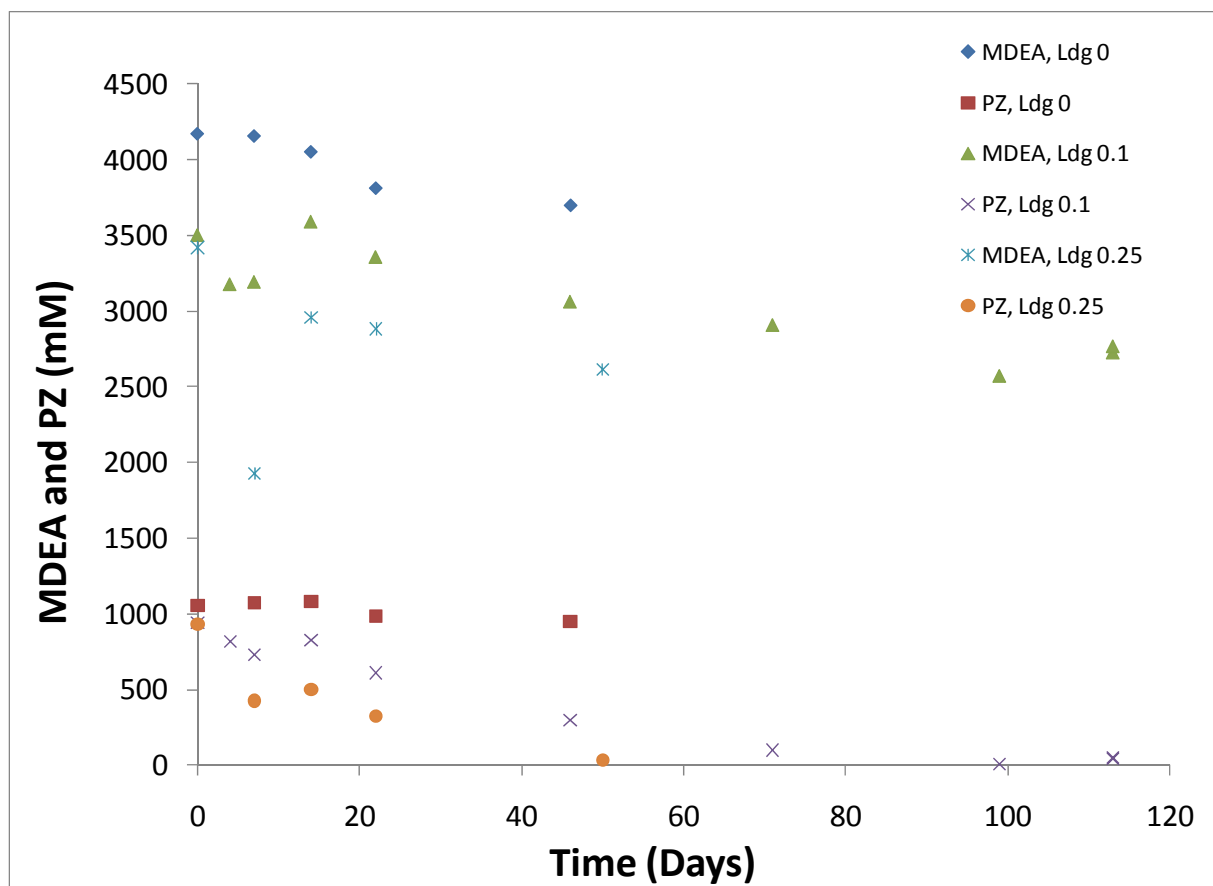


Figure 10: Thermal degradation of 7 m MDEA/2 m PZ at 135 °C

PZ derivatives (MPZ, DMPZ, AEP, and NPZ) were accounted for and compared to the loss of PZ itself. The average unaccounted-for PZ was approximately 48% after the initial three days of degradation, and was generally around 53% towards the end of the thermal degradation experiment (113 days). The recovery of PZ functional groups as major amine products indicates that approximately 50% of the PZ is actually degraded to other types of compounds, indicating ring breakage and opening to form polymers and possibly urea structures lacking amine functionality; these products do not appear as separated products using the cation chromatography method.

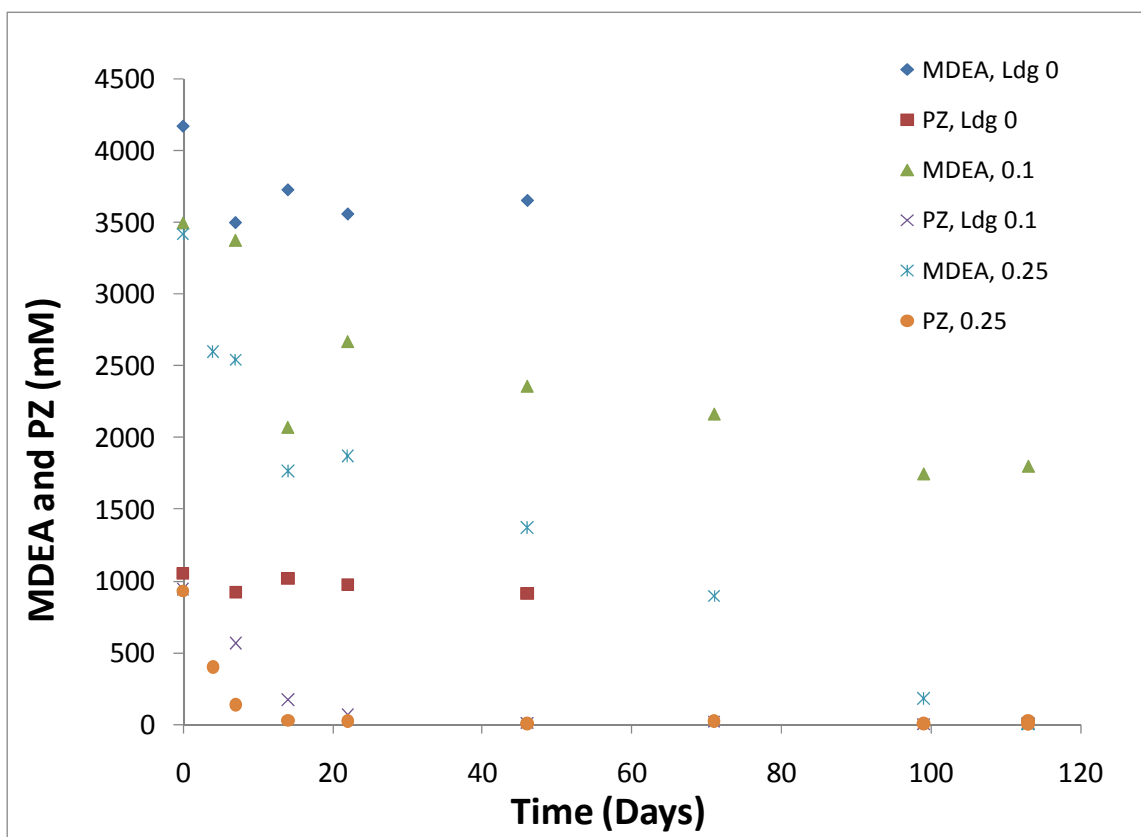


Figure 11: Thermal degradation of 7 m MDEA/2 m PZ at 150 °C

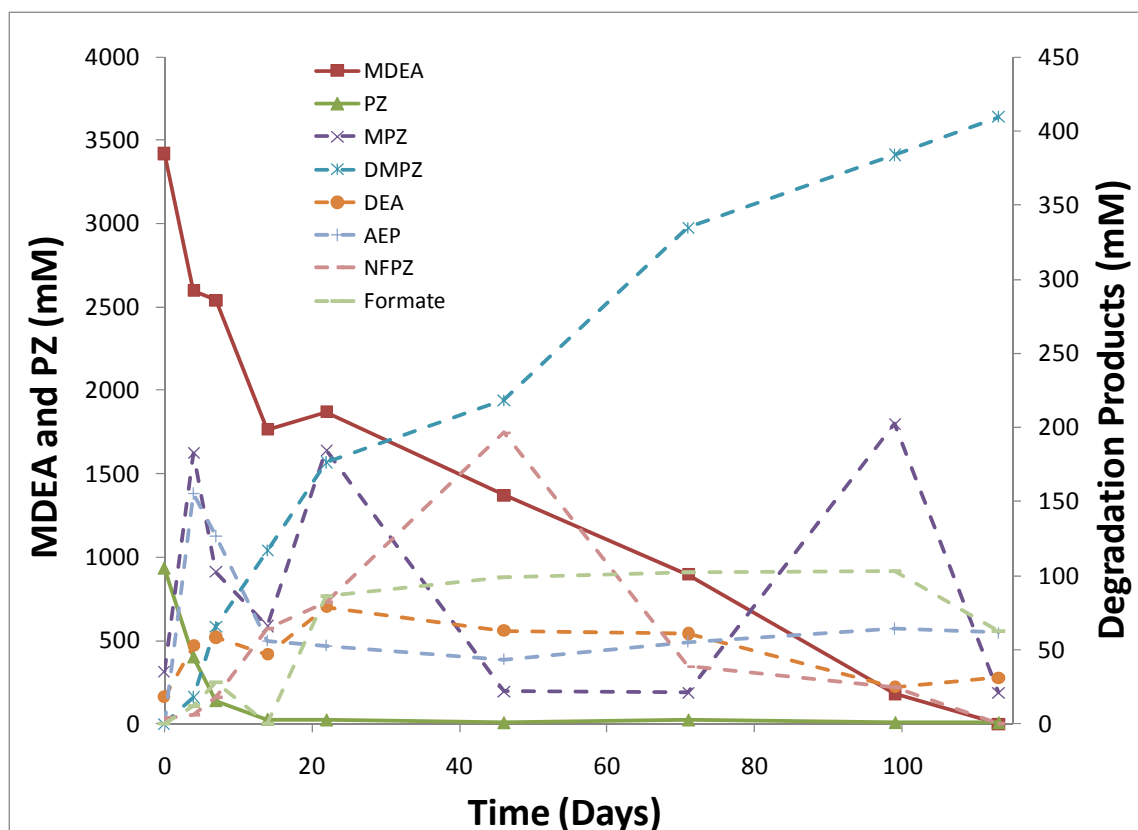


Figure 12: Degradation products in thermally degraded 7 m MDEA/2 m PZ (150 °C)

Conclusions

Experiments using the ISDA and the low-gas oxidative degradation apparatus isolated key oxidative degradation mechanisms in 7 m MDEA as well as the blend 7 m MDEA/2 m PZ. MDEA in the blend oxidizes to DEA, which then oxidizes to bicine. When MAE is formed in these experiments with 7 m MDEA and the blend, MAE will subsequently oxidize to HES.

When 6 m MDEA/1 m MAE was cycled, the production of DEA was either suppressed or masked for most of the experiment. This effect was further evidenced by the suppression of bicine production. Further, in this experiment, all indicators of amine degradation including formate, total formate and primary and secondary amine production and parent amine (MDEA) and alkalinity loss were suppressed, indicating either a competition for oxygen to oxidize MAE to HES, or a general suppression of overall oxidation.

HES was synthesized and identified as a single, stand alone peak using the HPLC amino acid method. The concentration of HES at the end of experiment C-21, where 7 m MDEA/2 m PZ was cycled from 55 to 120 °C, was approximately 192 mM, which represented approximately 10.5% of lost carbon as MDEA and PZ loss.

When oxidative degradation effects in 7 m DEA in low gas experiment OD-6 were isolated, The major amine degradation product was MEA, which was rapidly formed in correlation with rapid initial loss of DEA (18.2 mM/hr). Total formate was approximately 10X formate alone, and glycolamide formed rapidly, but behaved as a reaction intermediate, decreasing in concentration after approximately 150 hours. In low gas experiment OD-7, 7 m MAE was degraded at 55 °C,

and a rapid loss in MAE concentration was measured, accompanied by the production of MEA, HES, and total formate. MEA and HES both reached a steady state concentration after approximately 150 hours. As observed in OD-6, total formate was ~10X formate concentration. This observation for 7 m DEA and 7 m MAE degraded in low gas system is in contrast to cycling experiments with 7 m MDEA and 7 m MDEA/2 m PZ, and blends with other amendments/amines where a two to one ratio of total formate to formate has generally been observed, indicating that the amides (measured as formate) are at approximately the same concentration as formate. A comparison to Figure 1 of this report, which is a plot of degradation products in cycled 6 m MDEA/1 m MAE, demonstrates the contrast in these low gas results to a cycled blend. It is unclear at this time whether the higher temperature associated with cycled solvents is the reason for creating a much greater proportion of amides to heat stable salts, or if this is simply evidence of oxidative effects in an MDEA-based solvent.

Oxidative degradation mechanisms have been postulated for the degradation of MDEA and the generation of DEA, MAE, bicine, and HES in 7 m MDEA and 7 m MDEA/2 m PZ. In each case, the pathway relies on the presence of free radicals to initiate an e^- abstraction from an α -carbon on the amine, a subsequent H^+ abstraction, and the formation of a hydroperoxide compound which will decompose to an amine/amino acid and an aldehyde. When generating the amino acid HES, it is believed that MAE will form an enamine before rearranging to form an aldehyde, which is then oxidized to HES.

7 m MDEA/2 m PZ generally did not thermally degrade over the range of 120 to 150 °C in unloaded solutions when studied using Swagelok® sample cylinders for isolation of thermal degradation. However, lean ($\alpha = 0.1$) and rich ($\alpha = 0.25$) solutions of the solvent readily degraded both components over the temperature range of 120 to 150 °C. At 135 and 150 °C, the fraction PZ remaining was essentially zero within 50 and 15 days, respectively. Thermal degradation led to the formation of PZ derivatives including MPZ, DMPZ, AEP, and NPZ. When their concentrations are compared to those of PZ loss, only ~50% of the PZ functional group can be accounted for. DMAE appeared towards the end of the experiment, rather than the beginning, indicating that it is likely not a reaction intermediate, as observed by Chakma and Meisen (1997) in MDEA thermal degradation studies.

Future Work

Cycling experiment C-34 is currently underway and entails cycling 7 m MDEA/2 m PZ from 55 to 125 °C. Instead of loading the solvent with CO₂ prior to cycling, the solvent was treated with H₂SO₄ at 0.1 mol equiv H^+ /mol equiv alkalinity to create protonated MDEA (MDEAH⁺) in solution and catalyze or initiate degradation processes in 7 m MDEA/2 m PZ in the absence of carbamates which are known to catalyze polymerization reactions. We believe that one key to understanding degradation of this solvent blend lies with understanding how the presence of MDEAH⁺ causes other degradation processes to occur. For example, does the presence of MDEAH⁺ lead to arm switching that results in MPZ and DMPZ formation, and is this a significant pathway when only cycled to 125 °C? The data from C-34 will be compared to the data from C-30 which entailed cycling the blend to 125 °C, but at an initial loading of 0.14 mols CO₂/mol alkalinity.

At the beginning of the second quarter 2011, we completed two low gas experiments (C-8 and C-9) which entailed oxidatively degrading 7 m MDEA and 7 m MDEA/2 m PZ, respectively, at 70 °C. These two experiments are repeats of previous experiments conducted at 55 °C, and will

isolate oxidation only type mechanisms in these solvents. A full reporting of those experimental results will be made in the next quarterly report.

Finally, in the second quarter, we will initiate additional amino acid synthesis efforts to identify amino acids of MEA and PZ. The results of that work will be reported in detail in the next quarterly report.

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Oxidation and Analysis of a Field Sample of 9 molal Monoethanolamine

Quarterly Report for January 1 – March 31, 2011

by Alexander K. Voice

Supported by the Luminant Carbon Management Program

Department of Chemical Engineering

The University of Texas at Austin

April 30, 2011

Abstract

Analysis and oxidation of a field sample of 9 m monoethanolamine was carried out using 98 kPa O₂/ 2 kPa CO₂ at 55 °C for 17 days. The results were analyzed by anion chromatography, cation chromatography, total alkalinity titration, total nitrogen, total organic carbon, total inorganic carbon, HPLC with electrochemical detection, HPLC with UV and ELSD detection, GC-MS, and high resolution mass spectrometry.

The initial MEA loss rate was 18.4 mmol/kg/hr (for the first 24 hours). After that, the rate decreased substantially. The average rate was 7.4 mmol/kg/hr over the entire experiment (~400 hours).

The nitrogen mass balance was closed by 80–101% for the final samples (after >5 days of oxidation). 1-(2-hydroxyethyl)-imidazole was the largest degradation product. Amides and volatile ammonia accounted for most of the remaining nitrogen-containing products. Several novel products have also been suggested based on masses observed using high-resolution mass spectrometry.

HEI was synthesized from equimolar quantities of glyoxal, formaldehyde, and ammonia added to loaded, aqueous, MEA solution. The yield was close to 100% with excess glyoxal or formaldehyde, but only 80% with excess ammonia. HEI is somewhat thermally stable and is not produced during thermal degradation (high temperature, oxygen-free environment).

Some novel degradation products have been proposed based on formulas observed on high-resolution mass spectrometry. Many products (both old and new) were detected on GC-MS and LC-MS.

Qualitatively, the lab-scale oxidation experiment was observed to result in significantly more oxidation than occurs in a real system.

Previous Work

Several previous studies have been conducted on oxidation of MEA for carbon capture. Previous work reports data for oxidation rates of MEA at practical conditions, as well as identifying and quantifying products formed.

Oxidation Rates of MEA

Kindrick (1950) conducted oxidation of 2.5 M MEA at 80 °C with 50% oxygen and 50% CO₂. A metal coil placed in the reactor was used to generate metal catalyst for the oxidation reaction. After 100 hours of oxidation, the average rate of oxidation was determined to be 11.3 mM/hr (by analyzing the initial and final samples). Ammonia was the only product identified, although analysis of the solution showed that other non-alkaline nitrogen products were present.

Sexton (2008) conducted oxidation of 7 m MEA (~4M) at 55 °C with 98% O₂ and 2% CO₂ at 1 atm in the presence of 1 mM Fe²⁺. Over the course of 445 hours of oxidation, the oxidation rate fell from 11.6 mM/hr (between 0 and 144 hours) to 0.6 (between 213 and 445 hours). The average oxidation rate was 4.5 mM/hr over 445 hours.

Goff (2005) and Chi (2001) conducted oxidation of 7 m MEA at 55 °C with 98 kPa air and 2 kPa CO₂ in the presence of 0.1–1.0 mM Fe. The oxidation rate of MEA was not determined, but the ammonia production rate was 1–2 mM/hr at steady state.

LePaumier (2009) conducted oxidation of 4 mol/kg MEA at 140 °C with 2MPa air for 14 days. The average rate of oxidation was 2.3 mmol/kg/hr. This experiment was flawed because no metal catalyst was added to the reactor and because the batch was sealed (rather than flow through), allowing the oxygen partial pressure to decrease with time. This experiment also does not represent a real process in that the amine does not see oxygen high oxygen concentrations at 140 °C.

Since all of these experiments used various methods of introducing the oxygen into the system, there is the potential for the rate of the reaction to be controlled by the flux of oxygen into the solution. This is undoubtedly the case in LePaumier's work, where the high temperature significantly increases the rate of reaction in the bulk liquid, and the production of volatile products would have reduced the oxygen partial pressure.

Oxidation Products of MEA

Many products of MEA oxidation have been identified in previous works.

Strazisar (1999) determined that piperazinones as well as several other high molecular weight products were major degradation products found in a degraded MEA solution.

Rooney (1998) demonstrated that organic acids (including glycolate, acetate, formate, and oxalate) are produced during oxidation of MEA.

Koike (1988) first showed that hydroxyethyl formamide, the MEA amide of formate, was a major degradation product, and could be detected by treating degraded samples with hydroxide.

Sexton (2008) identified the mono- and di-amides of oxalate using the hydroxide treatment method. Nitrate and nitrite were also detected in degraded solutions. Hydroxyethyl formamide (HEF) and (previously unidentified) hydroxyethyl imidazole (HEI) accounted for 57% of degraded nitrogen from MEA; ammonia production from the solution was not monitored but likely accounted for much of the remainder (Figure 1).

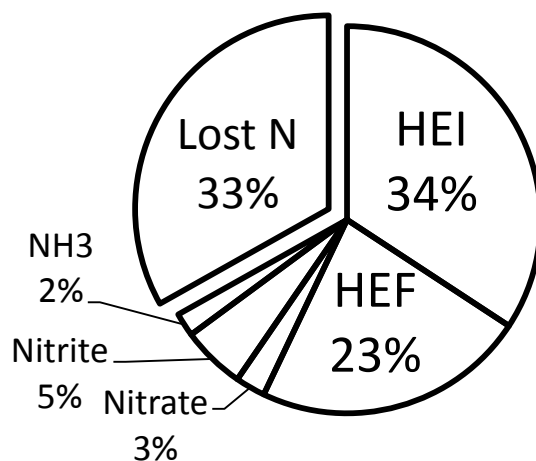


Figure 1: Nitrogen material balance for oxidation of 7 m MEA. Conditions: 55 °C, 98 kPa O₂, 2 kPa CO₂ (Sexton, 2008).

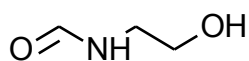
A summary of known oxidation products of MEA is shown below in Table 1

Table 1: Summary of known and suspected products of MEA oxidation

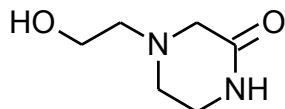
Known Fragmentation Products

Formate, oxalate, nitrate, nitrite, ammonia

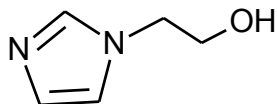
Likely Condensation Products



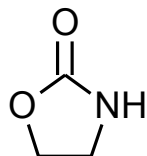
N-(2-hydroxyethyl)-formamide (HEF)



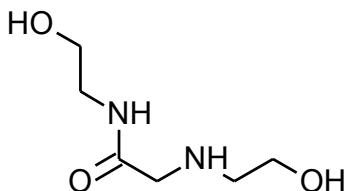
1-(2-hydroxyethyl)-4-piperazinone (HEPO)



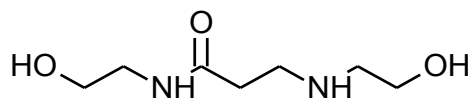
1-(2-hydroxyethyl)-imidazole (HEI)



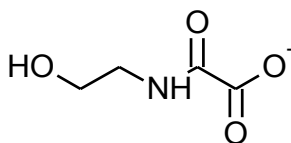
2-oxazolidinone



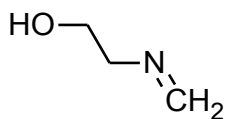
N-[(2-hydroxyethyl)-2-hydroxyethyl-amino]acetamide (HEHEAA)



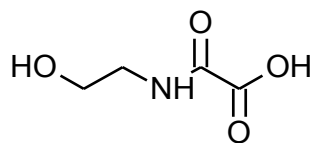
N-(2-hydroxyethyl)-3-[(2-hydroxyethyl)amino]propanamide (HEHEAP)



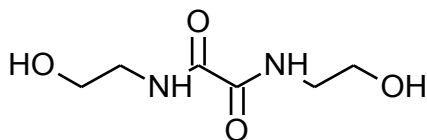
N-(2-Hydroxyethyl) oxalamide



2-(methylideneamino)ethanol



[(2-hydroxyethyl)amino](oxo)acetic acid



N,N'-di(2-hydroxyethyl)-oxal-diamide (diHEO)

Experimental Method

The oxidation experiment was conducted in the low gas flow apparatus, which has been described in previous literature (Sexton, 2008). The apparatus uses a jacketed glass reactor heated with recirculating water and outfitted with an agitator. Oxidation occurs by vigorously agitating the solution while maintaining a blanket of 98 kPa oxygen and 2 kPa CO₂. Oxygen

diffuses from the gas into the vortexing liquid. The gas enters a saturator before entering the reactor; water is added directly to the reactor daily to maintain the water balance using a level indicator. The experiment was carried out at 55 °C.

Analytical Methods

Samples were analyzed by numerous analytical methods: anion chromatography (for formate, oxalate, oxamate, nitrate, and nitrite), cation chromatography (for MEA and ammonia), GC-MS (assorted products), HPLC-ECD, HPLC-UV-ELSD, GC-MS, High resolution MS, titration (for total alkalinity), total nitrogen, total organic carbon, and total inorganic carbon. With the exception of the HPLC-UV-ELSD method, the details of these methods have been described in previous reports.

A new method for analysis of 1-(2-hydroxyethylimidazole) in degraded MEA solutions has been developed. The method uses a hydrophilic liquid-phase interaction (HILIC) elution scheme on a Phenomenex Luna 3 µm silica column with UV detection. A plot of the eluent ramp is shown in Figure 2.

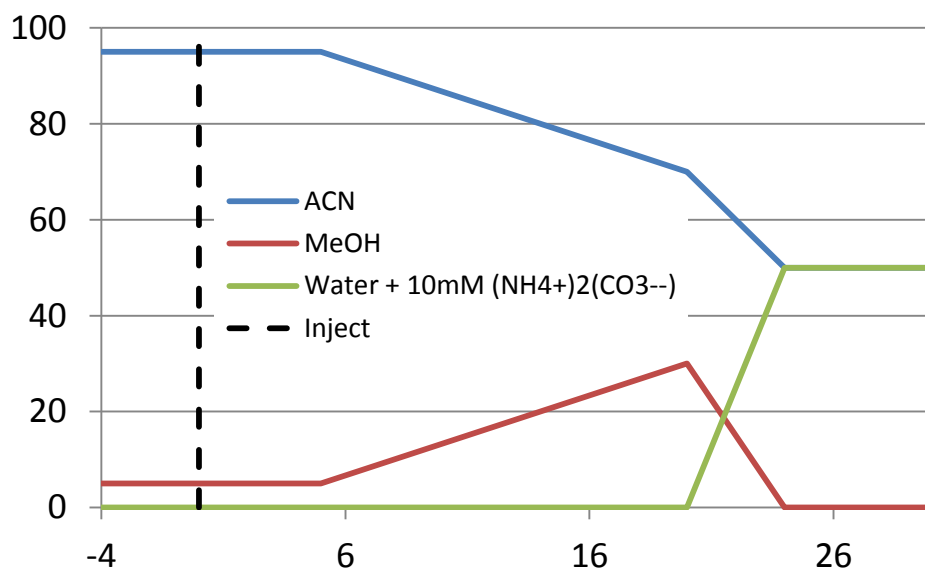


Figure 2: Eluent ramp for HILIC HPLC method for analysis of HEI in degraded MEA samples

The limit of quantification (LOQ) for this method was found to be 0.03 µg/g. The response was linear over four orders of magnitude (Figure 3). Thus quantification using this method is theoretically possible over six orders of magnitude (from 0.03 µg/g to 3000 µg/g).

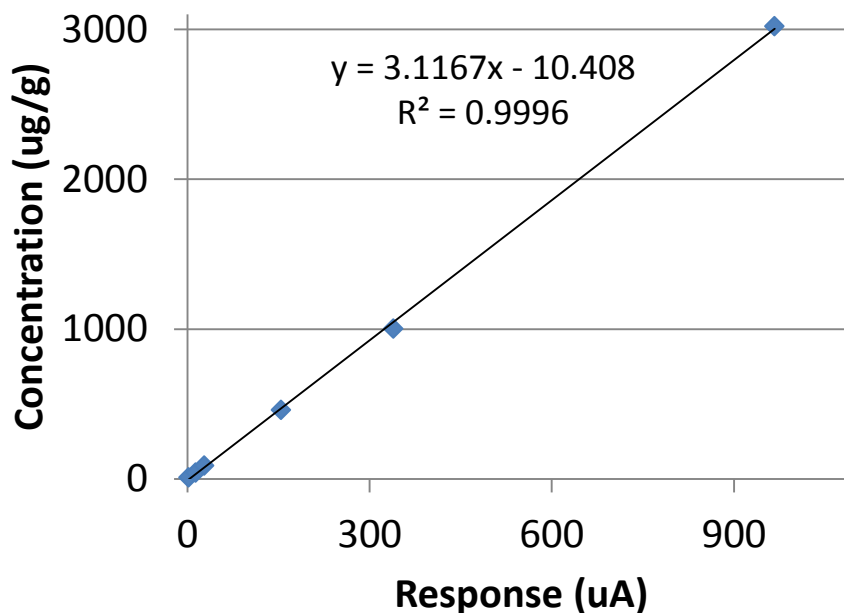


Figure 3: Calibration curve for HEI using the UV response from 8–3000µg/g

HEI was by far the most abundant UV absorber observed in degraded MEA. HEI is well-separated from other degradation products using this method (Figure 4). HEI was also the only major product observed on the ELSD using this method. The large increase in the baseline of the ELSD is caused by the introduction of water into the eluent mixture. Similarly, the water causes a drop in the UV baseline.

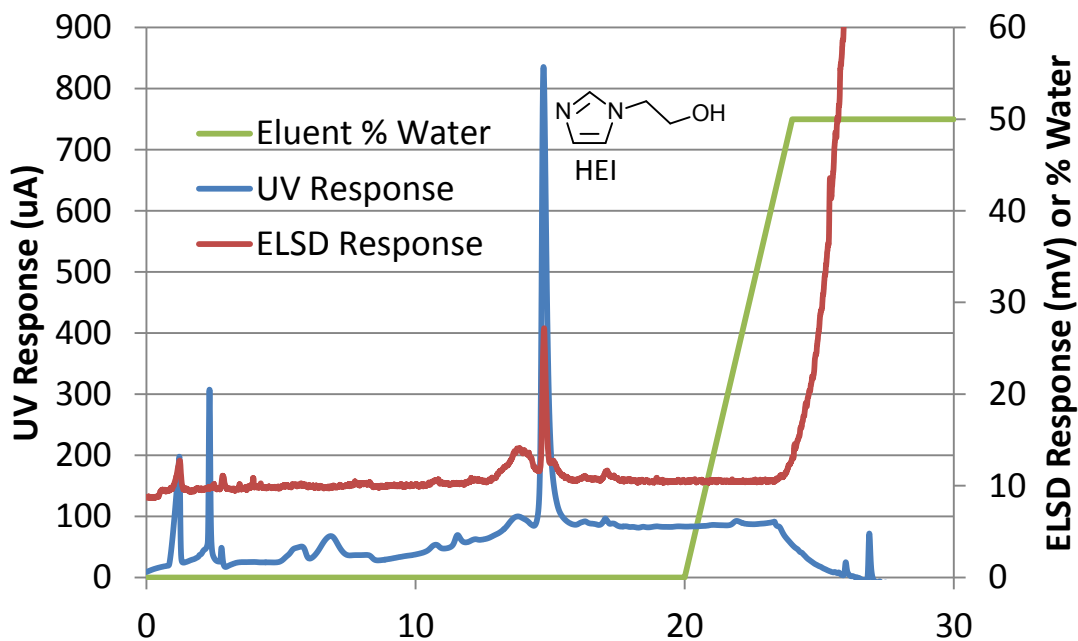


Figure 4: Chromatogram of the final sample of 9 m pilot plant MEA oxidized in the low gas flow reactor (55 °C, 98 kPa O₂, 2 kPa CO₂). 100x dilution in water.

Results

Experiments Summary

Several other oxidation experiments on MEA solutions have been selected for comparison with this work. These are summarized in Table 2. All of these experiments were carried out in the low gas flow (LGF) reactor at 55 °C with 98 kPa O₂ and 2 kPa CO₂. The metals concentration is reported, along with the MEA concentration at the start of the experiment and a regressed initial first order rate constant, k_1 . The k_1 value was determined by regressing the amine concentration as a function of time using following empirical expression, where C_0 is the initial concentration and k_1 is the only adjustable parameter (Table 2).

$$C(t) = C_0 / (1 + k_1 * t)$$

Table 2: Summary of selected LGF experiments on MEA solutions. Conditions (unless otherwise noted): 55 °C, 98 kPa O₂/2 kPa CO₂, agitation 1440 RPM. Fe (II), Cr (III), Ni (II) added as sulfate metal salts in dilute aqueous solution.

Solution	Catalyst (Fe/Cr/Ni) mM	C ₀ (experimental)	k ₁ (regressed) (day ⁻¹)	Source
7 m MEA (neat)	0.40 / 0.10 / 0.05	4.65	4.19e-2	Voice, 2010
7 m MEA (cycled)*	12.0 / 4.1 / 2.3	3.43	9.16e-2	Voice, 2010
7 m MEA (cycled + 100 mM Inh. A)	5.4 / 1.5 / 1.0	--	--	Voice, 2010
9 m MEA (field)	0.45 / 0.00 / 0.02	5.24	8.74e-2	This work

*135 °C for 2 weeks, 0.4 loading

HPLC-UV/ELSD

A reverse-phase HILIC method was used to elute separate degradation products in the degraded MEA solution. The major product observed on UV or ELSD was 1-(2-hydroxyethyl)-imidazole (HEI). This product was quantified using the UV response, which was found to be linear over four orders of magnitude of concentration.

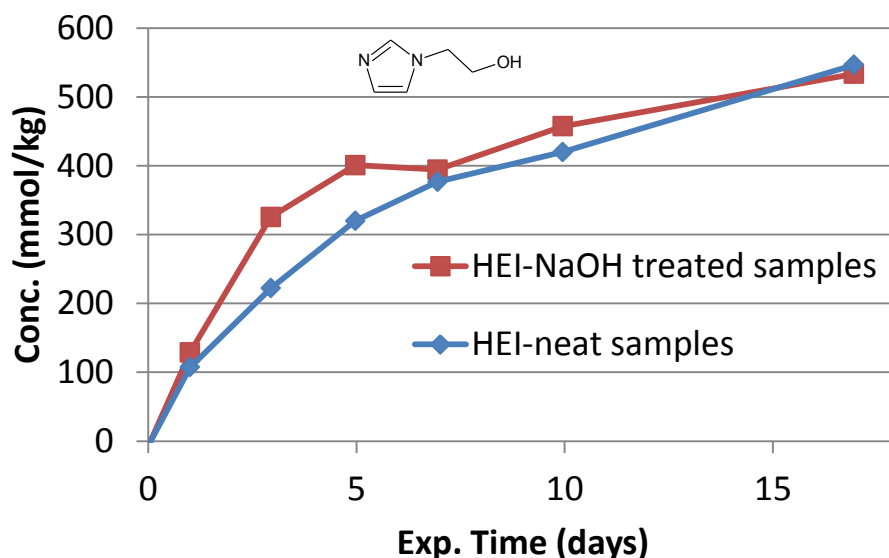


Figure 5: HEI production during oxidation of 9 m pilot plant MEA, analysis for neat and NaOH-treated samples. Conditions: 55 °C, 98 kPa O₂, 2 kPa CO₂.

HEI concentration was also determined for previous experiments, in which the sample was cycled once between an oxidative and high temperature environment. A summary of these experiments is shown below (Table 3).

Table 3: Summary of cycling experiments analyzed for HEI production

Solution	First step	Second step
7 m MEA (BASE)	Oxidation (55 °C, 98 kPa O ₂ , 2 kPa CO ₂), 2 weeks, metals: 0.40 mM Fe, 0.10 mM Cr, 0.05 mM Ni	--
7 m MEA (RSC)	Oxidation (55 °C, 98 kPa O ₂ , 2 kPa CO ₂), 2 days, metals: 0.40 mM Fe, 0.10 mM Cr, 0.05 mM Ni	Thermal degradation (135 °C, 42 days)
7 m MEA (SC4)	Thermal degradation (135 °C, 0.4 ldg, 2 weeks)	Oxidation (55 °C, 98 kPa O ₂ , 2 kPa CO ₂), 2 weeks, metals: 12.0 mM Fe, 4.1 Cr, 2.3 mM Ni
9 m MEA (pilot plant) (PP9)	Oxidation (55 °C, 98 kPa O ₂ , 2 kPa CO ₂), 2 weeks, metals: 0.45 mM Fe, 0.00 mM Cr, 0.02 mM Ni	

The production of HEI during the experiments BASE, PP9, and SC4 is shown in Figure 6. Very little HEI was produced during thermal degradation for SC4. The rate of HEI production was

much higher in PP9 (which used a 9 m MEA solution from a pilot plant) than in BASE, which used a neat, 7 m MEA solution. Easily oxidizable compounds in the pilot plant sample could be oxidized rapidly to glyoxal, formaldehyde, and ammonia. These would in turn react with MEA to produce HEI (as discussed in detail later).

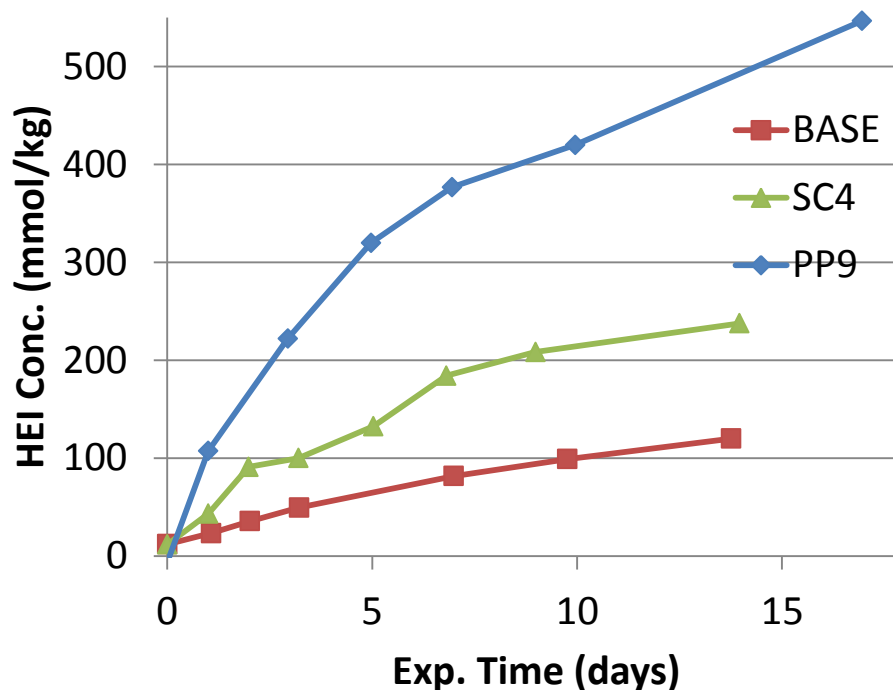


Figure 6: HEI production during oxidation of various aqueous MEA solutions. Conditions: 55 °C, 98 kPa O₂, 2 kPa CO₂. BASE (red) = neat 7 m MEA; SC4 (green) = thermally degraded MEA at 135 °C for 2 weeks; PP9 (blue) = 9 m pilot plant MEA.

The results from RSC show that when the oxidized sample is placed in the oven, products in the solution (e.g. imines, amines, and aldehydes) react to form a significant amount of HEI. The HEI is moderately thermally stable but is shown to degrade slowly over time. The constant rate of HEI loss at 135 °C was 1.49 mmol/kg/day.

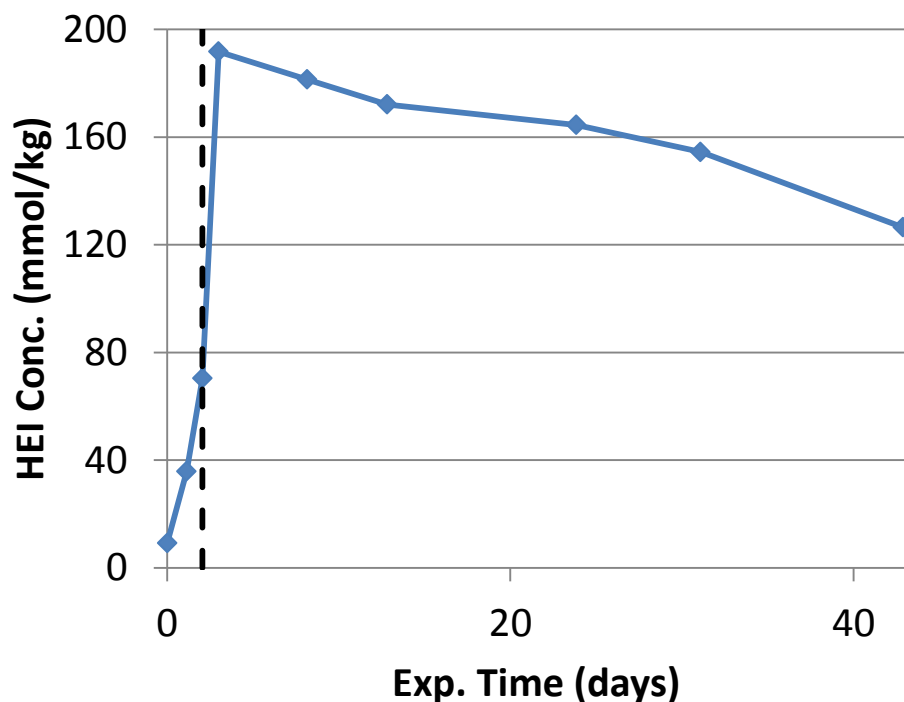


Figure 7: Oxidation followed by thermal degradation showing stability of HEI.
Conditions: Oxidation – 98 kPa O₂, 2 kPa CO₂, 55 °C; Thermal degradation – 135 °C.
Dotted line indicates when the solution was transferred to the oven.

HEI is likely produced by reaction of MEA, glyoxal, formaldehyde, and ammonia as shown below (Figure 8). This pathway was proposed by Noriyuki (2005).

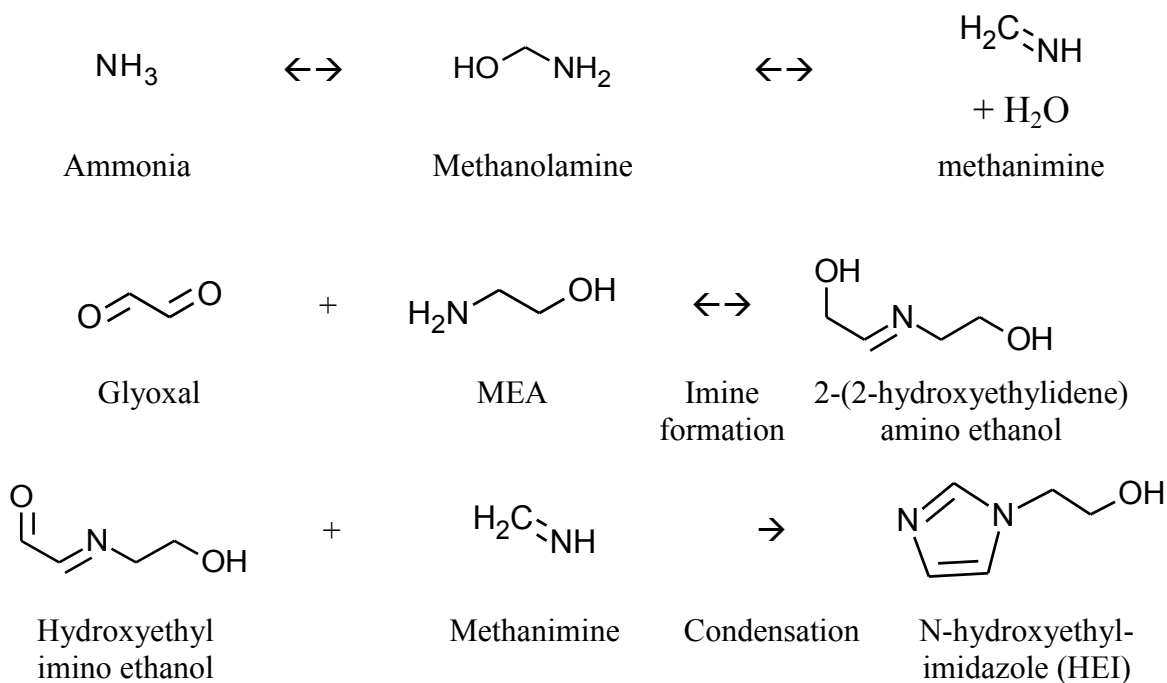


Figure 8: Pathway for production of HEI from condensation of oxidative fragmentation

products

This possible reaction scheme was tested by mixing various concentrations of glyoxal, ammonia, and formaldehyde with excess loaded, aqueous 7 m MEA. The solution was heated to 55°C and stirred for 24 hours, before analyzing for HEI production (Table 4).

Table 4: Synthesis of HEI by mixing loaded, aqueous 7 m MEA with various amounts of glyoxal, formaldehyde, and ammonium carbonate. Values are in mmol/kg, limiting reagent shown in bold, 2x excess reagent shown in italics.

Mix	MEA	Glyoxal	Formaldehyde	$(\text{NH}_4^+)_2(\text{CO}_3^{2-})$	HEI
1	3.803	<i>0.741</i>	0.386	0.178	0.349
2	3.886	0.390	<i>0.790</i>	0.194	0.393
3	3.940	0.383	0.403	<i>0.401</i>	0.326

The percent yield relative to each component is shown in Figure 9. This demonstrates that all four components are required for the reaction to take place. The highest conversion of the other components was achieved when formaldehyde was in excess relative to ammonia and glyoxal.

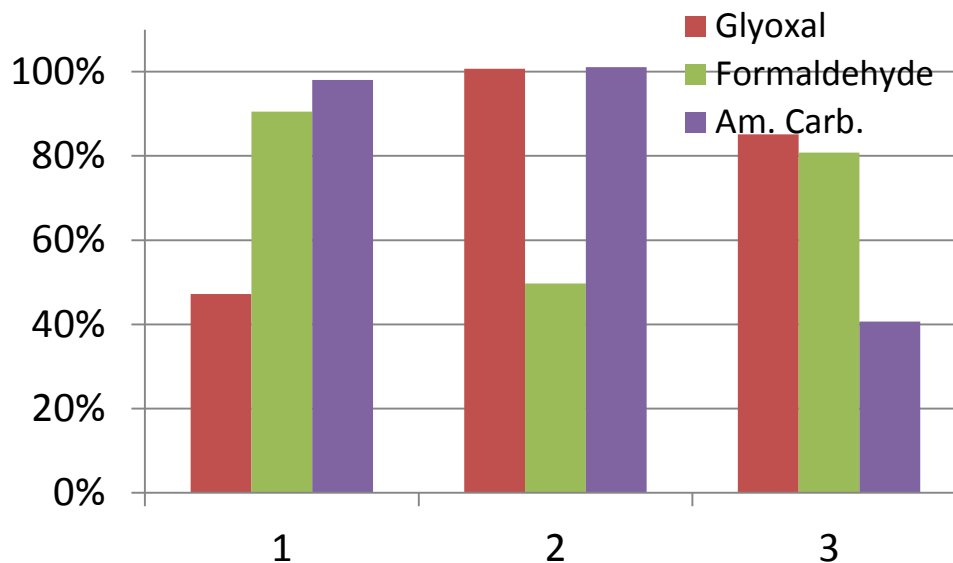


Figure 9: HEI yield for three mixtures of glyoxal, formaldehyde, and ammonium carbonate in various proportions in aqueous 7 m MEA loaded to 0.4 loading. The yield is shown relative to glyoxal, formaldehyde, or ammonia in each mixture.

Additional samples were taken after two days and seven days. The results of the time series are shown below in Figure 10. The yield is given relative to the limiting reagent: for the case where glyoxal and formaldehyde were in excess (blue and red curves), ammonia was the limiting reagent. For the case where ammonia was used in excess, glyoxal was the limiting reagent.

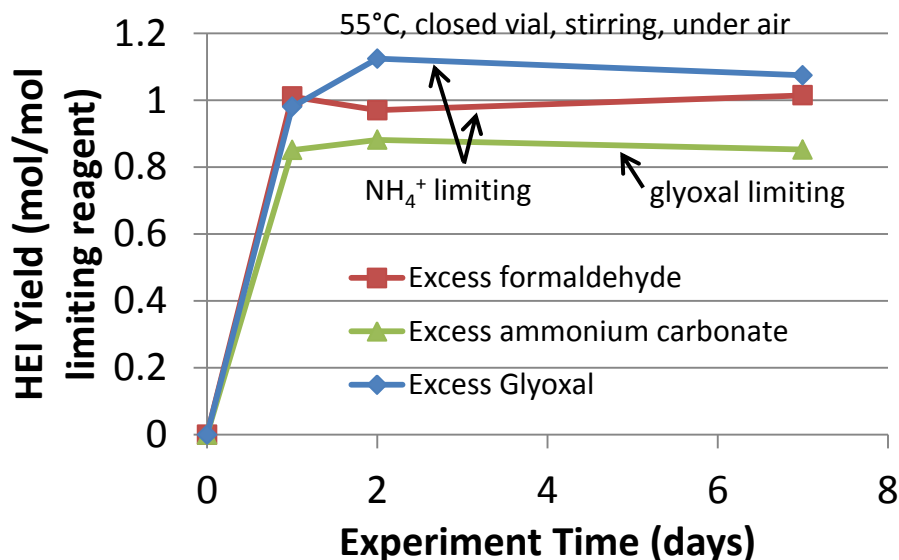


Figure 10: Time-series of HEI synthesis from glyoxal, formaldehyde, CO₂ loaded MEA, and ammonium carbonate.

In the case where glyoxal is in excess, the yield exceeds 100%. This may be because glyoxal is an oxidizing compound, and generates additional NH₃ and formaldehyde by reacting with MEA. These then go on to react with glyoxal to form HEI. In all three cases, the yield did not change significantly after two days or seven days. When glyoxal was in excess, the solution turned deep red after one day. The excess formaldehyde solution was somewhat red after one day and gradually became the same color as the glyoxal solution. The ammonium carbonate solution turned pale yellow, but did not turn red even after seven days.

HPLC-Electrochemical Detection

Samples were analyzed on HPLC using electrochemical detection with an anion exchange column for separating amino acids. A mixture of sodium acetate and sodium hydroxide are used to set the pH of the eluent. As the acidity of the eluent increases, amino acids retained on the column as anions are converted into zwitterions, which no longer stick to the column.

Hydroxyethyl glycine (Figure 11) and another amino acid (Figure 12) were observed in this experiment. Since a standard was not available, the response was calibrated using a glycine standard. Neither of these products represents a significant part of the material balance.

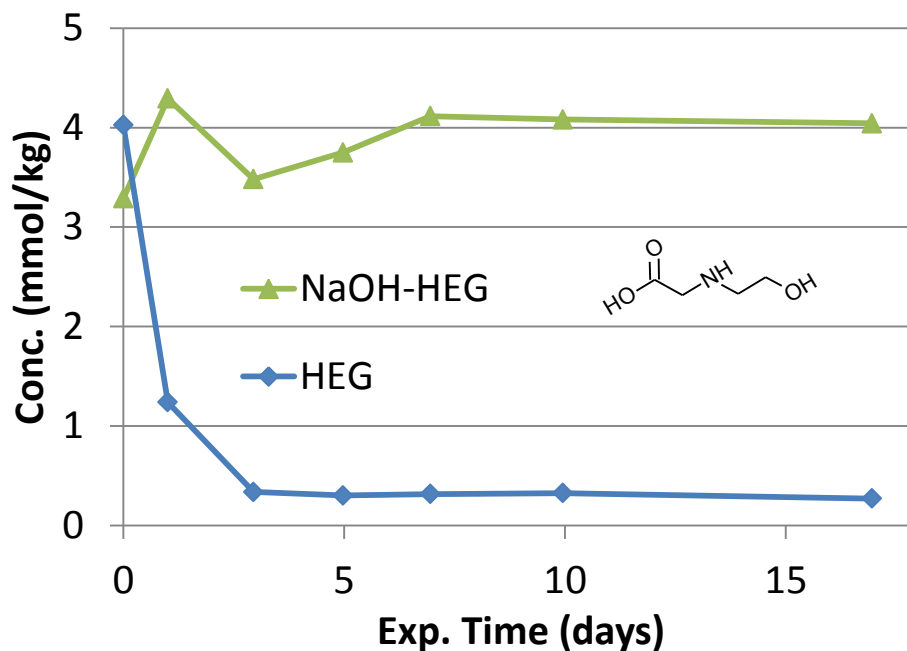


Figure 11: Hydroxyethyl glycine present in neat and NaOH treated samples during oxidation of 9 m pilot plant MEA. Conditions: 55 °C, 98 kPa O₂, 2 kPa CO₂.

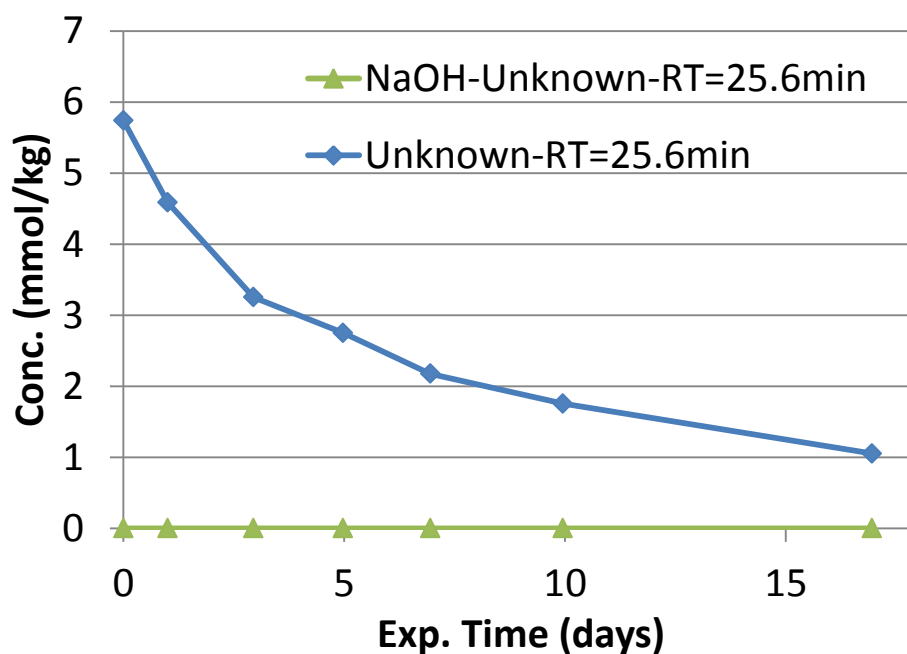


Figure 12: Unknown amino acid (RT = 25.6) present in neat and NaOH treated samples during oxidation of 9 m pilot plant MEA. Conditions: 55 °C, 98 kPa O₂, 2 kPa CO₂.

Anion Chromatography

Samples were analyzed by anion chromatography for concentrations of formate, oxalate, hydroxyethyl oxamate, nitrate, and nitrite. Glycolate and acetate did not appear in significant concentrations relative to other anionic species (Figure 13).

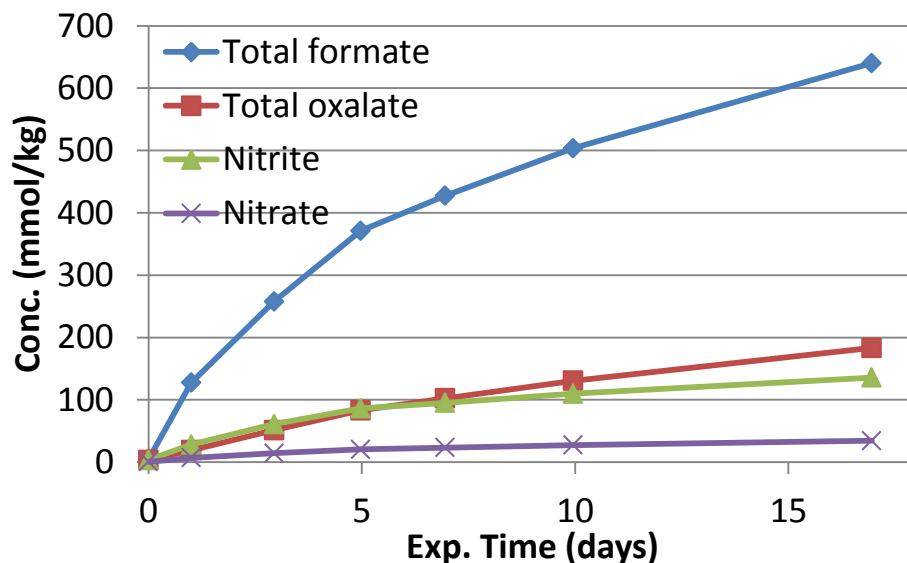


Figure 13: Anions production from 9 m pilot plant MEA in an oxidative environment. Conditions: 55 °C, 98 kPa O₂, 2 kPa CO₂, 1400 RPM agitation.

The results of formate, oxalate, nitrate, and nitrite production for four experiments are compared in Figures 14–17.

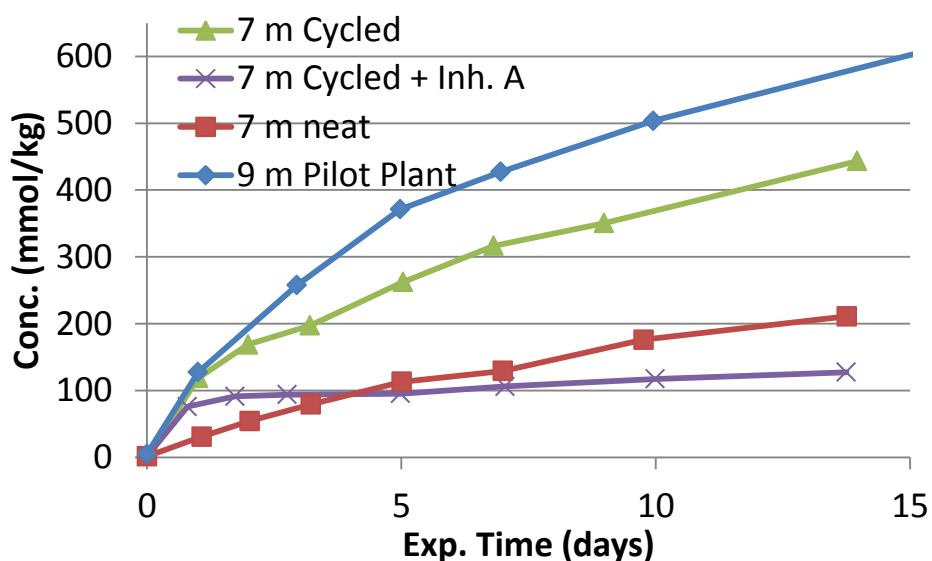


Figure 14: Total formate production in oxidized MEA solutions. Conditions: 55 °C, 98 kPa O₂, 2 kPa CO₂, 1400 RPM agitation.

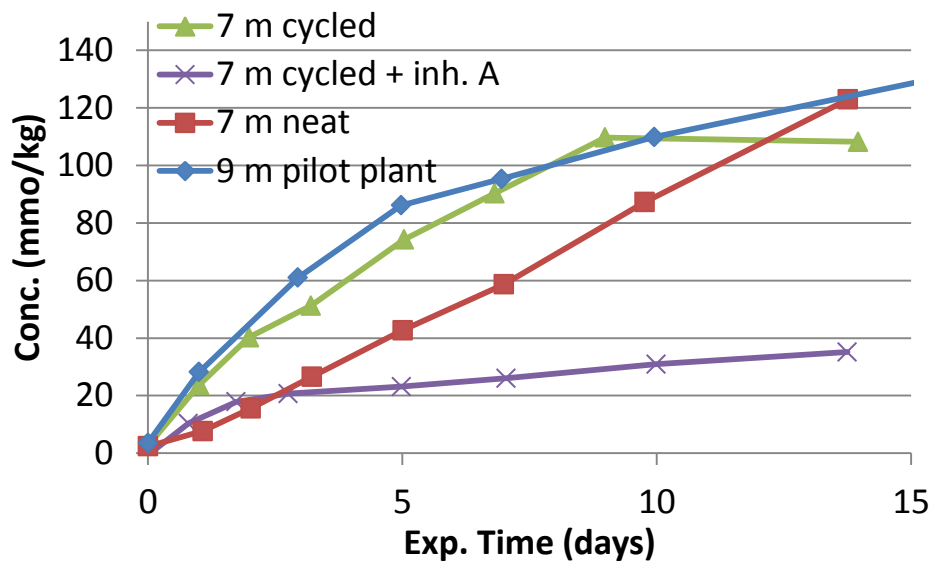


Figure 15: Total oxalate production in oxidized MEA solutions. Conditions: 55 °C, 98 kPa O₂, 2 kPa CO₂, 1400 RPM agitation.

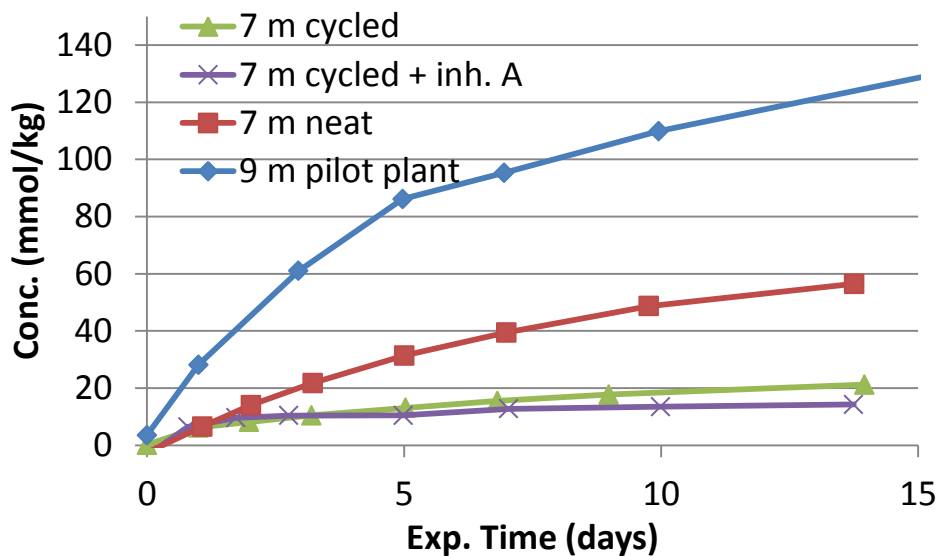


Figure 16: Nitrite production in oxidized MEA solutions. Conditions: 55 °C, 98 kPa O₂, 2 kPa CO₂, 1400 RPM agitation.

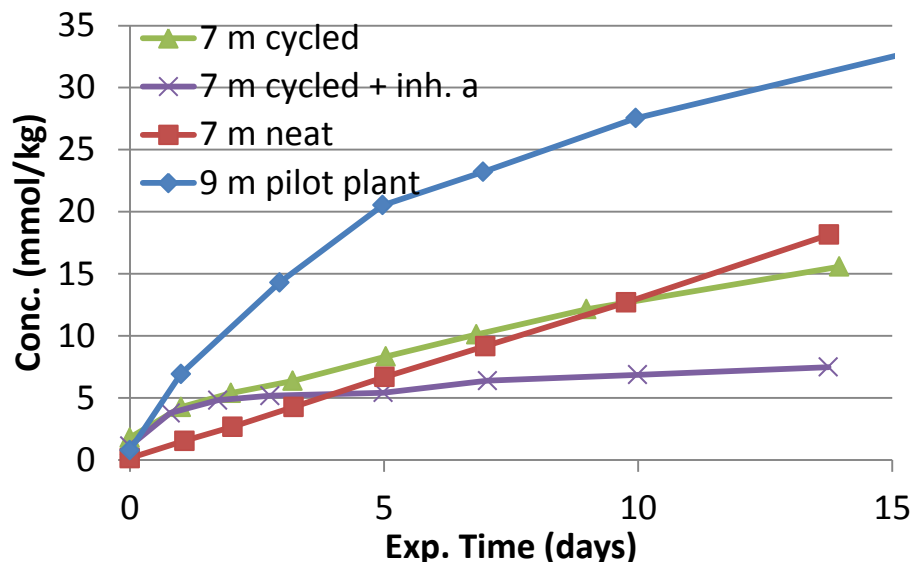


Figure 17: Nitrate production in oxidized MEA solutions. Conditions: 55 °C, 98 kPa O₂, 2 kPa CO₂, 1400 RPM agitation.

Cation Chromatography

Samples were analyzed with cation chromatography to determine the concentrations of MEA and ammonia during the experiment. For the 9 m MEA pilot plant sample, the MEA concentration decreased significantly over the course of the experiment. The initial MEA loss rate was 18.4 mmol/kg/hr (for the first day). After that, the rate decreased substantially. The average rate was 7.4 mmol/kg/hr over the entire experiment. The result is compared with a previous experiment, oxidation of neat 7 m MEA at the same conditions (Figure 18).

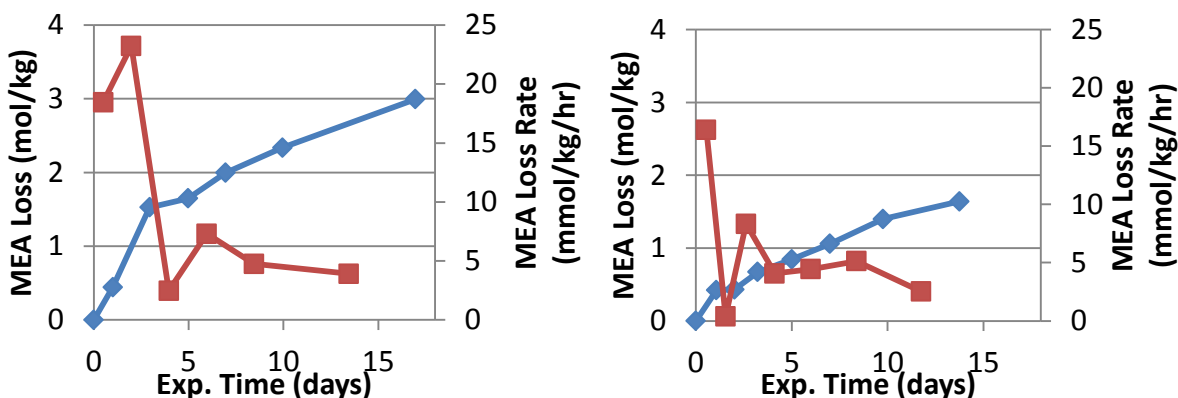


Figure 18: MEA loss and MEA loss rate during oxidation of 9 m pilot plant MEA (left) and neat 7 m MEA with 0.4 mM Fe, 0.1 mM Cr, and 0.05 mM Ni (right). Conditions: 55 °C, 98 kPa O₂, 2 kPa CO₂, 1400 RPM agitation.

Results from this experiment are compared with two other experiments by accounting for first order concentration effects (Figure 19). A simple model is used to do this, where the ratio of MEA loss to MEA concentration is equal to a constant rate (Equation 1).

$$\text{MEA Loss (mol/kg)} / \text{MEA Conc. (mol/kg)} = a \cdot t \quad (1)$$

Figure 19: MEA loss and model fit for three oxidation experiments using 7 and 9 m MEA. Conditions: 55 °C, 98 kPa O₂, 2 kPa CO₂, 1400 RPM agitation.

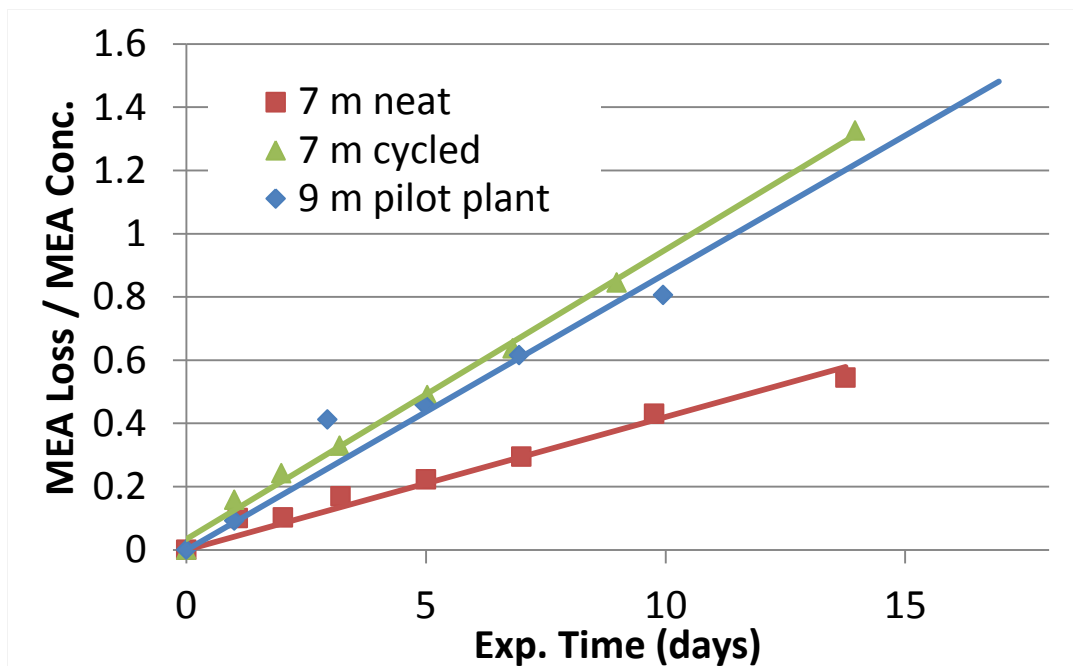


Table 5: Summary of experiments and regressed parameters. Conditions: 55 °C, 98 kPa O₂, 2 kPa CO₂, 1400 RPM agitation.

MEA Conc.	Treatment	Catalyst (Fe/Cr/Ni) mM	C ₀ (experimental)	k ₁ (day ⁻¹)
7 m	Neat	0.40 / 0.10 / 0.05	4.65	4.19e-2
7 m	135 °C, ldg.=0.4, 2 weeks	12.0 / 4.1 / 2.3	3.43	9.16e-2
9 m	Pilot plant	0.45 / 0.00 / 0.02	5.24	8.74e-2

Ammonia concentration was also determined for this experiment. The dissolved ammonia concentration reaches a maximum after two days and then begins to drop (Figure 20). Ammonia would be sufficiently volatile to leave the reactor with the exiting gas. Ammonia is also expected to react with aldehydes in the liquid phase to form imines and hemi-aminals.

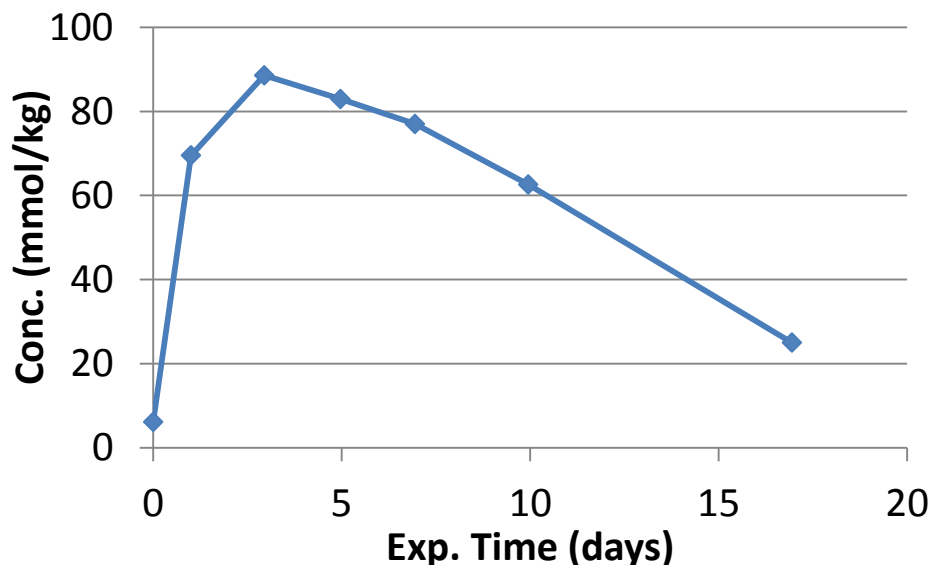


Figure 20: Dissolved ammonia production during oxidation of 9 m pilot plant MEA. Conditions: 55 °C, 98 kPa O₂, 2 kPa CO₂, 1400 RPM agitation.

Total Alkalinity, Total Nitrogen and Total Carbon Analysis

Samples were analyzed for total nitrogen and total organic carbon by a catalyzed combustion method. The instrument was calibrated using the initial sample, thus only the percent of initial N or C is reported. The organic carbon concentration did not change significantly over the course of the experiment, however the total nitrogen concentration dropped by approximately ~10% (Figure 21).

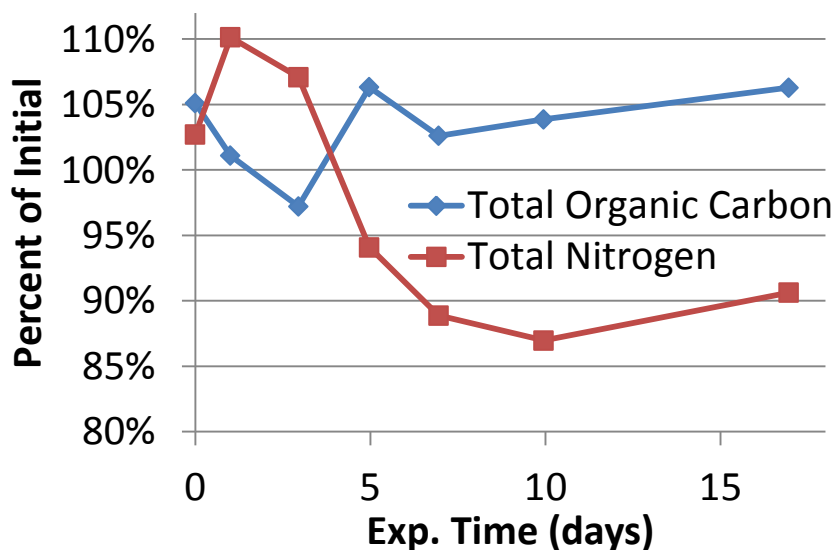


Figure 21: Total organic carbon and total nitrogen relative to the initial sample during oxidation of 9 m pilot plant MEA. Conditions: 55 °C, 98 kPa O₂, 2 kPa CO₂, 1400 RPM agitation.

Samples were also analyzed by for total alkalinity using an acid titration with sulfuric acid. The total alkalinity of the solution almost exactly matches the MEA concentration, demonstrating that there are very few if any alkaline degradation products (Figure 22).

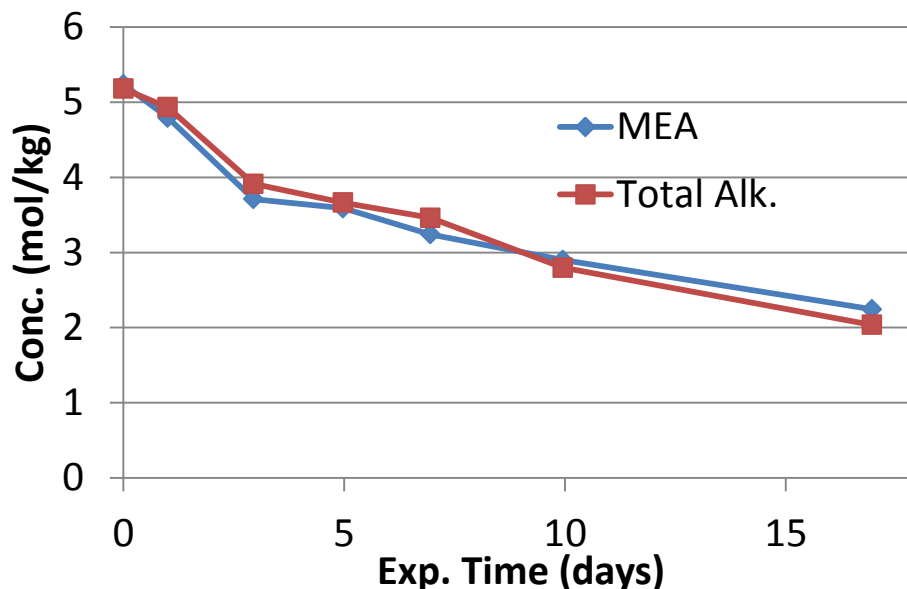


Figure 22: Comparison of total alkalinity and MEA concentration during oxidation of 9 m pilot plant MEA. Conditions: 55 °C, 98 kPa O₂, 2 kPa CO₂, 1400 RPM agitation.

The total inorganic carbon increases initially, then decreases. This is likely because the solution started at a very low loading and absorbed CO₂ during the first few days. As degradation products accumulated, the loading decreased (Figure 23)

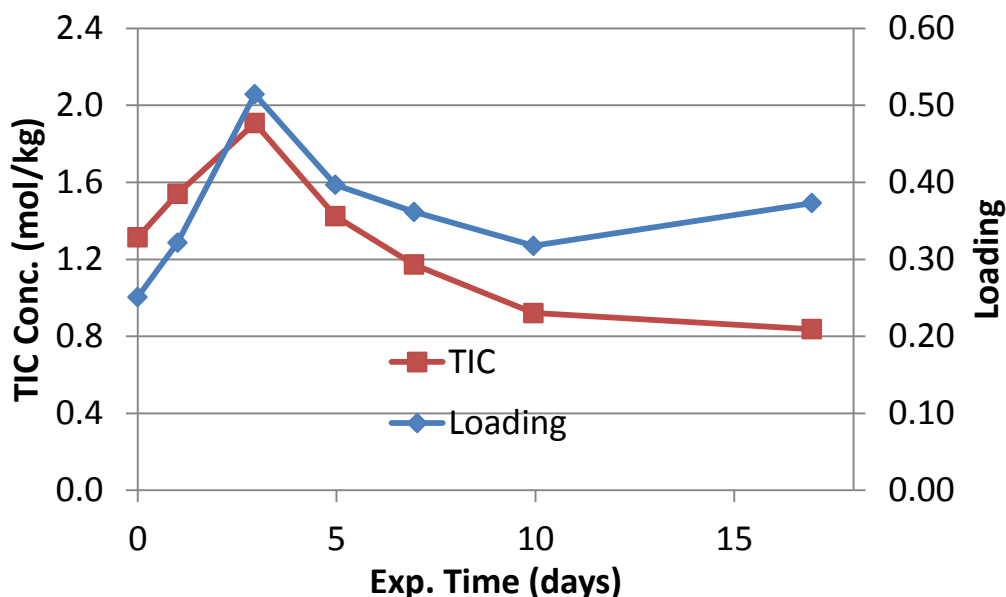


Figure 23: Total inorganic carbon concentration during oxidation of 9 m pilot plant MEA. Conditions: 55 °C, 98 kPa O₂, 2 kPa CO₂, 1400 RPM agitation.

Material Balance

The nitrogen material balance was closed to 80–101% for the middle and final samples (Figure 24, Table 6). The material balance was calculated by subtracting the sum of all nitrogen in degradation products from the amount of degraded MEA (Equation 2).

$$\frac{\sum \text{amides, HEI, volatile losses, other N species}}{MEA_i - MEA_f} \quad (2)$$

Volatile losses were calculated by loss of total nitrogen (Equation 3), where N_T is the fraction of total nitrogen detected relative to the initial sample (recall that the instrument was calibrated using the initial sample, therefore only the absolute total nitrogen loss can be calculated).

$$\text{volatile loss} = N_T * MEA_i \quad (3)$$

HEI, amides, and volatile losses (most likely volatile ammonia) accounted for most of the material balance, whereas nitrate, nitrite, dissolved ammonia, and hydroxyethyl glycine accounted less than 10% of the material balance for most samples. A summary of all raw data is provided in Appendix A.

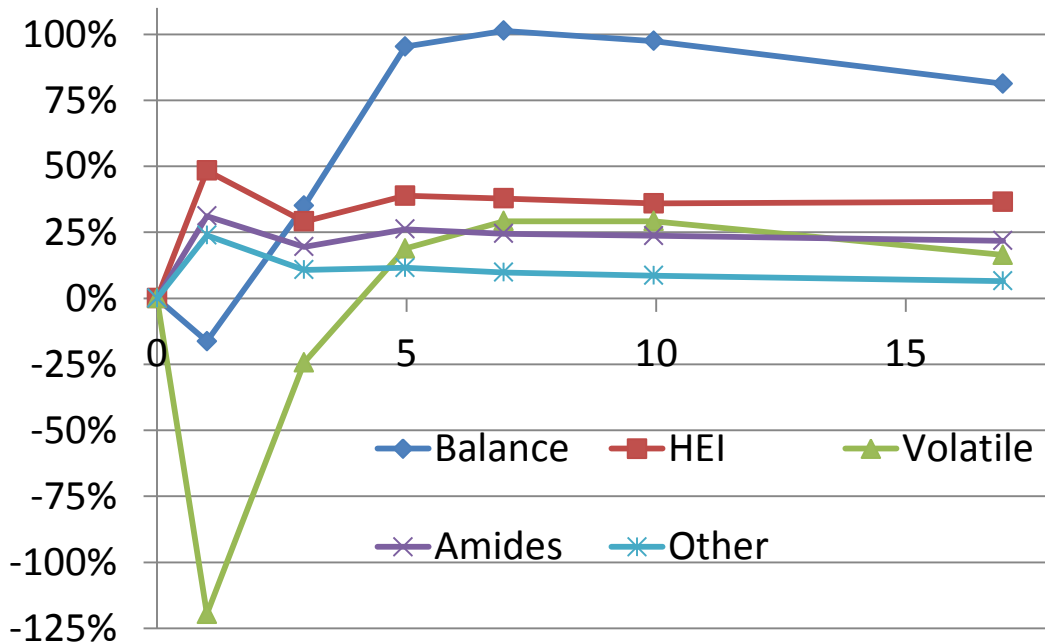


Figure 24: Nitrogen material balance during oxidation of 9 m pilot plant MEA

Table 6: Tabulated data for nitrogen material balance during oxidation of 9 m pilot plant MEA

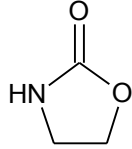
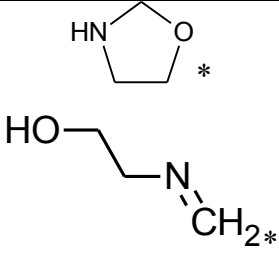
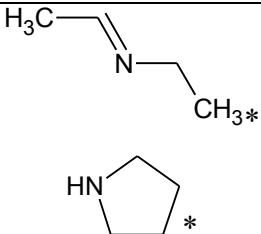
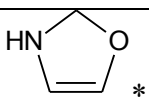
Days	Balance	HEI	Volatile	Amides	Other
0.0	--	--	--	--	--
1.0	-16%	48%	-120%	31%	24%
2.9	35%	29%	-24%	19%	11%

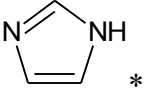
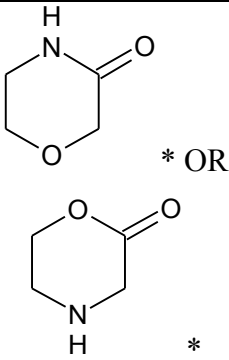
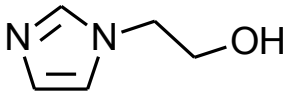
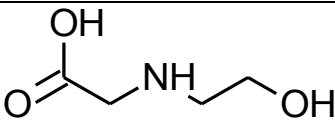
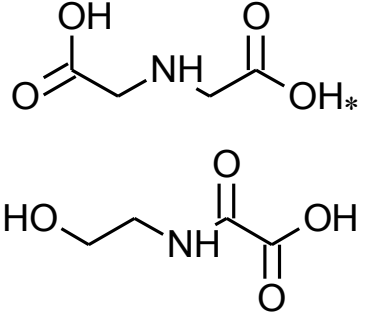
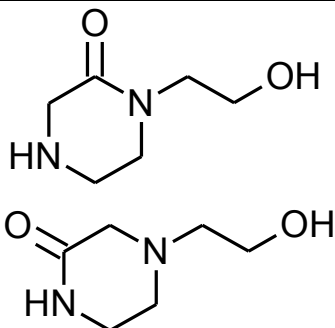
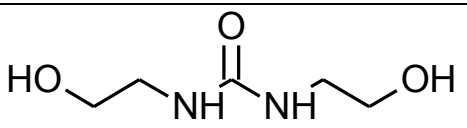
5.0	95%	39%	19%	26%	12%
6.9	101%	38%	29%	24%	10%
10.0	97%	36%	29%	24%	9%
17.0	81%	37%	16%	22%	7%

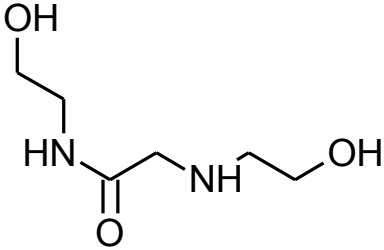
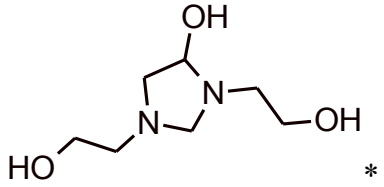
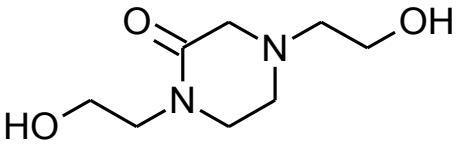
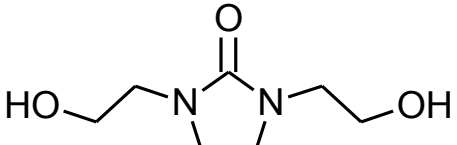
High-Resolution Mass Spectrometry Qualitative Analysis

The initial sample received from the pilot plant was analyzed by high-resolution mass spectrometry. This yielded the exact mass (which can be used to predict the molecular formula) of m+h peaks observed using direct injection. Chemical ionization was used to produce only the parent m+h masses and avoid fragmentation. In Table 7, the masses observed, along with their relative intensity on the low-resolution CI mass spectrometer, are listed. A possible structure is also given for some masses.

Table 7: Exact masses, relative abundance, and possible structures observed using high resolution chemical ionization direct injection mass spectrometry of a 9 m pilot plant sample

<u>Exact Mass</u>	<u>Molecular Formula</u>	<u>DBE</u>	<u>Relative abundance (Full scan)</u>	<u>Possible Compound(s)</u>	<u>Possible Structure</u>
88.0760	$C_4H_{10}NO^+$	0.5	49	Oxazolidone	
74.0606	$C_3H_8NO^+$	0.5	18	1,3-oxazolidine 2-methylidene-aminoethanol	
72.0813	$C_4H_{10}N^+$	0.5	6	N-ethylethanamine	
72.0449	$C_3H_6NO^+$	1.5	6	2,3-dihydro-1,3-oxazole	

69.0453	$C_3H_5N_2^+$	2.5	1	Imidazole	
102.0556	$C_4H_8NO_2^+$	1.5	18	Morpholin-3-one / Morpholin-2-one	
102.0919	$C_5H_{12}NO^+$	0.5	18		
113.0716	$C_5H_9N_2O^+$	2.5	100	1-(2-hydroxyethyl)imidazole	
120.0660	$C_4H_{10}NO_3^+$	0.5	28	Hydroxyethyl glycine	
134.0818	$C_5H_{12}NO_3^+$	0.5	37	Imino diacetic acid; 1-(2-hydroxyethyl)-oxalamide	
145.0976	$C_6H_{13}N_2O_2^+$	1.5	55	hydroxyethyl piperazinone	
149.0925	$C_5H_{13}N_2O_3^+$	0.5	16	1,3-bis-hydroxyethyl urea	

163.1082	$C_6H_{15}N_2O_3^+$	0.5	88	N-(2-hydroxyethyl)-2-[(2-hydroxyethyl)amino]acetamide	
177.1240	$C_7H_{17}N_2O_3^+$	0.5	68	1,3-bis (2-hydroxyethyl)imidazolidin-4-ol	
189.1239	$C_8H_{17}N_2O_3^+$	1.5	25	1,4-bis-hydroxyethyl-piperazin-2-one	
175.1081	$C_7H_{15}N_2O_3^+$	1.5	13	1,3-bis-hydroxyethyl-imidazolidinone	
244.1657	$C_{11}H_{22}N_3O_3^+$	2.5	15		
242.1503	$C_{11}H_{20}N_3O_3^+$	2.5	10		

*Indicates not previously reported

A pathway for production of HEI was proposed above. The pathway for imidazole would be the same, except that it would involve the reaction of two mols of ammonia with one mol of glyoxal and one mol of formaldehyde. Additional pathways for some of these products are proposed below.

In general these pathways involve the fast reaction of known fragments (principally the condensation of amines with aldehydes to form imines, which hydrolyze to hemi-aminals), followed by a slower nucleophilic substitution or oxidation reaction. All of the larger products should originally come from the reaction of fragments produced during oxidation with MEA:

- Ammonia
- Hydroxyacetaldehyde $\rightarrow$ (oxidizes) $\rightarrow$ glyoxal
- Formaldehyde

1,3-oxazolidine

MEA reacts with formaldehyde to form 2-(methylidene amino) ethanol. This product may hydrolyze to 2-[(hydroxymethyl)amino]ethanol. This compound is subject to internal attack, where the OH on the ethanol replaces the hydroxyl group to form the 5-membered ring.

2-hydroxyethyl glycine (HEG)

MEA reacts with 2-hydroxy acetaldehyde to form the imine derivative. This compound hydrolyzes to form the hemi-aminal. The imine bond flips and hydrolyzes to form 2-[(2-hydroxyethyl)amino]ethane-1,1-diol. This diol is in equilibrium with the corresponding aldehyde. The aldehyde is oxidized in place to 2-hydroxyethyl glycine.

N-(2-hydroxyethyl)-2-[(2-hydroxyethyl) amino] acetamide

The aldehyde from the last step of the HEG pathway reacts with MEA to form another imine before being oxidized. This imine hydrolyzes and is oxidized in place to the amide.

Morpholin-2-one

The carboxylic acid group in HEG is subject to internal nucleophilic attack by the hydroxyethyl group to form the six-membered ring.

Iminodiacetic acid

This compound could be produced from direct oxidation of the hydroxyl group on hydroxyethyl glycine to the corresponding carboxylic acid.

4-(2-Hydroxyethyl)-2-piperazinone OR 1-(2-hydroxyethyl)-2-piperazinone

There are two possible pathways to this product. One involves the reaction of glyoxal with 1-(2-hydroxyethyl) ethylenediamine, as described by Treybig (1989). The second involves the cyclization of N-(2-hydroxyethyl)-2-[(2-hydroxyethyl) amino] acetamide (which in turn is generated from HEG, as described above) by internal attack of one of the nitrogens on the alpha carbon to the hydroxyl group, forming the six-membered ring.

1,3-bis (2-hydroxyethyl)-4-imidazolidinol

This compound is two MEA molecules attached to a formaldehyde and a 2-hydroxyacetaldehyde in a five-membered ring. The formation of this compound would occur by the same types of reactions described above (reaction of MEA + aldehyde to form imines and hemi-aminals; cyclization by internal nucleophilic attack where hydroxyl is the leaving group).

1,3-bis-(2-hydroxyethyl) urea AND 1,3-bis-(2-hydroxyethyl) imidazolidinone

These thermal degradation products are likely formed from reaction of MEA with CO₂ at high temperature via nucleophilic substitution reactions.

LC-MS Qualitative Analysis

The 9 m pilot plant sample was analyzed for degradation products using two methods (Table 8). Both the standard reverse-phase method and the HILIC method used a 10 mM ammonium carbonate buffer, methanol, and acetonitrile. The undiluted sample was injected at time zero. For the final sample (after 17 days of oxidation) a 20x dilution in water was used.

Table 8: Eluent ramp for two LCMS methods used for analysis of degradation products in 9 m MEA

<u><i>Reverse-phase Method</i></u>				<u><i>HILIC Method</i></u>			
Time	10 mM NH ₄ ⁺	MeOH	MeCN	Time	10 mM NH ₄ ⁺	MeOH	MeCN
-4.00	100	0	0	-4.00	0	5	95

3.00	100	0	0	5.00	0	5	95
10.00	95	5	0	20.00	0	70	30
20.00	50	50	0	24.00	50	0	50
30.00	30	50	20	30.00	50	0	50

Figures 25–28 show the chromatograms from this analysis. Four chromatograms are shown, the first two show the total ion current response with m+h peak assignments for the 9 m MEA pilot plant sample as received, using the two different chromatography methods. The second two show the same thing, but for the final sample after 17 days of oxidation. These post-oxidation samples were also diluted 20x in water due to the higher concentration of products present. For the HILIC method, HEI is the main peak observed on LCMS (Figure 26).

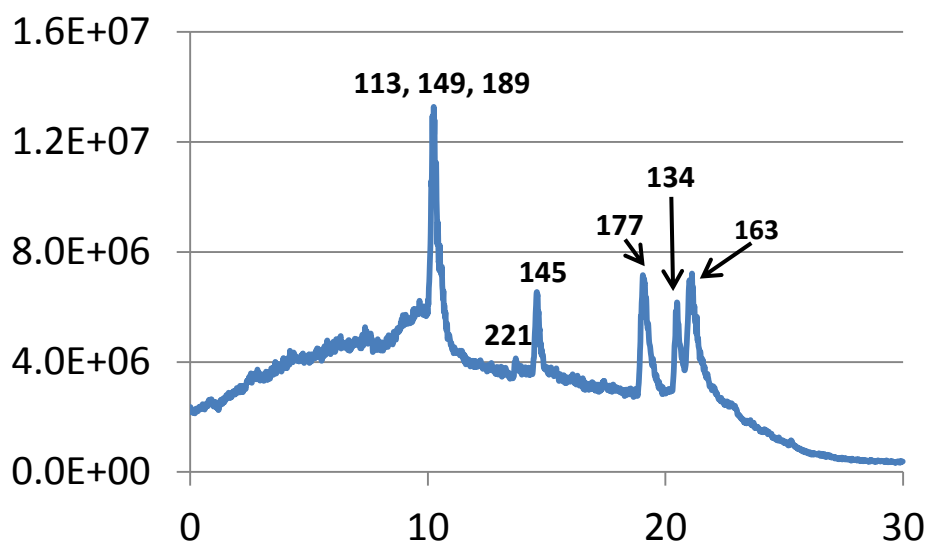


Figure 25: LC-MS chromatogram (HILIC method) for 9 molal pilot plant sample. Eluents: aqueous 10 mM ammonium carbonate, methanol, acetonitrile. Peak assignments indicate m+h observed on the mass spectrometer.

Table 9: Peak areas and retention times for LC-MS chromatogram (HILIC method, above) for 9 molal pilot plant sample. Eluents: aqueous 10 mM ammonium carbonate, methanol, acetonitrile. Peak assignments indicate m+h observed on the mass spectrometer.

Retention Time (min)	Mass(es) (m+h)	TIC Area	Possible Formula(s)	Possible Structure(s)
10.25	113, 149, 189	157.6e6	$C_5H_9N_2O^+$ $C_5H_{13}N_2O_3^+$ $C_8H_{17}N_2O_3^+$	

13.70	221	7.2e6	??	??
14.59	145	42.3e6	$C_6H_{13}N_2O_2^+$	
19.05	177	104.8e6	$C_7H_{17}N_2O_3^+$	
20.48	134	52.5e6	$C_5H_{12}NO_3^+$	
21.08	163	147.0e6	$C_6H_{15}N_2O_3^+$	

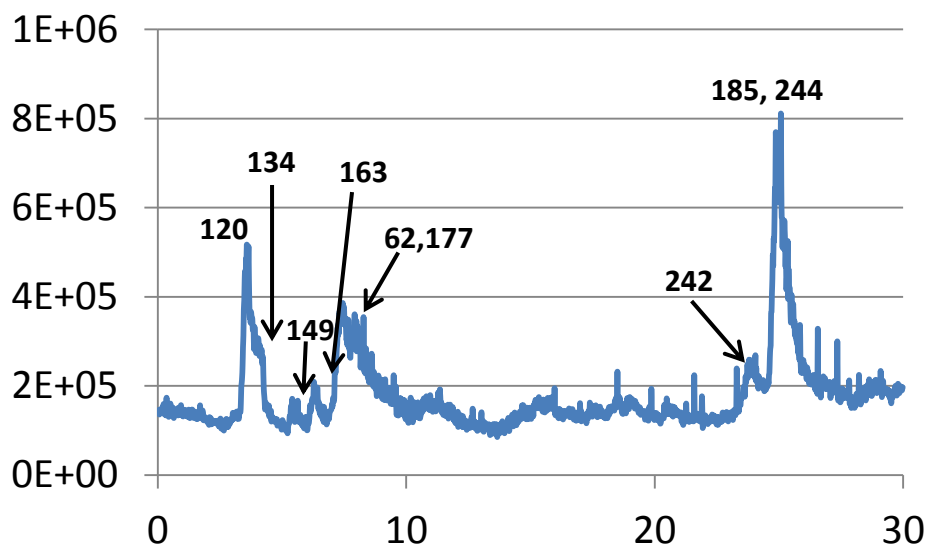


Figure 26: LC-MS chromatogram (standard reverse-phase method) for 9 molal pilot plant sample. Eluents: aqueous 10 mM ammonium carbonate, methanol, acetonitrile. Peak assignments indicate m+h observed on the mass spectrometer.

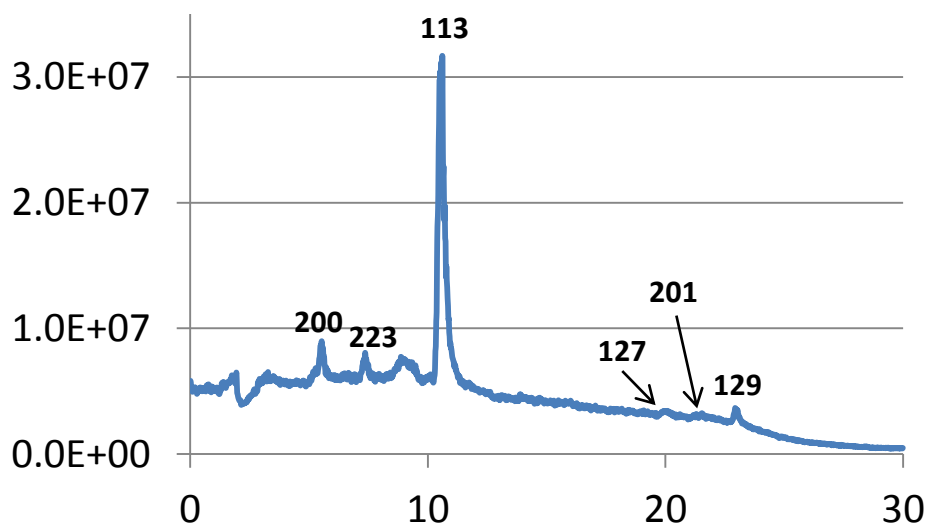


Figure 27: LC-MS chromatogram (HILIC method) for 9 molal pilot plant sample after 17 days of oxidation, 20x dilution in water. Eluents: aqueous 10 mM ammonium carbonate, methanol, acetonitrile. Peak assignments indicate m+h observed on the mass spectrometer.

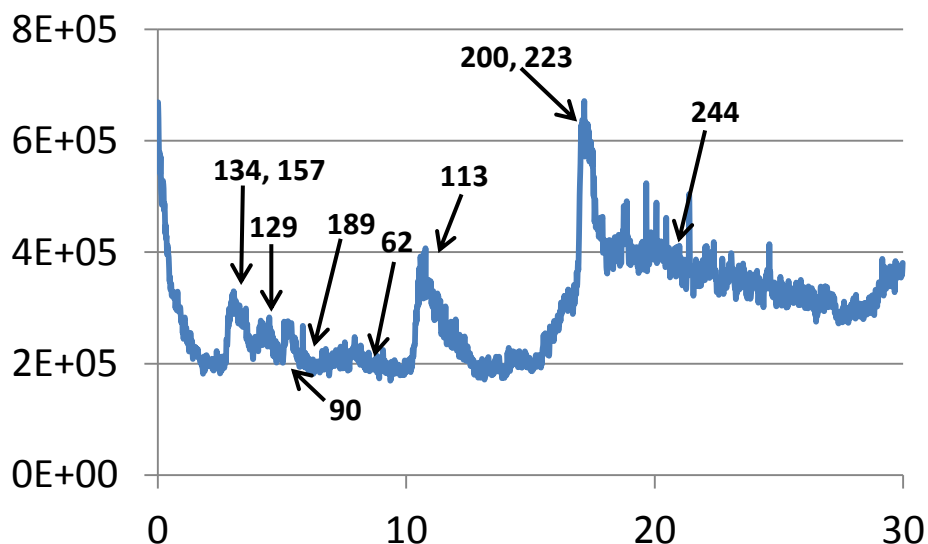


Figure 28: LC-MS chromatogram (standard reverse-phase method) for 9 molal pilot plant sample after 17 days of oxidation, 20x dilution in water. Eluents: aqueous 10 mM ammonium carbonate, methanol, acetonitrile. Peak assignments indicate $m+h$ observed on the mass spectrometer.

After oxidation, a compound with $m+h = 200$ is observed on LC-MS on both methods. This compound is a strong UV absorber at 254nm^{-1} and somewhat at 280nm^{-1} , but is not visible at 210. It is also not visible on LC-MS after treatment with concentrated sodium hydroxide, indicating that it likely contains an amide bond. Although the compound is unknown, the formula is $\text{C}_8\text{H}_{14}\text{N}_3\text{O}_3^+$ and the double bond equivalent is 3.5.

GC-MS Qualitative Analysis

Initial and final samples were analyzed qualitatively by GC-MS. Several peaks were observed in the initial sample (Figure 29). Some of these were possibly identified using the data from high-resolution mass spectrometry described above. The relative areas of various components in the initial sample are shown in Figure 30.

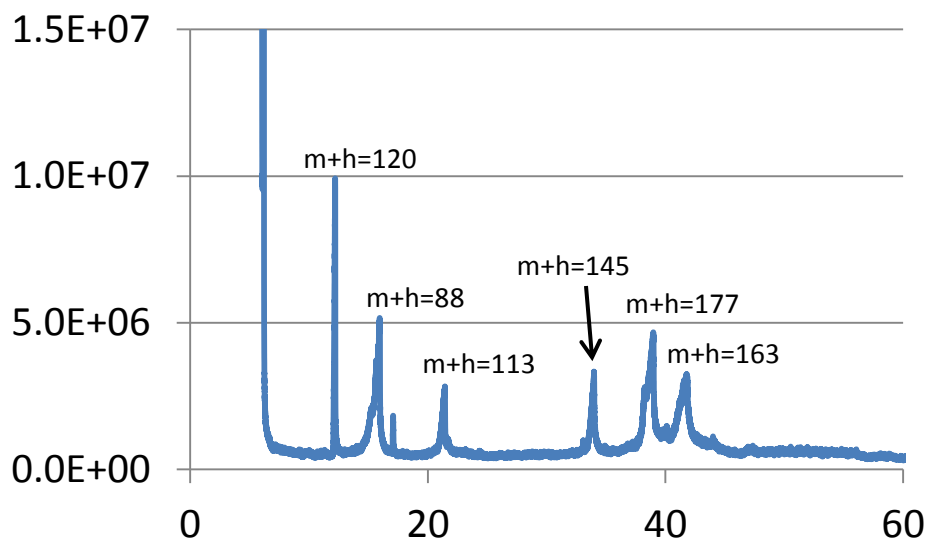


Figure 29: Analysis of a 9 m MEA pilot plant sample by GC-MS with chemical ionization.

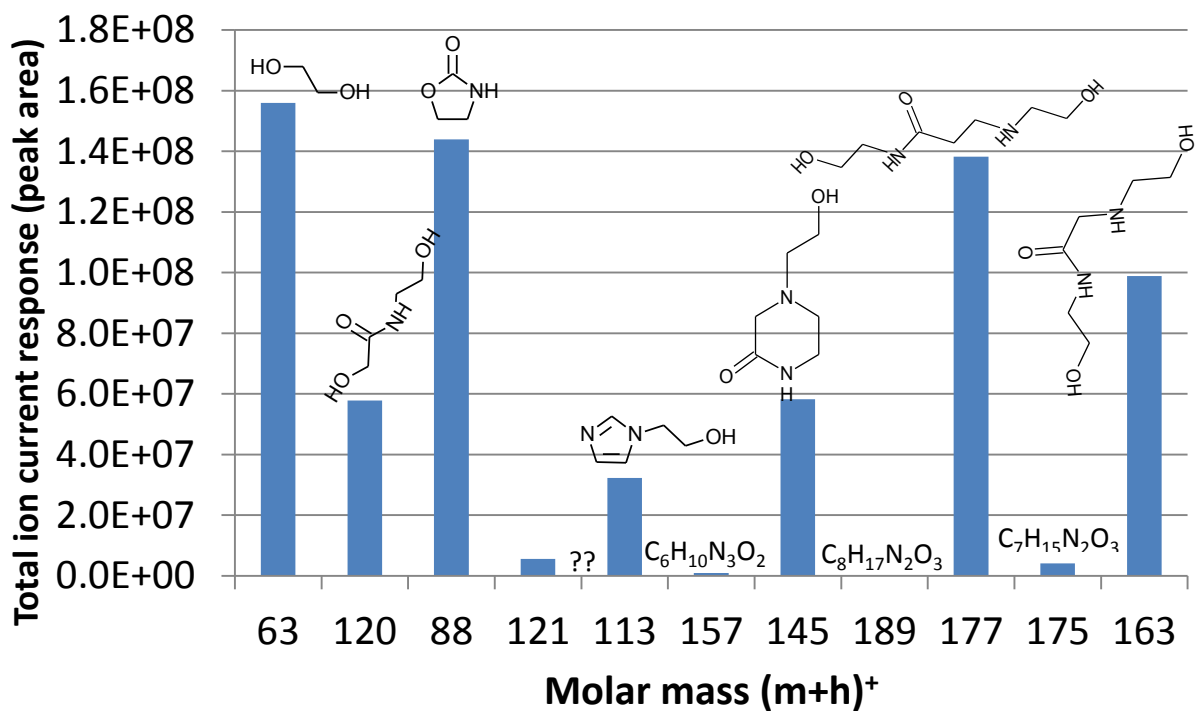


Figure 30: Response (GC-MS area) of some masses detected by GC-MS in a 9 m MEA pilot plant sample.

The final sample contained three major peaks, all of which were much larger than any peaks in the initial sample (note the scale on Figure 31 is much higher than Figure 29). These peaks are oxazolidone, hydroxyethyl formamide, and hydroxyethyl imidazole.

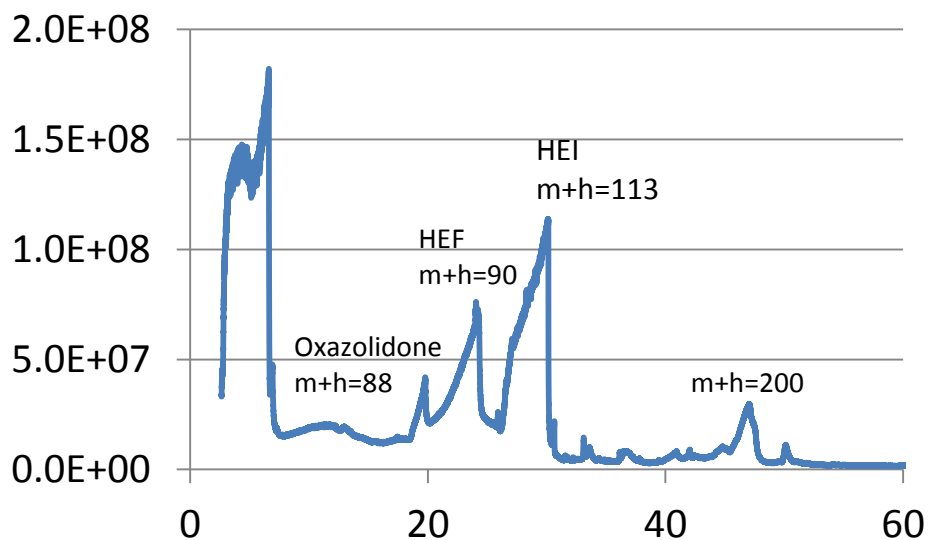


Figure 31: Chromatogram for GC-MS analysis of 9 m pilot plant sample after 17 days of oxidation. Chemical ionization, no split.

Split-injection was also used, which reduces the amount of time that the sample spends in the high-temperature injector (from up to a minute to less than a second). Under these conditions, oxazolidone was not observed and a different molecule with $m+h = 47$ was observed. This is likely the formic acid peak. Oxazolidone is likely produced in the high temperature injector, and is thus an “artificial” degradation product. The other major peaks (HEI and HEF) are both quantified using liquid chromatography methods.

Appendix A

Analysis of oxidized 9 m pilot plant samples by various analytical methods

Sample	Date	Time	Days	MEA (mol/kg)	Total Alk. (mol/kg)
0	1/21/2011	3:32 PM	0.00	5.24	5.18
1	1/22/2011	3:35 PM	1.00	4.79	4.93
2	1/24/2011	2:14 PM	2.95	3.71	3.91
3	1/26/2011	2:54 PM	4.97	3.59	3.66
4	1/28/2011	2:19 PM	6.95	3.24	3.46
5	1/31/2011	2:25 PM	9.95	2.90	2.80
6	2/7/2011	2:23 PM	16.95	2.24	2.04

<u>NH₃ (mmol/kg)</u>	<u>TIC (mol/kg)</u>	<u>TOC (% Initial)</u>	<u>TN (% Initial)</u>	<u>Loading (TIC/MEA)</u>
6.11	1.314	105%	103%	0.25
69.51	1.541	101%	110%	0.32
88.56	1.908	97%	107%	0.51
82.94	1.424	106%	94%	0.40
77.01	1.173	103%	89%	0.36
62.60	0.921	104%	87%	0.32
24.96	0.837	106%	91%	0.37

<u>Total Formate (mmol/kg)</u>	<u>Total Oxalate (mmol/kg)</u>	<u>Nitrite (mmol/kg)</u>	<u>Nitrate (mmol/kg)</u>	<u>Formate (mmol/kg)</u>	<u>Oxalate (mmol/kg)</u>	<u>Oxamate (mmol/kg)</u>
4.9	3.5	3.5	0.8	5.4	1.7	4.8
127.4	19.1	28.2	6.9	14.0	1.9	9.8
257.6	51.2	61.0	14.3	31.0	3.1	25.1
371.1	83.1	86.1	20.5	49.4	4.8	47.3
427.2	102.4	95.3	23.2	66.0	6.4	64.8
503.5	130.6	109.9	27.5	96.9	9.8	94.3
640.2	183.3	135.7	34.4	169.8	17.5	149.6

<u>HEG</u> (mmol/kg)	<u>UK, RT=25.6</u> (mmol/kg)	<u>NaOH HEG</u> (mmol/kg)	<u>NaOH UK,</u> <u>RT=25.6</u> (mmol/kg)	<u>HEI</u> (mmol/kg)	<u>NaOH-HEI</u> (mmol/kg)
4.03	5.74	3.29	0.00	-6.7	-7.8
1.24	4.59	4.29	0.00	107.2	128.9
0.34	3.25	3.48	0.00	222.2	325.7
0.30	2.75	3.75	0.00	319.9	400.9
0.32	2.18	4.12	0.00	376.7	394.4
0.33	1.76	4.08	0.00	419.9	457.3
0.27	1.05	4.04	0.00	546.7	533.6

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Nitrosamine Formation in CO₂ Capture by Piperazine

Quarterly Report for January 1 – March 31, 2011

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Supported by the Luminant Carbon Management Program

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Abstract

Secondary amines may react with nitrite to produce carcinogenic products called nitrosamines. They were first described in the chemical literature over 150 years ago, but since the discovery of their carcinogenic properties in 1956 by Barnes and Magee; there has been an explosion of interest in their chemistry and particularly in methods of destroying them. Piperazine (PZ) is an amine of interest in our study and nitrosation products of PZ are N-nitrosopiperazine (MNPZ) and N-N, dinitrosopiperazine (DNPZ).

Four experiment were performed this quarter to measure the reaction of nitrite with 8 m loaded PZ at 60 °C with 0.4 mM Fe⁺²/0.1 mM Cr⁺²/0.05 mM Ni⁺². The experiments included exposure to no gas with added nitrite, to air/CO₂ with added nitrite, or to air/CO₂/NO₂. The reaction rate of nitrite with 8 m loaded PZ is not changed by contacting the solution with oxygen.

Nitrite accumulates when the solution is contacted with gas containing oxygen and NO₂.

We continued to develop a method for detecting and measuring dinitrosopiperazine (DNPZ) and mononitrosopiperazine (MNPZ) using liquid chromatography followed by mass spectrometry (LC-MS) or a UV detector.

Introduction

Nitrosamine production occurs when secondary amines such as piperazine (PZ) undergo a nitrosation reaction in the presence of nitrite ions. The nitrosation reaction behind this formation has been known for over 150 years, but the carcinogenic properties of its products were discovered about 60 years ago.

PZ is an effective promoter for carbon dioxide removal from gas streams. The rate constant is an order of magnitude higher than a primary amine, but the reaction between PZ and nitrite may cause nitrosopiperazine formation.

The purpose of this research is to study the kinetics of the reaction between 8 m loaded PZ ($\alpha = 0.3$) and nitrite. There are two main sources of nitrite in a CO₂ capture process using PZ: flue gas and amine oxidation products in the absorber. Experiments have been ongoing to determine the effect of nitrite concentration, temperature, amine concentration, formaldehyde, and acidity

on nitrite and PZ reaction, and a method is being developed for detecting and measuring MNPZ and DNPZ. Results reported previously show that the reaction is a first order reaction with respect to the nitrite concentration and total PZ concentration. An acidic environment accelerates the reaction between PZ and nitrite, but not as much as using loaded PZ with CO₂, and while formaldehyde acts as a catalyst, it increases the rate of reaction only slightly.

Our aim is to find out if there is any evidence of nitrosamines in a CO₂ capture process using PZ. A method has been established for detecting standard DNPZ using 80% methanol and 20% water as dilution solvent and then injecting the sample to liquid chromatography followed by mass spectrometry (LC-MS). Now this method is being developed to detect and measure MNPZ and DNPZ in a solution of 8 m loaded PZ. To achieve better separation peaks of MNPZ and DNPZ, a solution of 10% methanol and 90% water with a 30-minute cycle time has been used for liquid chromatography.

A new detection method using HPLC is being developed. The best method is to use standard reverse phase 5% Acetonitrile to 50% Acetonitrile in water buffered with ammonium formate to detect standard MNPZ and DNPZ in a solution of methanol. Studies are under development to build calibration curve for detecting MNPZ and DNPZ in unknown samples.

Theory of nitrosation reaction

The most regularly used reagent for nitrosation is nitrous acid, generated in aqueous acid solution from a nitrite salt, typically sodium nitrite. Nitrous acid exists in aqueous solution in equilibrium with dinitrogen trioxide N_2O_3 , Equation 1, an effective nitrosating species which can be observed as nitrosonium nitrite (Equation 2).



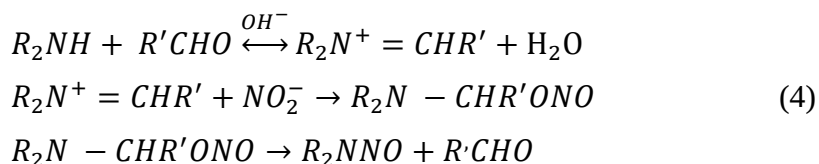
The rate equation, Equation 3, has been established for a range of amines.

$$\text{Rate} = k[HNO_2]^2[A] \quad (3)$$

This is the rate equation expected for rate limiting attack by an equilibrium concentration of N_2O_3 on amine, and the third order rate constant k in Equation 3 is given by $k_2k_{N_2O_3}$, where k_2 is the second order rate constant for N_2O_3 attack and $k_{N_2O_3}$ is the equilibrium constant for N_2O_3 formation.

In a CO₂ capture plant using PZ, the pH of the system is high, so the acidic condition which promotes formation of N_2O_3 as an important nitrosation reagent is not available but there are sources of nitrite ions in different sections of the plant. Normally nitrite has no capacity for effecting nitrosation. However, in the presence of some carbonyl-containing catalysts, nitrosation can be achieved in neutral and basic solution.

Catalysts include formaldehyde, chloral, benzaldehyde derivatives, and pyridox. Reaction 4 is particularly effective for the conversion of secondary amines to nitrosamines.



Product formation was efficient with the formation of an iminium ion intermediate, which reacts with nitrite ions giving a dialkylamino nitrite ester which breaks down rapidly and intramolecularly to give nitrosamine and regenerate the catalyst. This pathway has been suggested for the reaction of secondary amines with solid sodium nitrite in halogenated solvents (Roller et al., 1980).

Experimental Methods

A solution of 8 moles of PZ in 1 kg water was prepared and 4.8 moles of CO₂ was introduced to the solution to have 8 m loaded PZ ($\alpha = 0.3$). This solution was used in further experiments for kinetic study.

Kinetics of PZ nitrosation

Initial experiments started with 8 m loaded PZ and 50 mmolal sodium nitrite (NaNO₂) at 60 °C which is the absorber temperature, and the effect of temperature, acidity, and catalyst on the reaction has been studied by analyzing the concentration of nitrite during the course of each reaction, and the activation energy of reaction was calculated.

Following these experiments, the reaction of 8 m loaded PZ and 50 mmolal NaNO₂ in the presence of stainless steel mixture (Fe²⁺, Ni⁺, and Cu²⁺) was considered because it is closer to absorber conditions in a real CO₂ capture process. The loss rate of nitrite is a first order function of nitrite but the rate of reaction is lower than without the presence of metals (Figure 1).

In the process of absorbing CO₂ by amine solution, flue gas, which contains mainly air and CO₂ with small amounts of NO₂ and other gasses, contacts the amine solution. Three experiments were conducted to simulate this process using 8 m loaded PZ in contact with:

- Low gas flow containing 97% O₂, 2% CO₂, and 1% NO₂ for 2 weeks;
- High gas flow containing 97% O₂, 2% CO₂, and 1% NO₂ for 5 days;
- Low gas flow containing 98% O₂, 2% CO₂, and 50 mmol NaNO₂ for 7 days.

NaNO₂ has been used, because there is a possibility for having nitrite ion from oxidative degradation of amine in absorber.

Results show that in a continuous process of contacting gas and PZ solution containing nitrite, the rate of nitrite concentration loss is lower than when the process is done in batch condition (Figure 2).

The reaction of both low and high flow rate gas containing NO₂ shows an accumulation of nitrite in solution, but analysis shows that some of the entering nitrite reacted with the amine solution or exited the system (Figures 6, 7), and as expected, the rate of nitrite accumulation in the high gas flow reaction is considerably more than in low flue gas.

Nitrosamine detection and measurement

A method has been established for detecting standard DNPZ using a solution of 80% methanol and 20% water as dilution solvent and then injecting the sample to liquid chromatography followed by mass spectrometry (LC-MS). The method is now being developed to detect and measure MNPZ and DNPZ in a solution of 8 molal loaded PZ. To achieve better separation

peaks of MNPZ and DNPZ, a solution of 10% methanol and 90% water with a 30-minute cycle time has been used for liquid chromatography.

A new method using HPLC is under development. The best method is to use standard reverse phase 5% Acetonitrile - 50% Acetonitrile in water buffered with ammonium formate to detecting standard MNPZ and DNPZ in a solution of methanol. Studies are under development to build calibration curve for detecting MNPZ and DNPZ in unknown samples.

Both apparatuses, LC/MS and HPLC, are being used for detecting and measuring nitrosopiperazine (MNPZ and DNPZ) and later by comparing the results, the most accurate method will be chosen.

Kinetics of nitrite reaction with loaded piperazine

The disappearance of nitrite suggests that nitrite reacts with PZ by a first order reaction in both total PZ and total nitrite:

$$\text{Rate (mol/day-kg}_{\text{solution}}) = k_2 [\text{PZ}]_T [\text{NO}_2^-]$$

where the concentrations are given in mol/kg_{solution}.

In a given experiment the total piperazine $[\text{PZ}]_T$ is assumed to be constant and the loss of PZ follows first order behavior, so the rate constant, k_2 , is determined from the fit of data given by:

$$\text{Ln}[\text{NO}_2^-] = \text{Ln} [\text{NO}_2^-]_0 - k_2 t$$

or

$$\text{Ln}[\text{NO}_2^-] = \text{Ln} [\text{NO}_2^-]_0 - k_2 [\text{PZ}]_T t$$

where $k_2 = b/[\text{PZ}]_T$

The rate constant, k_2 , is further correlated as a function of temperature using the Arrhenius expression:

$$k_2 = (k_2)_{\text{ref}} e^{(-E/RT)}$$

$$\text{Ln}(k_2) = \text{ln}(k_2)_{60^\circ\text{C}} + (E/R)(1/T - 1/333)$$

Results

Results of the kinetic study of PZ nitrosation are presented in Table 1 and Figure 1. The reaction between 8 m loaded PZ and 50 mmolal NaNO_2 , which has been selected as the concentration of nitrite for nitrosation reaction based on recent experiments, has been demonstrated at 21, 60, and 75 °C over 6 days. Samples have been taken once a day and diluted to 100X with DI water to be analyzed by anion chromatography for nitrite disappearance. Results show that all three reactions follow a linear path on a log/linear plot so the slope of each line is the first order reaction rate constant at each temperature.

Using following equation, reaction rate constant (k_2) has been calculated for each temperature;

$$\text{Ln}[\text{NO}_2^-] = \text{Ln} [\text{NO}_2^-]_0 - k_2 [\text{PZ}]_T t$$

The results of all conducted experiments are presented in Table 1, including reaction rate constant of each for comparing different reaction conditions. An average reaction rate constant at 60 °C has been defined for the reaction of PZ and nitrite which is 0.0463 kg/mole-day.

Formaldehyde is a well known catalyst in nitrosation reaction, but results show that the reaction rate of 8 m loaded PZ and 50 mmol nitrite in the presence of formaldehyde is slightly higher than without catalyst (Figure 1). Loaded PZ has more reactivity with nitrite; this might be related to the acidic behavior of CO₂ and water in solution, but results of reaction of 8 m unloaded PZ and 50 mmol NaNO₂ when we adjust the pH of reaction to the pH of loaded solution by H₂SO₄ show that pH is not the acceleration factor for loaded PZ reaction and this might be because of producing piperazine carbamate which reacts with nitrite ion faster and easier. By adding SS metal mixture, the rate of nitrite disappearance decreased and, as shown in Figure 1 and Table 2, the reaction rate constant is about the same as in the presence of acid.

It seems that SS metal solution has the same effect when amine solution reacts with nitrite directly as when amine solution containing nitrite is contacting a low gas flow mixture of O₂ and CO₂ (Figure 1).

The results of the experiments those conducted to study the reaction of 8 m loaded PZ and a gas mixture containing O₂, CO₂, and NO₂ (Figures 2 & 3) show that at the end of the course of experiments we do have some nitrite but less than that entered at first moment. This means either nitrite reacted with PZ or it just left the system with gas flow.

In the low gas flow experiment, the flow rate was 100 ml/min of gas containing 97% O₂, 2% CO₂, and 1% NO₂. 4.8 mmole of nitrite entered the reactor during the experiment and 3.2 mmole of total nitrite ion remained in the reactor at the end of experiment, which means that 1.6 mmole (33%) disappeared either by reaction or by exiting with the gas.

In the high gas flow experiment, the flow rate of gas is 7.7 L/min which contains 97% O₂, 2% CO₂, and 1% NO₂. The amount of nitrite which entered the reactor was 99 mmole during the experiment and the amount of total nitrite ion remaining in the reactor was 29.9 mmole at the end of experiment, which means that 60 moles (60%) disappeared either by reaction or just leaving the reactor with exiting gas. Analytical methods for detecting any products of PZ and nitrite reaction are needed.

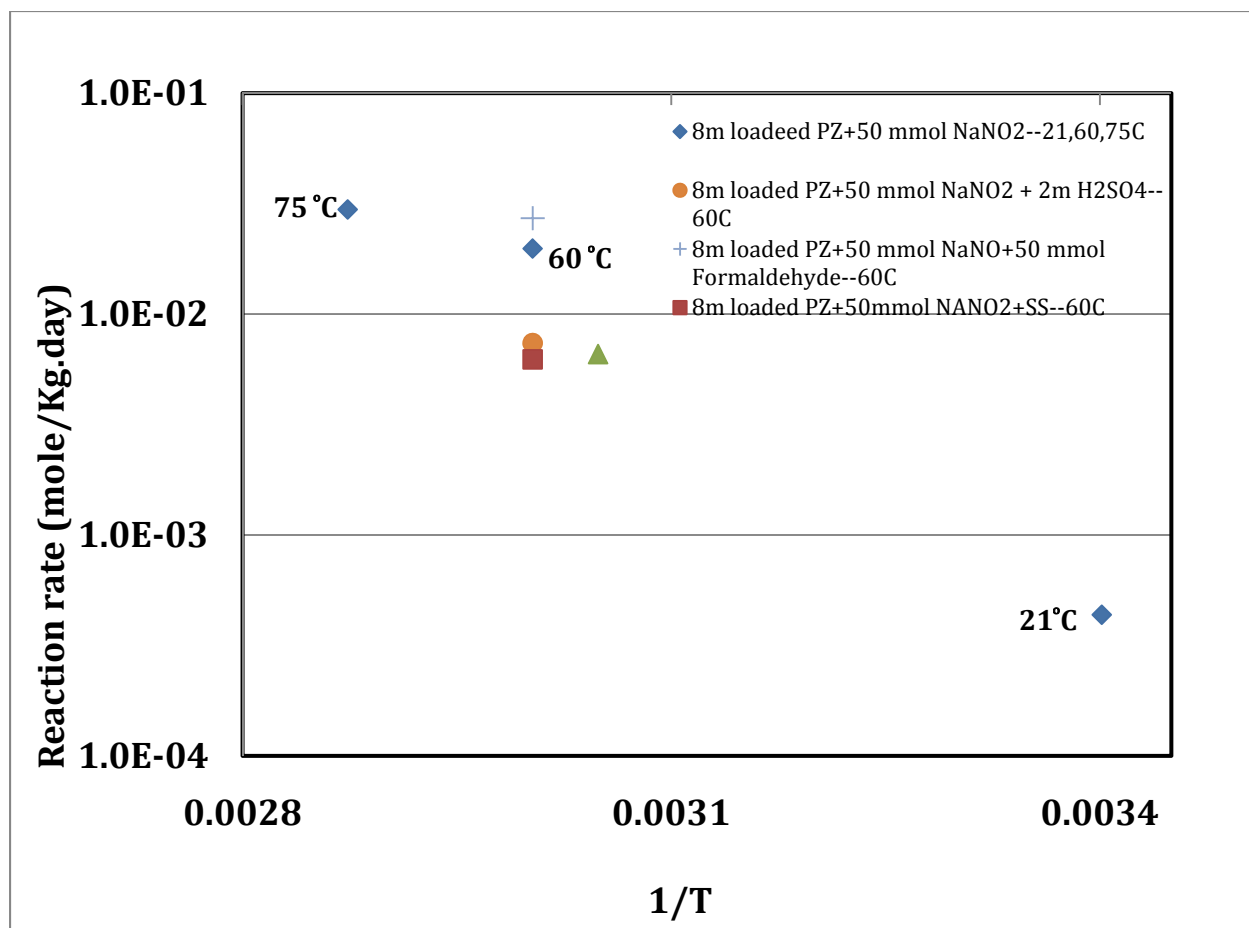


Figure 1: Reaction rate of PZ and nitrite under different conditions with respect to temperature (1/T)

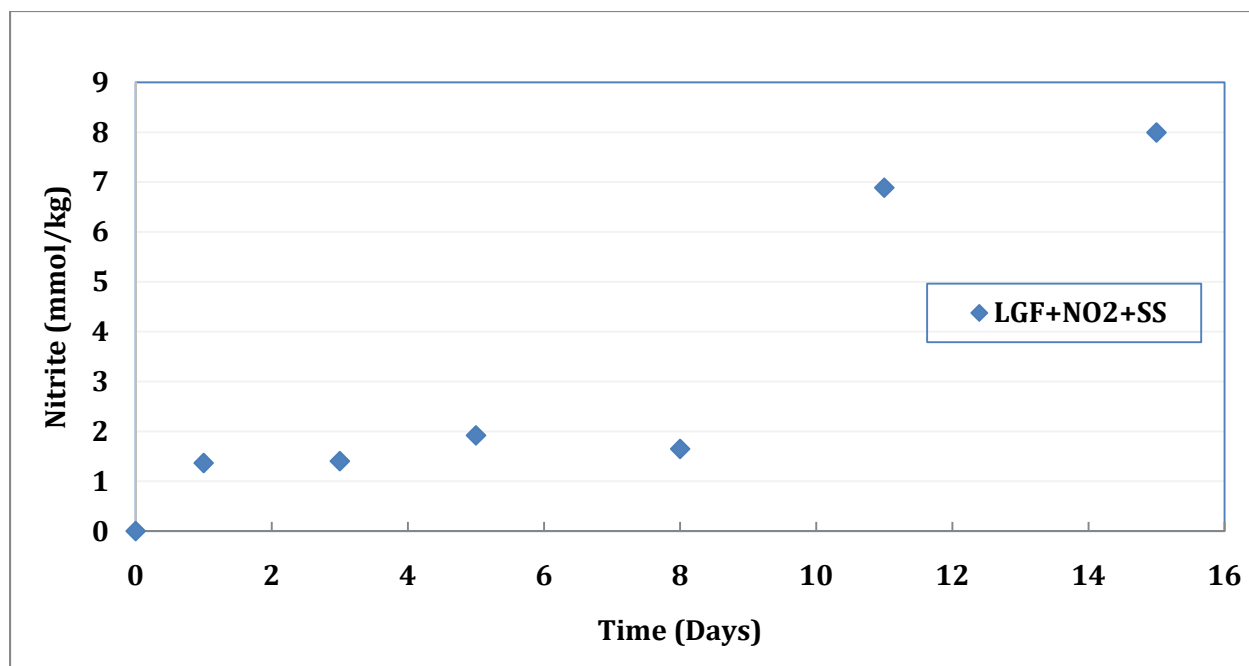


Figure 2: Nitrite accumulation from the reaction of 8 m loaded PZ and 50 ppm NO₂ in low gas flow experiment

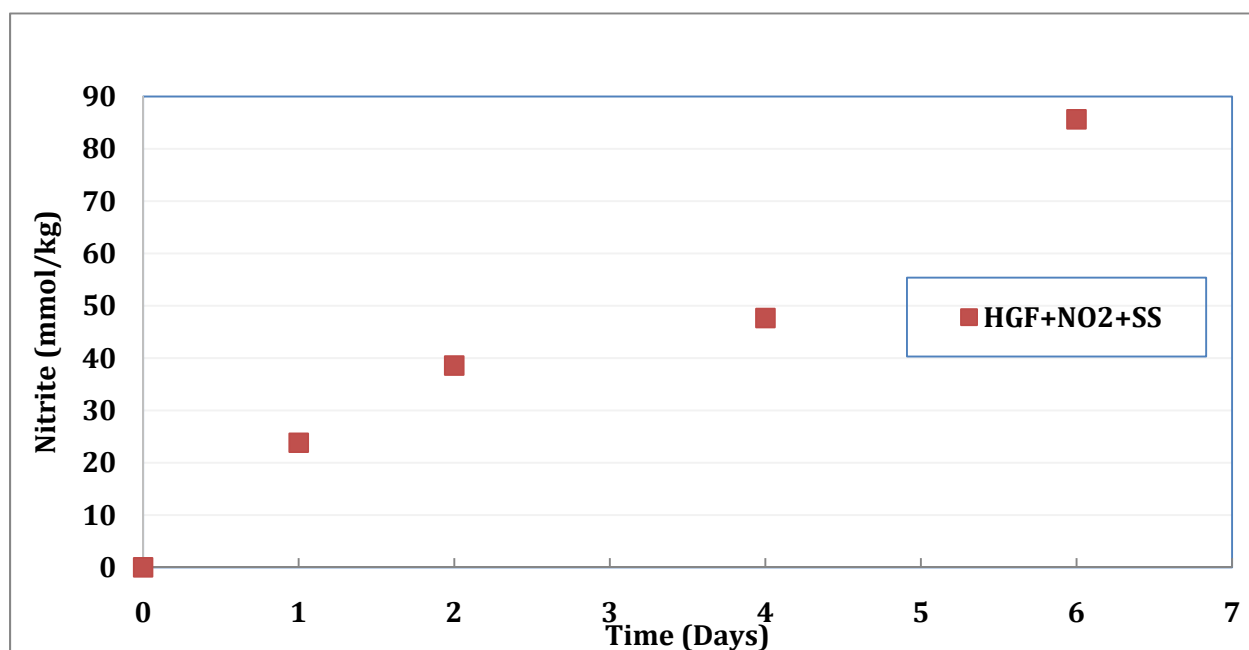


Figure 3: Nitrite accumulation the reaction of 8 m loaded PZ and 50 ppm NO₂ in high gas flow experiment

Table 1: Reaction rate constant for different reaction conditions

	T (°C)	[PZ] _T (mole/kg)	CO ₂ loading	NaNO ₂ (mmole/kg)	SS Metals	Formaldehyde (mmole/kg)	H ₂ SO ₄ (m)	NO ₂ (mmol/kg)	k ₂ (kg/mole. day)
Amine solution in contact with Nitrite	60	8	0.3	50	-	-	-	-	0.0467
	60	8	0.3	50	-	50	-	-	0.0675
	60	8	0.3	50	-	-	2	-	0.018
	21	8	0.3	50	-	-	-	-	0.00104
	75	8	0.3	50	-	-	-	-	0.07
	60	8	0.3	50	√	-	-	-	0.00623
Low gas flow	60	8	0.3	50	√	-	-	-	0.00695
Low gas flow	60	8	0.3	-	√	-	-	50	-
High Gas flow	60	8	0.3	-	√	-	-	50	-

The reaction activation energy is obtained from the slope of $\ln(k_2)$ versus reciprocal temperature as in Figure 2.

Direct injection of Dinitrosopiperazine to Mass Spectrometry (MS)

Standard DNPZ has been synthesized by using method USP 24. By diluting standard DNPZ in a solution of 80% methanol and 20% water, and then injecting new samples to the MS, mass spectrometry shows a peak at m/z of 145 which is DNPZ (Figure 4). 100 xs has been chosen as the standard dilution factor for future experiments.

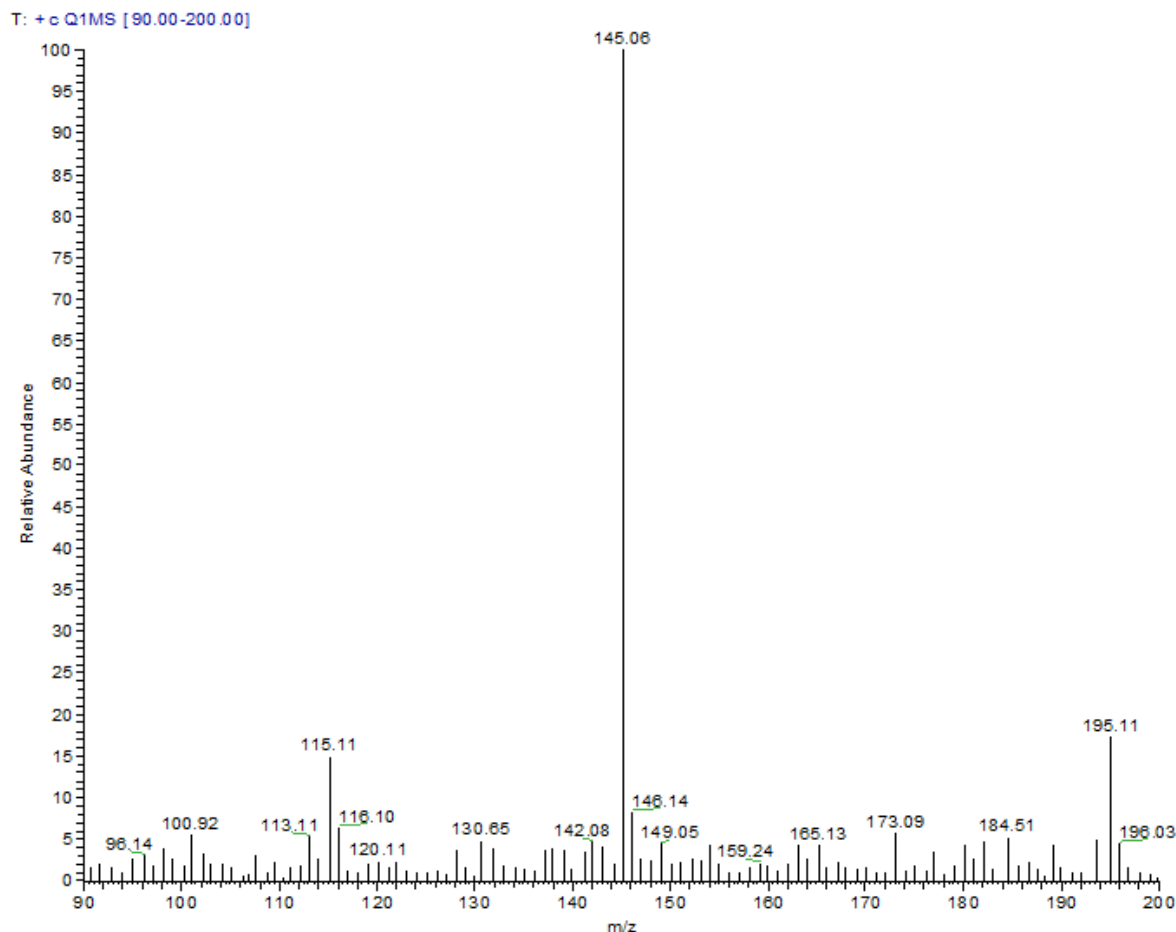


**Figure 4: Mass spectrum of a sample of dinitrosopiperazine in methanol and water.
(Relative abundance and m/z)**

Rather than a big peak of DNPZ, there is a small amount of MNPZ in the injected sample as shown in Figure 4. m/z of 116.1 represents the molecular weight of MNPZ which is 115.

Quantifying Dinitrosopiperazine by Liquid chromatography and Mass Spectrometry (LC-MS)

LC-MS was used to quantify DNPZ. Samples were diluted in 89% methanol/20% water and analyzed by LC/MS with a reverse phase column and at different concentrations. The areas under the peaks in chromatograms are related to the concentration of each standard, so a calibration curve has been established with a sensitivity of 5×10^{-5} (Figure 5).

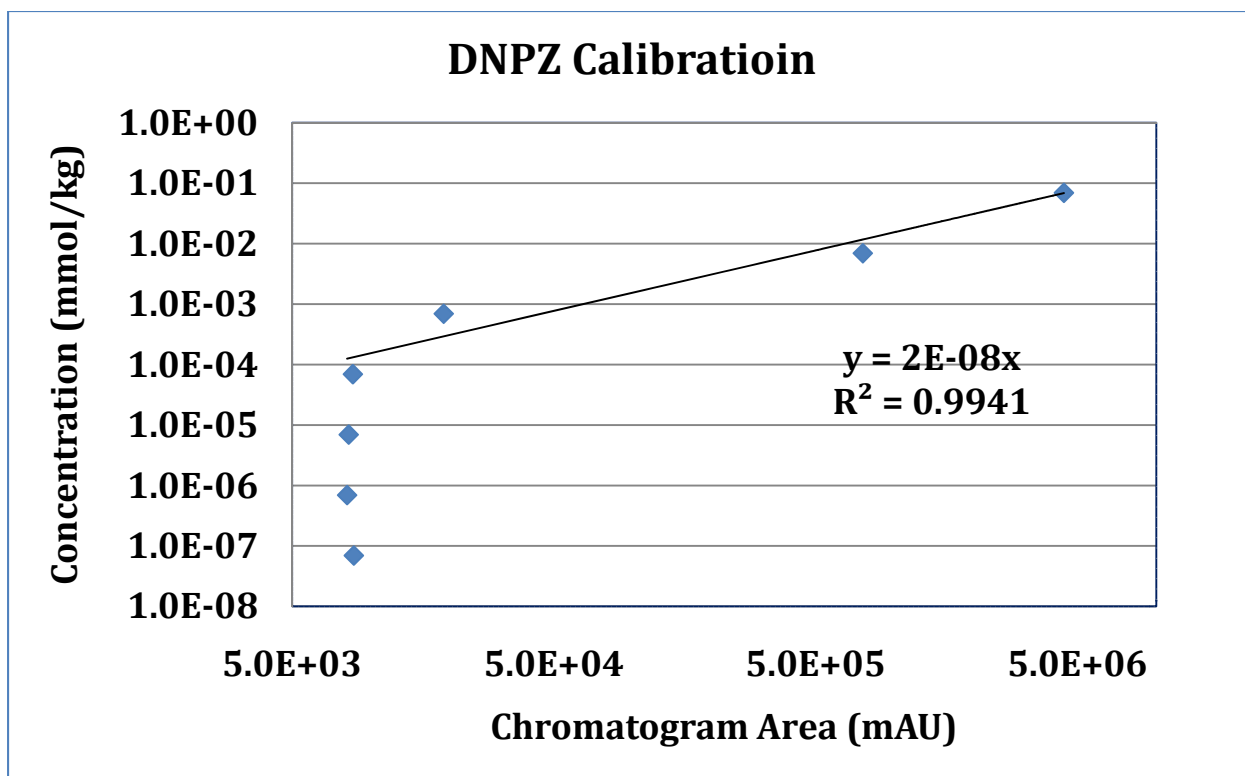


Figure 5: Calibration curve for standard DNPZ, with a detection limit of 9×10^{-5} mmol/kg

Figure 5 shows the chromatogram area related to the different concentrations of DNPZ, and the respective calibration curve which is linear. This will be used when a sample with unknown concentration of DNPZ is injected into the LC-MS.

Detecting MNPZ and DNPZ in a solution of PZ using LC-MS

The DNPZ detection method has been applied to samples of purchased standard MNPZ, but results show that the method should be refined; therefore we have investigated a better method for both MNPZ and DNPZ detection especially in the presence of other species in solution. The mobile phase of the new method contains 10% methanol and 90% water with a rate of 200 $\mu\text{l}/\text{min}$ during 30 minutes. In this method, there is better separation of PZ, MNPZ, and DNPZ. Figure 6 shows the detection of PZ, MNPZ, and DNPZ in a solution of amine and nitrosamines.

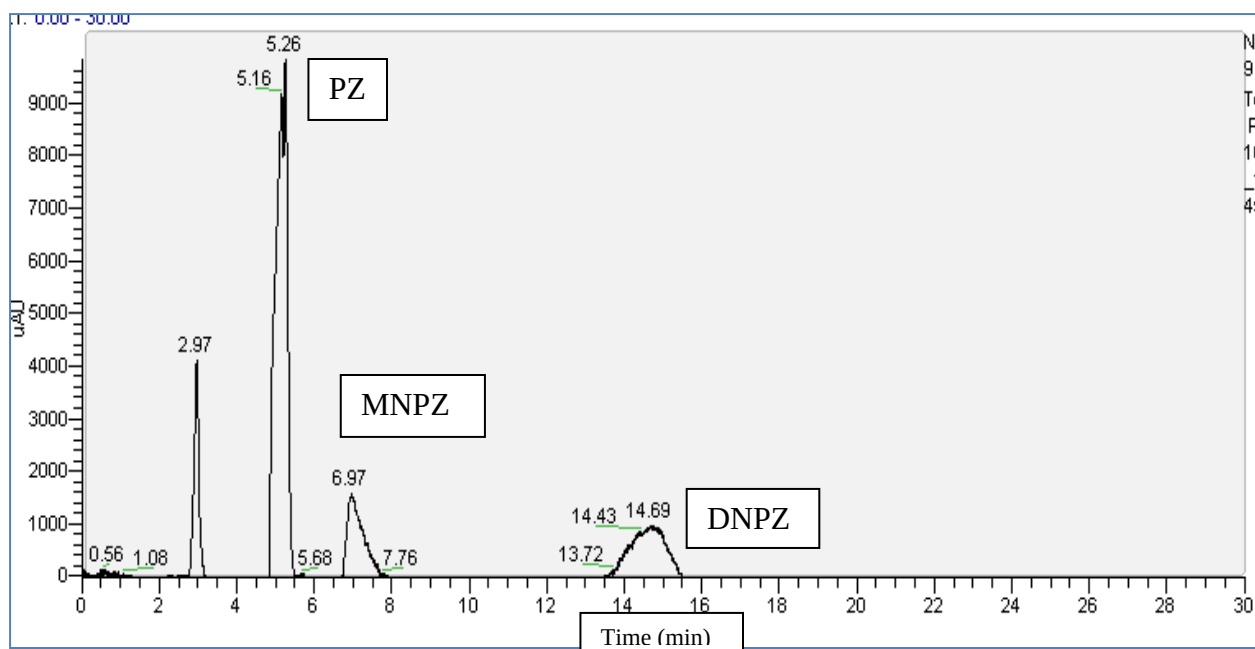


Figure 6: Chromatogram of PZ, MNPZ, and DNPZ, when the mobile phase contains 10% Methanol and 90% water

Detecting MNPZ and DNPZ in a solution of PZ sing HPLC

A new detection method has been applied to standard solutions of MNPZ, DNPZ, and a solution of PZ containing MNPZ and DNPZ using HPLC. The best method is to use standard reverse phase 5% Acetonitrile - 50% Acetonitrile in water buffered with ammonium formate to detecting standard MNPZ and DNPZ in a solution of methanol. Studies are under development to build calibration curve for detecting MNPZ and DNPZ in unknown samples.

Primary results show that MNPZ and DNPZ are detectable but PZ is not detectable with HPLC. Figure 7 shows a chromatogram of a sample containing MNPZ, DNPZ, and PZ. MNPZ gives better detection peak while DNPZ has a wider peak, which might be because of some impurities in DNPZ standards.

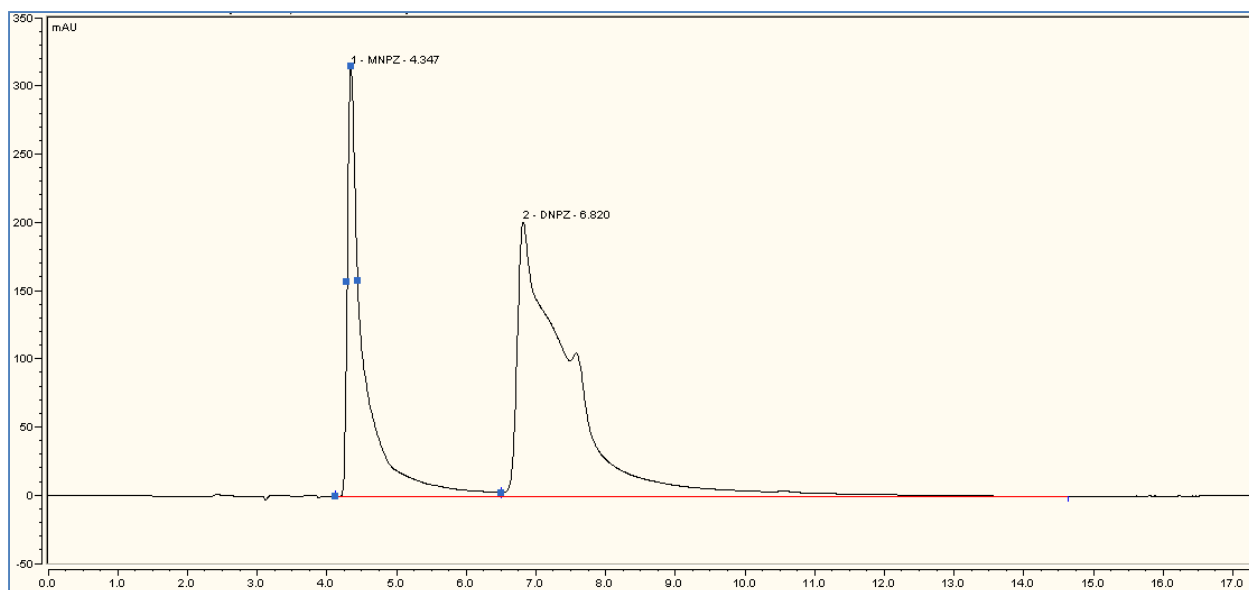


Figure 7: Chromatogram of 500 ppm of MNPZ and DNPZ in PZ, using HPLC

Comparing the results of LC-MS and HPLC for unknown samples

Samples were injected in to both LC-MS and HPLC to compare the analysis and select the most accurate way to detect and measure nitrosopiperazines.

Figure 8 shows the results of samples from high gas flow experiments at the beginning, middle, and end of the course of experiments. There are three clear peaks that show PZ, MNPZ, and DNPZ. However chromatograms show evidence of MNPZ and DNPZ, but by developing the reaction, MNPZ and DNPZ disappear. Applying the peak area of these results and the calibration curves show that the concentration of MNPZ and DNPZ is very low and less than 6×10^{-5} mmol/kg at the beginning.

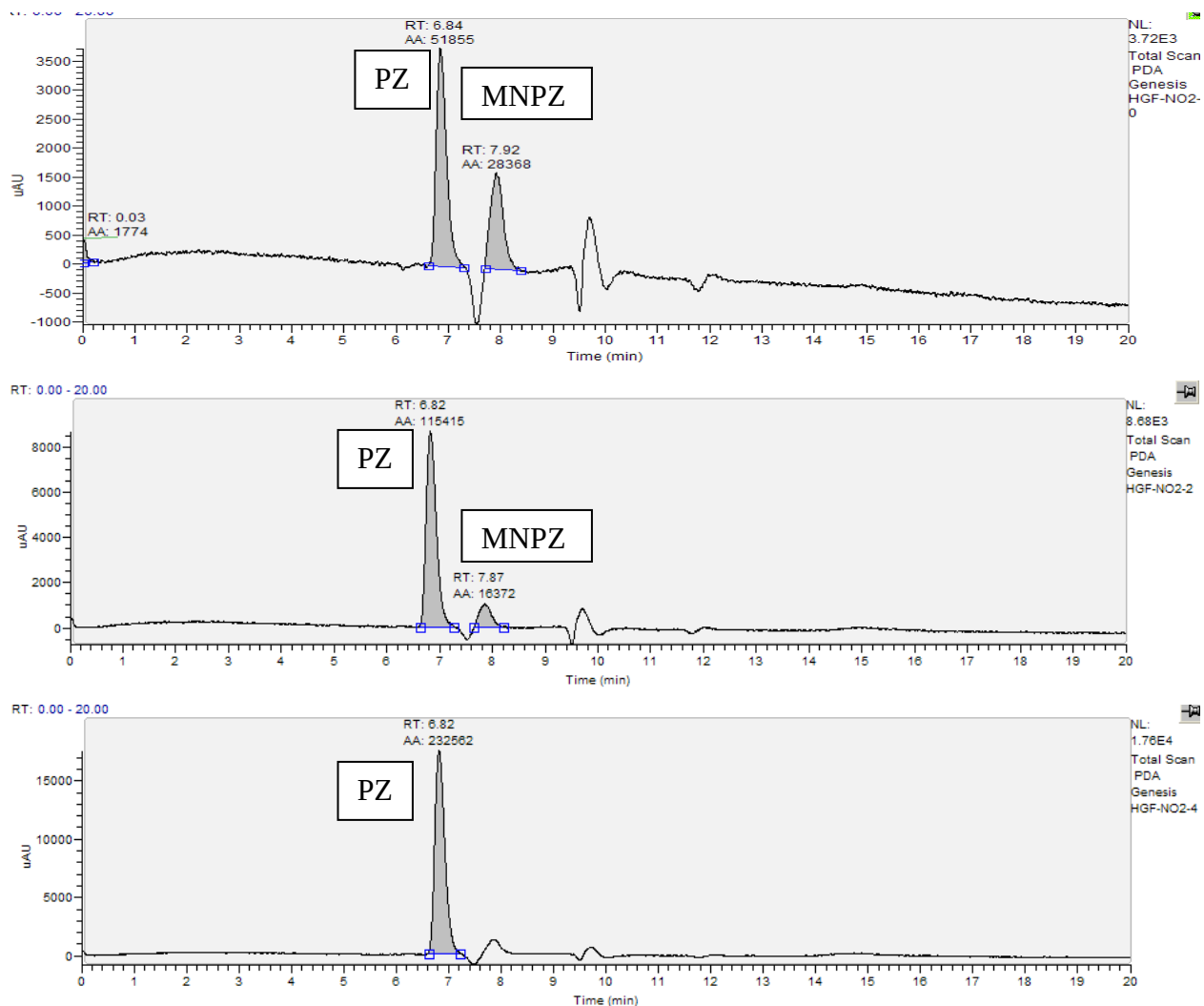


Figure 8: Chromatogram of reaction products of HGF experiments at the beginning, middle, and end of the reaction, analyzed by LC-MS

Figure 9 shows the same samples as Figure 8 but analyzed by HPLC. HPLC shows good response to standard MNPZ, but as shown in Figure 8, it does not have the accuracy of LC-MS.

HPLC does show the production of an unknown component during the reaction which has a retention time close to that of MNPZ and DNPZ. Since this could be something other than MNPZ or DNPZ, another analytical method (MS) should be used to identify this new product.

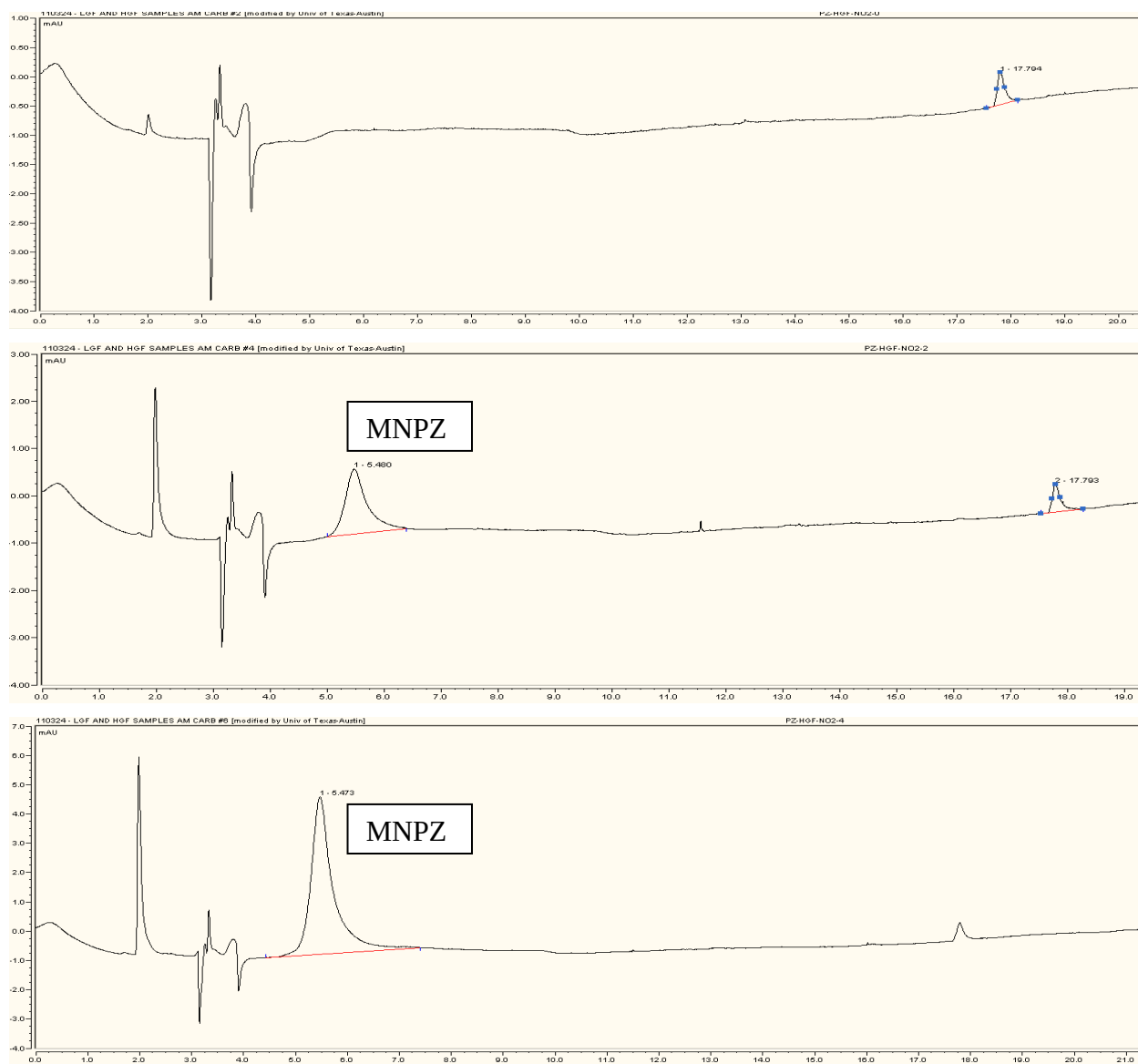


Figure 9: Chromatogram of reaction products of HGF experiments at the beginning, middle, and end of reaction, analyzed by HPLC

The same analysis has been done for the low gas flow experiment (Figures 10, 11).

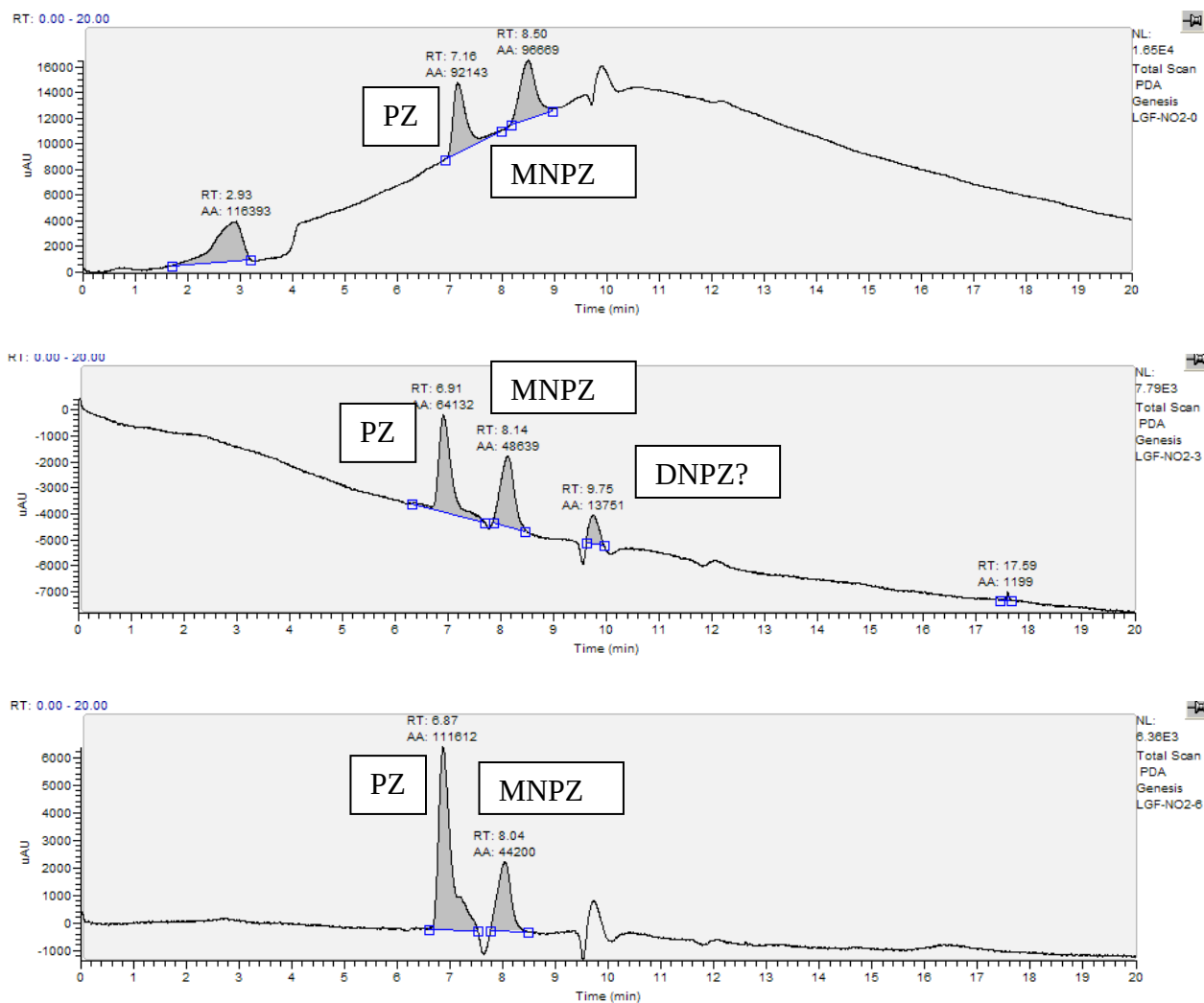


Figure 10: Chromatogram of reaction products of LGF experiments at the beginning, middle, and end of reaction, analyzed by LC-MS.

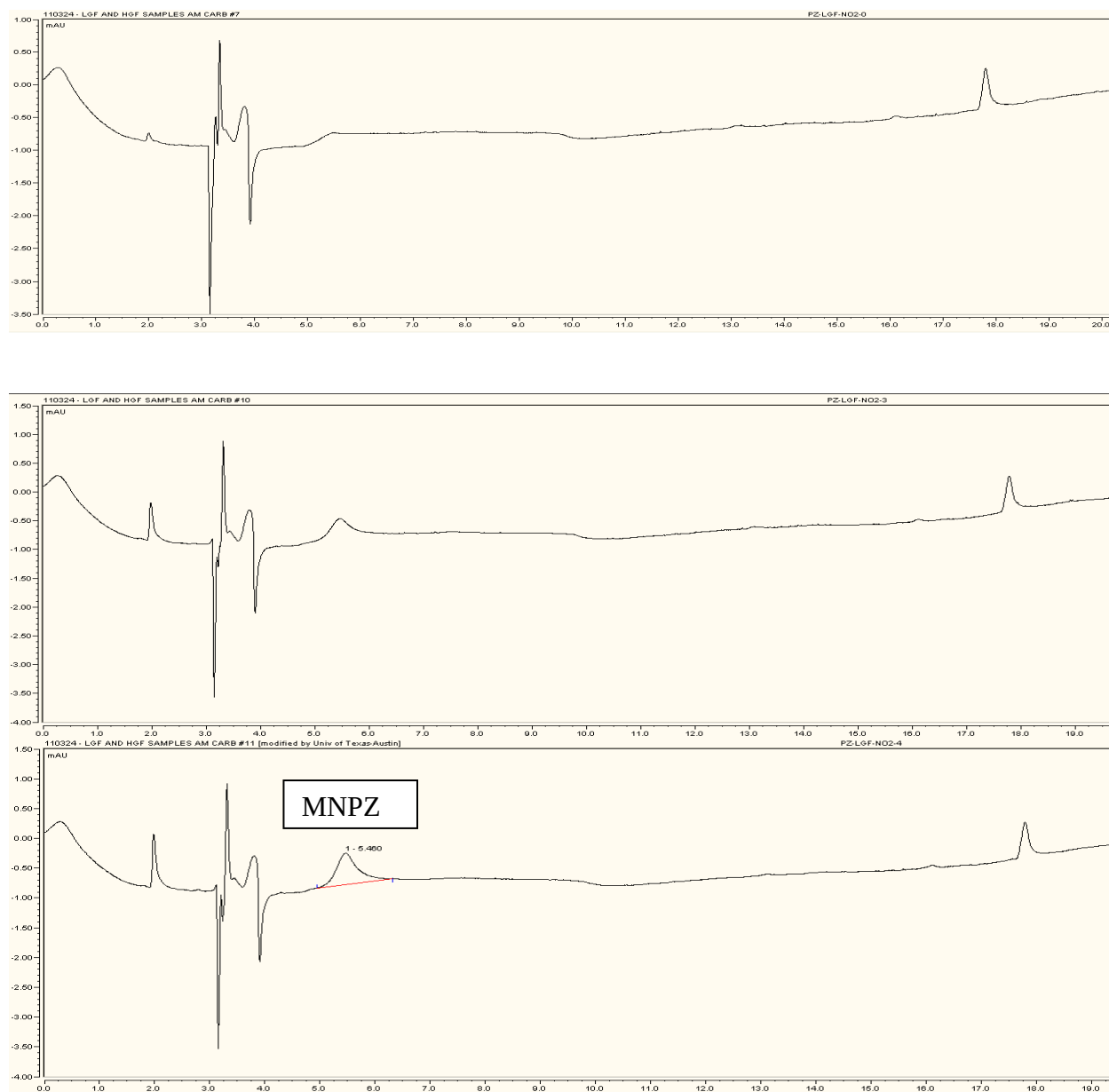


Figure 11: Chromatogram of reaction products of LGF experiments at the beginning, middle, and end of reaction, analyzed by HPLC

Conclusions

Standard dinitrosopiperazine (DNPZ) can be measured by LC-MS using a reverse phase column, with a detection limit of 6E-5 mmol/kg.

The reaction of nitrite with 8 m loaded PZ is first order in nitrite and first order in total PZ concentration, and the reaction rate constant has been calculated as 0.0463 kg/mol-day. Loaded PZ reacts with nitrite faster than with than unloaded PZ or with acidified PZ. A stainless steel metal mixture decreases the reaction rate of 8 m loaded PZ with nitrite. The reaction of 8 m loaded PZ and nitrite in low gas flow conditions has the same reaction rate constant as without any gas flow.

30% of nitrite entering the low gas flow reactor in contact with amine solution containing SS metal mixture either is absorbed by amine or exits the system very slowly.

60% of nitrite entering the high gas flow reactor in contact with amine solution containing SS metal mixture either is absorbed by amine or leaves the system very rapidly.

Future Work

A method for analyzing nitrosamine in reaction products will be finalized. Samples from pilot plant will be analyzed looking for nitroso products.

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Reclaiming for Amine-Based CO₂ Capture

Quarterly Report for January 1 – March 31, 2011

by Steven Fulk

Supported by the Luminant Carbon Management Program

Department of Chemical Engineering

The University of Texas at Austin

April 30, 2011

Abstract

In this quarter, liquid-liquid equilibrium experiments were investigated as a means of recycling oxidation inhibitors. Phase separation experiments consisted of heating solution to 60 °C in an agitated isothermal glass-jacketed beaker followed by additions of anhydrous K₂CO₃ to unloaded solutions and KOH to loaded solutions. Additions of K₂CO₃ to an 8 m PZ solution containing Inhibitor A led to formation of two liquid phases below a total solution loading of 0.365 moles CO₂/mole alkalinity. For a total solution loading of 0.365, K⁺ and CO₂ were 50 and 60 times more concentrated in the bottom phase, respectively. PZ and Inh A were 335 and 1.92 times more concentrated in the top phase, respectively. Adding anhydrous KOH to an 8 m PZ, 0.30 loaded solution containing Inh A precipitated instead of liquid-liquid separating.

The pKa of the free amine functionality group of FPZ was measured by titration with 0.01 M HCl. The pKa of FPZ was measured at 7.807.

A 20 m PZ, 0.1 loaded solution was thermally degraded in 316 SS cylinders with Swagelok[®] endcaps in a forced convection oven at 175 °C for a period of ten weeks to simulate degradation in a thermal reclaimer. Samples were transferred each week to a glass vial with a nitrogen-sparged headspace. The average loss of total alkalinity, PZ, and CO₂ was 0.185, 0.212, and 0.093 moles/kg, respectively. The ratio of total alkalinity and PZ loss to CO₂ loss was 1.990 and 2.280, respectively. FPZ was the dominant degradation product followed by formate, NH₄⁺, and EDA. Fe and Ni increased to 450 ppm over a period of 10 weeks. Glycolate, oxalate, nitrite, nitrate, HEP, DMPZ, and Cr were found in negligible amounts.

A two-stage integrated thermal reclaimer was simulated in Aspen Plus[®] using the Fawkes thermodynamic framework with MDEA as a surrogate for a collection of contaminants for thermodynamic modeling purposes. 1×10^{-4} – 1×10^{-3} percent of the lean stream flow rate was able to remove contaminants produced at a rate of 1×10^{-5} moles per mole CO₂ captured. The make-up and disposal costs varied between \$0.3–\$1.5/MT CO₂ captured for varying reclaimer pressure while the energy cost was determined to be independent of reclaimer design.

Goals for next quarter include continued phase characterization experiments for contaminant and inhibitor separation using liquid-liquid separation. Thermal degradation experiments for solutions containing KOH, KHCO₃, and K₂CO₃, to mimic neutralized reclaiming solutions, will be analyzed.

Introduction

Alkanolamines have been used to treat acid gases since 1930 (GPSA, 2004). Since then, the need to develop new solvents to increase system capacity and optimize to meet economic and environmental concerns has become increasingly important. Although new and better solvents have been and are continually being developed to meet some of these demands, process contaminants are becoming increasingly problematic. As carbon capture matures and applications shift from simulated to real flue gas, issues related to pollutants will become more problematic, especially for coal-fired power plants. System contaminants pose a number of problems such as increased solvent make-up costs, reduced system capacity due to amine degradation, waste disposal costs, equipment corrosion, and environmental concerns related to greenhouse gas and nitrosamine emissions.

Many methods for removing contaminants, or reclaiming, have been developed. Reclaiming methods include filtration and adsorption, thermal reclaiming, ion exchange, electrodialysis, foam fractionation, and sulfate crystallization. Each system operates on a different separation principle, and thus each process will have inherent advantages and disadvantages.

The overall goals of reclaiming are to separate and return amine, water, and inhibitors to the absorption/stripping system while purging contaminants in the most cost-effective and environmentally friendly manner.

Experimental Methods

Liquid-Liquid Equilibrium

Liquid-liquid separation is a potential way to separate and recycle inhibitors from contaminants in a CO₂ capture system. Phase separation may also reduce the total volume sent to additional reclaiming systems.

The liquid-liquid equilibrium apparatus used consists of a 100 mL jacketed beaker, a Lauda E-100 Ecoline Staredition circulating water bath, and a Corning model PC-220 Laboratory Stirrer/Hot Plate. A diagram of the apparatus can be seen in Figure 1 below.

Experiments began by filling the jacketed beaker with 50–75 mL of amine solution containing Inh A. A magnetic stir-bar was placed in the solution and the beaker was sealed with a rubber stopper with an inserted thermometer. The sealed beaker was then placed on a magnetic stirrer and the circulating water bath was connected to the inlet and outlet connections of the beaker jacket. Stirring and jacket circulation was then initiated. Sequential additions of K₂CO₃ were added to unloaded solutions, and anhydrous KOH was added to loaded solutions. The solution temperature and phase behavior was monitored for a period of one hour between each addition of either K₂CO₃ or KOH.

Samples were analyzed using total alkalinity (acid titration), total inorganic carbon analysis (TIC), and cation chromatography to determine amine, additive, and CO₂ concentrations in each phase. The specific analytical procedures are discussed in the Analytical Methods section of this report.

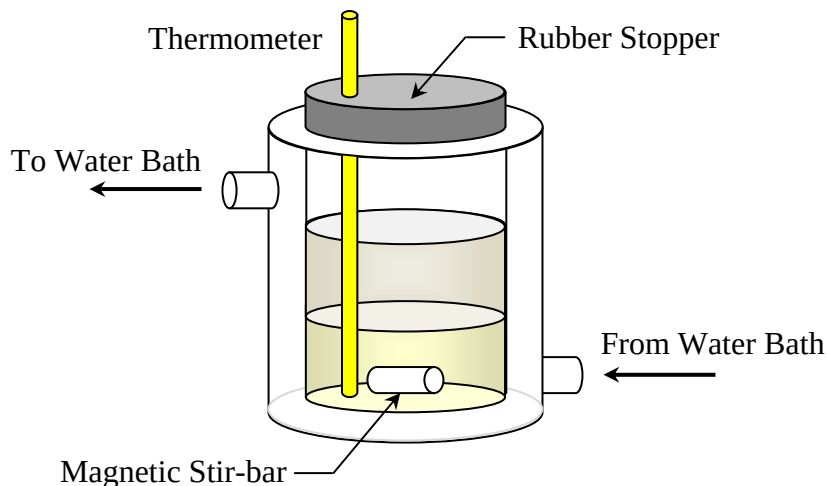


Figure 1: Liquid-Liquid Equilibrium Apparatus

pKa Measurements

The pKa for N-Formyl Piperazine (FPZ) was measured by titration. 25 mL of a 0.01 M FPZ solution was placed in a 150 mL tall-profile beaker with a magnetic stir-rod. The beaker was placed on a Metrohm-Peak 835 Titrando system for agitation and manual pH measurement. The solution was titrated with 0.01 M HCl in 1 mL increments. The pH was measured between each HCl addition using the attached pH probe. Measurements were made every 10–20 seconds to eliminate any acidic hydrolysis effects of the amide back to amine and formate. The solution was titrated until the pH dropped below 2.7.

Thermal Degradation

Thermal degradation experiments began by filling 0.5" ID 316 SS tubes with Swagelok® endcaps with approximately 10 mL of solution. The cylinders were placed in a forced convection oven maintained at 175 °C for a period of 10–15 weeks. Cylinders were sampled each week to produce a time series of thermally degraded samples. Samples that were solid at ambient conditions were reheated in the stainless steel cylinder placed in a water bath before being transferred to 15 mL glass sample vials. The headspace of each sample vial was purged with nitrogen to eliminate any oxidation during the period of sampling and analysis.

Analytical Methods

Dilutions

Many of the analytical methods and sampling techniques performed this quarter required dilutions to achieve the desired concentration ranges or to prevent crystallization of the sampled material. Dilutions are performed gravimetrically by weighing a sample in a beaker, taring the balance, and weighing an amount of water added to the sample. The solution is then stirred and transferred to the appropriate vial.

Total Alkalinity (Acid Titration)

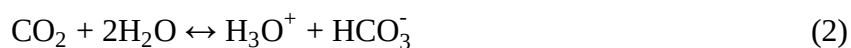
The total alkalinity of solutions was determined by titration with 0.2 N H₂SO₄ using a Metrohm-Peak 835 Titrando with an auto-dispenser. In this method, a sample of known mass is diluted by

water in a tall-profile titration beaker and is then titrated with acid. Once titration is complete, the volume of acid used to reach the equivalence point, nominally a pH of 3.9, is used to calculate the total alkalinity of the solution. Acidic titration is not selective for any particular species and therefore reports the total alkalinity of the solution regardless of the mix of components displaying alkaline behavior. Typical sample masses and dilution factors for acid titration are 0.2 g and 300x, respectively.

For a more detailed description of the Total Alkalinity procedure, please see Appendix A.3 of Hilliard (2008).

Total Inorganic Carbon Analysis (TIC)

The Total Inorganic Carbon analysis was used to quantify CO₂ loading in samples. Generally, a sample of known mass is injected into a port containing 30 wt % H₃PO₄ where the sample is acidified and CO₂ is produced according to the following equilibrium equations:



The CO₂ is then carried by a nitrogen stream to a Horiba PIR 2000 CO₂ analyzer where voltage response versus time data is sent to a computer for tabulation. A plot of voltage against time for a given experimental run reveals a series of peaks corresponding to sample injections. The area of a given injection peak provides a means of calculating the amount of CO₂ contained in a sample when compared to injections of a carbon standard. The carbon standard used for this analysis technique was a buffered K₂CO₃/KHCO₃ 1000 ppm by mass standard.

Injection volume depends on the concentration of CO₂ in the sample; consequently, the dilution factor of the sample plays a role in fine-tuning injection volumes to fall in the appropriate voltage range of the CO₂ analyzer. Once the solutions were diluted properly, the injection volumes were adjusted to achieve a voltage response of approximately 0.5 V. The injection volume of samples ranged from 25-45 µL. After all of the samples were injected in triplicate, five different volumes of the 1000 ppm by mass carbon standard were injected with a voltage response range encompassing all of the sample responses to create a calibration curve. The calibration curve was then used to calculate the moles of CO₂ contained in a sample. CO₂ concentration information given by TIC used in conjunction with amine concentration information from cation chromatography allows calculation of loading (moles CO₂/mol alkalinity) of the samples.

For a more detailed description of the TIC procedure, see Appendix B.2–B.7 of Hilliard (2008).

Cation Chromatography

Cation chromatography was performed this quarter using a Dionex ICS-2500 IC with an auto-sampler and a gradient pump providing a linear eluent concentration profile using methanesulfonic acid to quantify the amount of Ammonium (NH₄⁺), Ethylenediamine (EDA), Piperazine (PZ), N-Formyl Piperazine (FPZ), 2-amino-2-methyl-1-propanol (AMP), 1-Methyl Piperazine (1-MPZ), 1,4-Dimethylpiperazine (DMPZ), 1-Ethyl Piperazine (1-EPZ), Hydroxyethyl Piperazine (HEP), and Aminoethylpiperazine (AEP) in sample solutions. A detailed description of the cation chromatography system and procedures is described in Section 3.2 of the dissertation by Sexton (2008).

Standards used for analysis were made by Stephanie Freeman; however, peak area assignments and cropping used in quantification of standards and products were all performed by the author.

Anion Chromatography

Anion chromatography was carried out using a Dionex ICS-3000 IC with a KOH eluent to determine the quantity of anions such as formate, acetate, glycolate, oxalate, sulfate, nitrate, nitrite, and chloride found in the sample solutions. A detailed description of this method and procedures is described in Section 3.1 of the dissertation by Sexton (2008).

Table 1 lists the specifications for the reagents used to make the standards for anion chromatography analysis.

Table 1: Anion Chromatography Chemical Reagent Specifications

Reagent	Supplier	Molecular Weight	Assay
Sodium Chloride	EM Science	58.44	99.0%
Sodium Sulfate	EM Science	142.04	99.9%
Sodium Nitrite	Fisher	69.00	99.0%
Sodium Nitrate	Fisher	84.99	100%
Potassium Formate	Alfa Aesar	84.12	99%
Sodium Acetate	Fisher	82.03	99.3%
Glycolic Acid, Anh.	Fisher	76.05	98.9%
Sodium Oxalate	Baker	134.00	99.9%

Standards were prepared by weighing appropriate amounts of each salt into a 250 mL beaker and adding enough water to produce a 2000 ppm solution of each compound. The 2000 ppm stock solution was diluted to produce additional standards.

NaOH Treatment for Amides

The formation of amides from the reaction of carboxylic acids and amines is significant in quantification of degradation products in amine scrubbing systems. Quantification of amides in a degradation sample is accomplished through basic hydrolysis of the amide to provide carboxylate salts, which are then quantified using the anion chromatography analytical method. Most degradation samples already contain appreciable quantities of carboxylate salts; therefore, the basic treatment method determines amide concentrations by difference in initial and base treated carboxylate concentrations.

The mechanism of the basic hydrolysis pathway occurs by nucleophilic addition of hydroxide to the amide carbonyl group, followed by amine elimination and hydroxide deprotonation (McMurry, 2007).

Samples are treated for amide quantification by mixing equal gravimetric amounts of sample with 5 N NaOH. The base-treated solutions are allowed to sit for 24 hours before anion chromatography analysis.

Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Simultaneous quantification of metals in thermal degradation samples is readily performed using atomic spectroscopy. Samples are sent to a nebulizer to produce a fine aerosol before

atomization and ionization in a plasma flame created by introducing argon gas into a time-varying electromagnetic field. Atoms and ions inside the plasma flame transition from excited to lower energy states producing emission spectra of sharp characteristic wavelengths. The argon plasma flame is maintained at 7000 K.

Four characteristic wavelengths are chosen for each element quantified using ICP-OES. Fe, Cr, and Ni were quantified for thermal degradation samples performed in stainless steel thermal cylinders. Table 2 shows metals quantified and their characteristic wavelengths. One wavelength was chosen to quantify the background emission intensity of argon. Calibration curves were made for each individual wavelength and were used to calculate an average concentration of each element measured.

Table 2: Characteristic Wavelengths for ICP-OES Metal Quantification

Element Analyzed	Measured Wavelengths (nm)			
Argon (Ar)	737.212			
Iron (Fe)	234.350	238.204	239.563	259.940
Chromium (Cr)	205.560	206.158	206.550	267.716
Nickel (Ni)	216.555	221.648	230.299	231.604

Quantification of metals in thermal degradation samples was performed using a Varian 710-ES Axial Inductively-Coupled Plasma Optical Emission Spectrometer. Samples were prepared at the proper concentration (25-100X), depending on metal concentration and particulate solubility, through dilution with DDI water and were acidified to 2% by mass using concentrated HNO₃. 10 mL of each sample and standard was prepared in a plastic vial.

Results

Liquid-Liquid Equilibrium

Two liquid-liquid experiments were performed this quarter. The first experiment was kept at a temperature of 60 °C and consisted of additions of K₂CO₃ to an unloaded 8 m PZ solution containing 0.1 mol Inh A per kg H₂O. K₂CO₃ was added in proportions such that the total solution loading would increase in 0.05 moles CO₂/mole alkalinity increments. The solution liquid-liquid separated at a loading range of 0.050–0.375 mol CO₃²⁻/equiv amine. At a loading of 0.375, precipitate formed in the bottom liquid phase. The top and bottom liquid phases were sampled at the final loading using a syringe. Table 3 shows the concentration of components in each phase as well as their selectivity towards their dominant phase. For example, the dominant phase of PZ is the top phase, so its selectivity is defined as the ratio of the top phase concentration to the bottom phase concentration. The dominant phase containing K⁺ is the bottom phase, so its selectivity is defined as the ratio of the bottom phase concentration to the top phase concentration.

The top phase contains mostly organic compounds and the bottom phase contains mostly aqueous and ionic compounds. The selectivity of most components is high; however, measurable Inh A selectivity is low.

As K₂CO₃ was added to the initial solution, the time required for dissolution and complete phase separation increased. Therefore, selectivity for each component may be higher for lower loadings.

Table 3: Phase Compositions for Liquid-Liquid Separation of 8 m PZ containing 0.1 moles Inh A/kg H₂O with approximately 0.375 Total* CO₂ Loading.

Compound	Top Phase	Bottom Phase	Selectivity	Method
K ⁺ (mmol/kg)	166	8249	50	Cation Chrom.
PZ (mmol/kg)	7673	23	334	Cation Chrom.
CO ₂ (mol/kg)	0.049	2.936	60	TIC
A (mol/kg)	0.098	0.051	1.92	--

* Total solution loading includes the CO₂ in the precipitate.

The second experiment was kept at a temperature of 60 °C and consisted of additions of anhydrous KOH to 0.3 loaded, 8 m PZ containing 0.1 mol Inh A per kg H₂O. KOH was added to the solution to mimic the addition of a strong base to a lean stream off the stripper, as is common practice in reclaiming operation. Addition of KOH should increase the pH of solution, converting all aqueous CO₂ and bicarbonate (HCO₃⁻) to carbonate (CO₃²⁻) according to Equations 1 and 2 shown in the Analytical Methods section above. Strong base is added to break heat-stable salts to free bound amine to increase overall recovery.

The solution precipitated a white powder on addition of anhydrous KOH and did not liquid-liquid phase separate. The precipitate in solution was likely HCO₃⁻ since HCO₃⁻ solubility is very low in PZ solutions, and all aqueous CO₂ must be converted to HCO₃⁻ prior to conversion to CO₃²⁻. Therefore, the solubility of HCO₃⁻ may prevent liquid-liquid phase separation of a reclaiming solution by addition of a strong base to a loaded solution.

Liquid-liquid phase separation might be possible by adding a strong base to a solution with low loading. The first experiment showed that even at low loadings, the solution formed two liquid phases. Also, at low loadings the concentration of HCO₃⁻ during reaction to CO₃²⁻ may be low enough that no precipitation occurs.

pKa Measurement

The pKa of the free amine group on FPZ (N-formyl piperazine) was measured by titration with HCl at ambient conditions with no ionic strength background salt. Figure 2 shows the resulting titration curve as well as the second derivative of pH with respect to volume of HCl. The endpoint of the titration is located at the inflection point of the pH versus volume curve ($d^2\text{pH}/dV^2 = 0$). According to the Henderson-Hasselbalch equation (Equation 3), the pKa equals the pH of the solution when half of the compound is deprotonated, or otherwise at half of the volume required to reach the equivalence point of the titration.

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) \quad (3)$$

The pKa for FPZ was calculated to be 7.807. At high pH reclaiming conditions in which a strong base is added to break heat-stable salts, FPZ will exist predominantly in its deprotonated form. The deprotonated form of FPZ is molecular, and therefore will be more volatile. Higher volatility of FPZ means that a thermal reclaiming system may not remove the majority of the compound as a nonvolatile unless it is hydrolyzed by hydroxide.

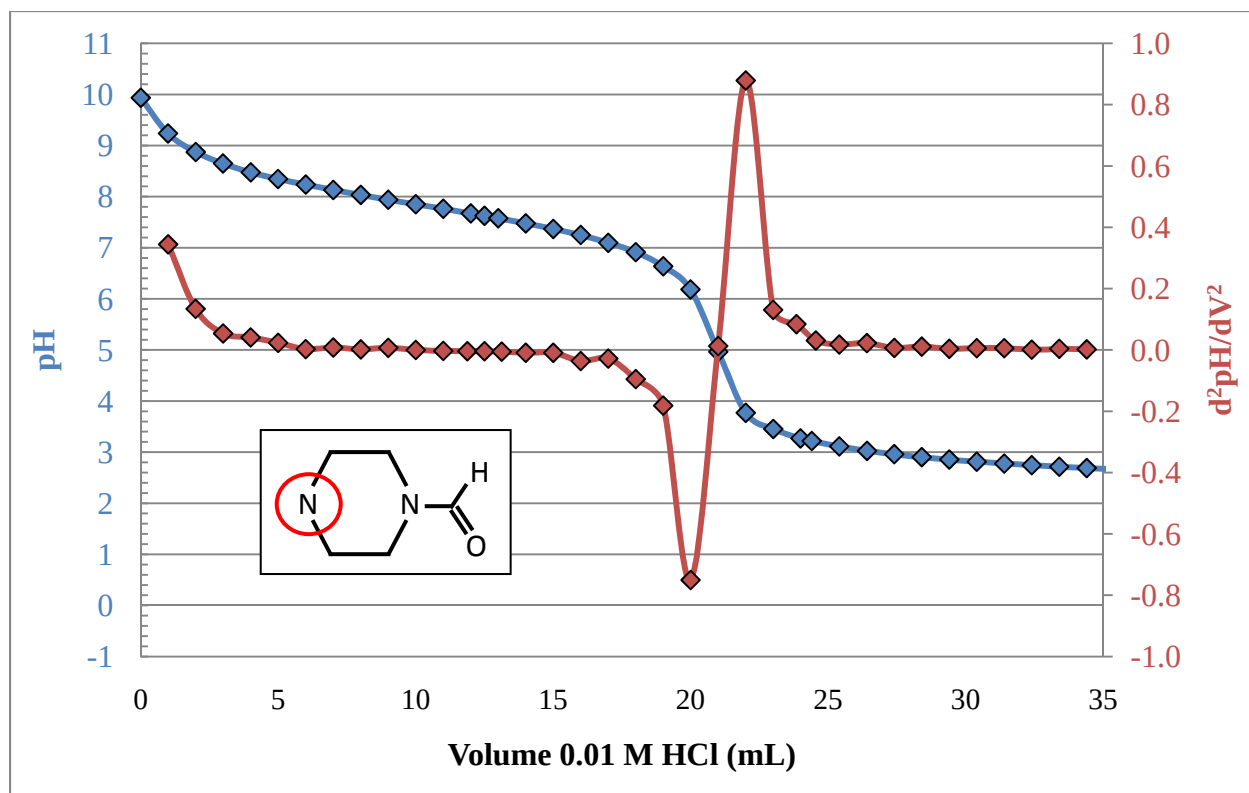


Figure 2: Titration of 0.01 M N-Formyl Piperazine with 0.01 M HCl

Thermal Degradation

In this quarter, a 20 m PZ, 0.1 mole CO₂ per mol alkalinity solution (TDE4) was thermally degraded for a period of 10 weeks at 175 °C to simulate thermal degradation characteristic to a reclaimer. The results are shown below in Figures 3–6.

The average loss rate of total alkalinity, PZ, and CO₂ is 0.185, 0.212, and 0.093 moles/kg/week, respectively. The ratio of total alkalinity and PZ loss to CO₂ loss is 1.990 and 2.280, respectively. FPZ was the dominant degradation product followed by formate, ammonium, and EDA. Glycolate and oxalate were determined to be insignificant carboxylate degradation products. Nitrite, nitrate, HEP, and DMPZ were found in negligible concentrations. Dissolved metals, particularly Fe and Ni, increased with thermal degradation time. Cr was found in negligible amounts.

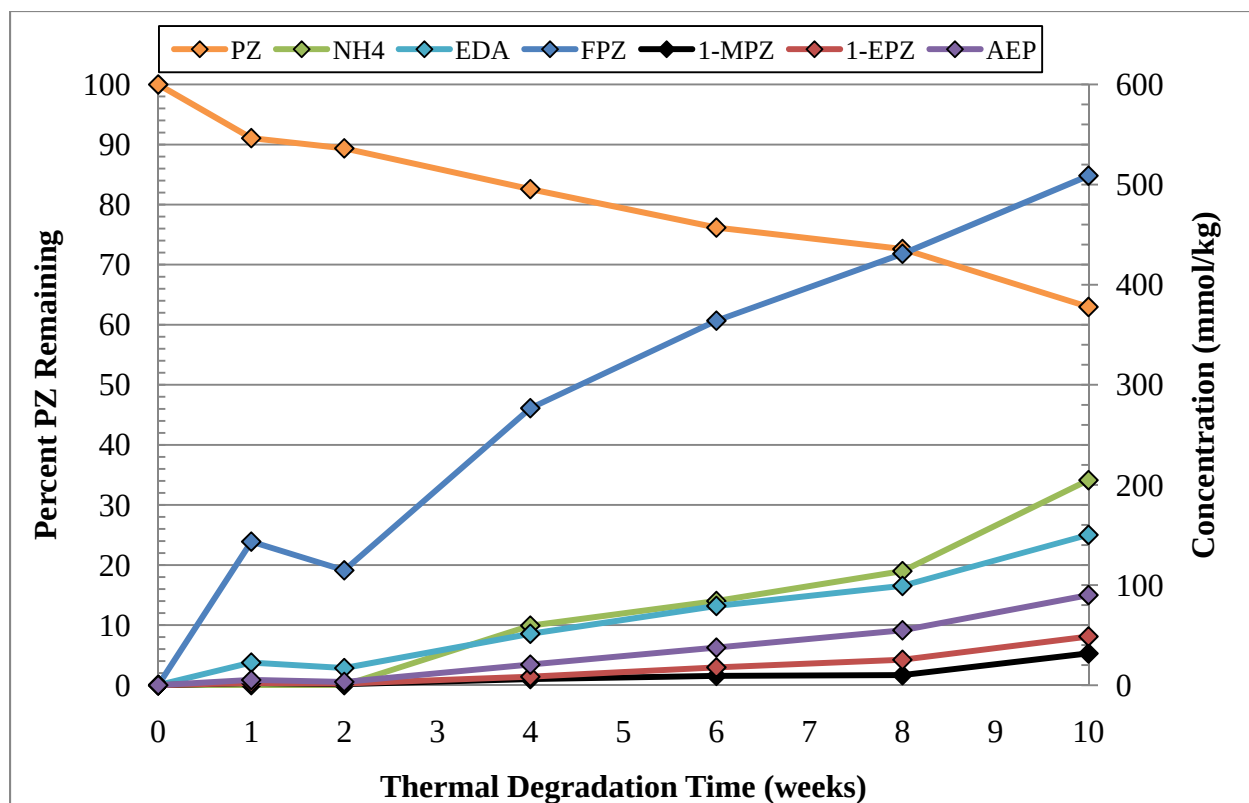


Figure 3: Concentration Profiles for TDE4 (20 m PZ, 0.1 mol CO₂/mol alkalinity, 175 °C)

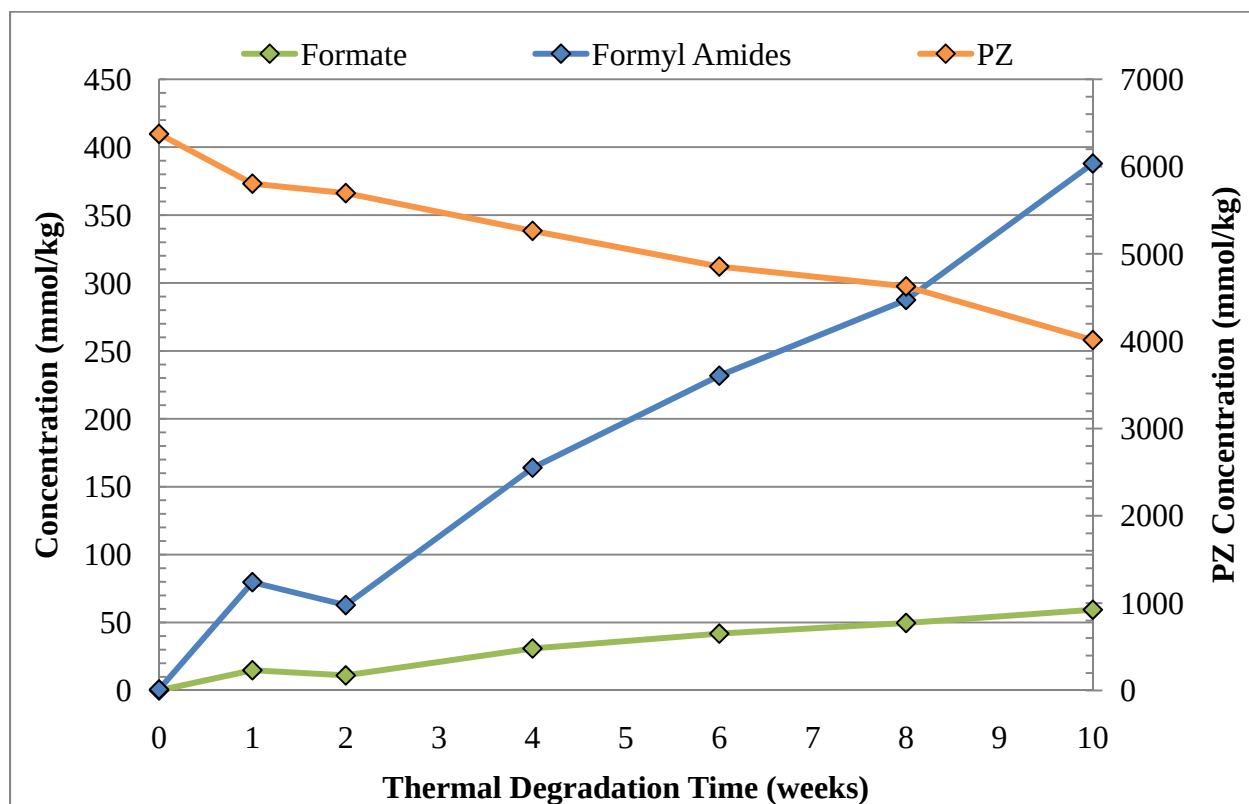


Figure 4: Concentration Profiles for TDE4 (20 m PZ, 0.1 mol CO₂/mol alkalinity, 175 °C)

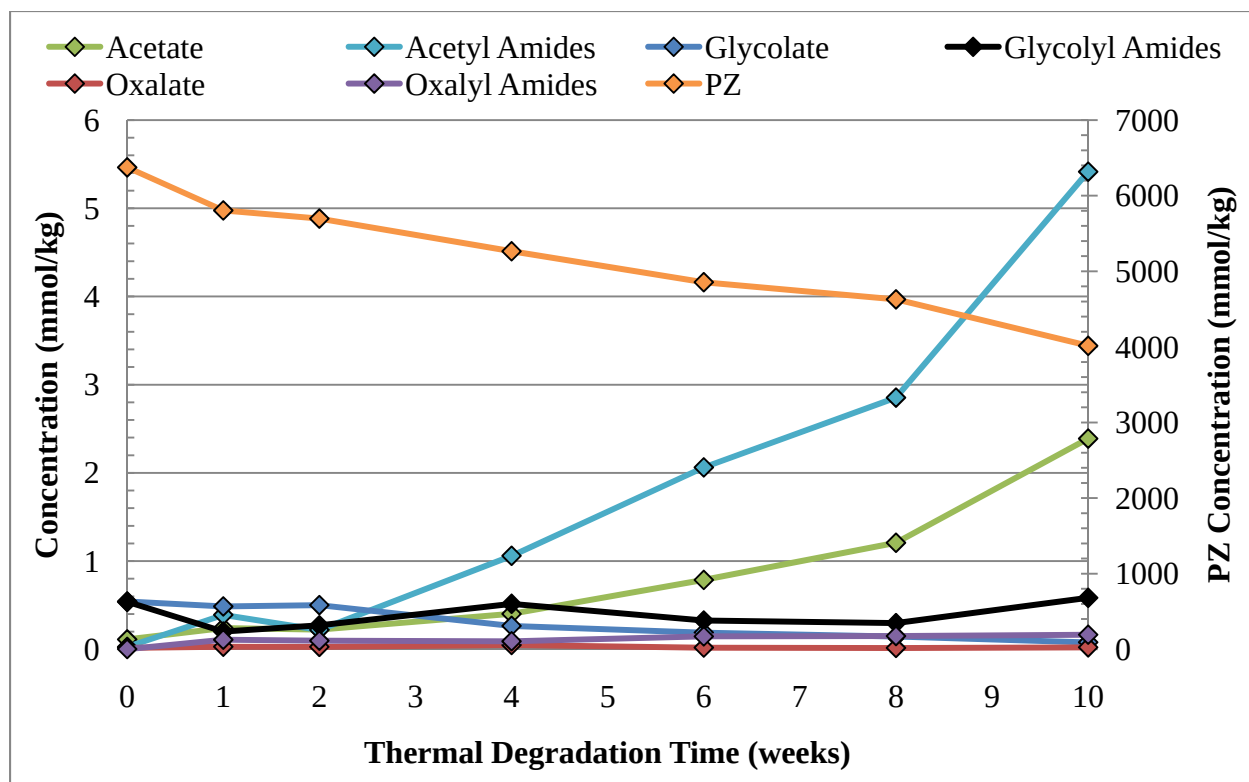


Figure 5: Concentration Profiles for TDE4 (20 m PZ, 0.1 mol CO₂/mol alkalinity, 175 °C)

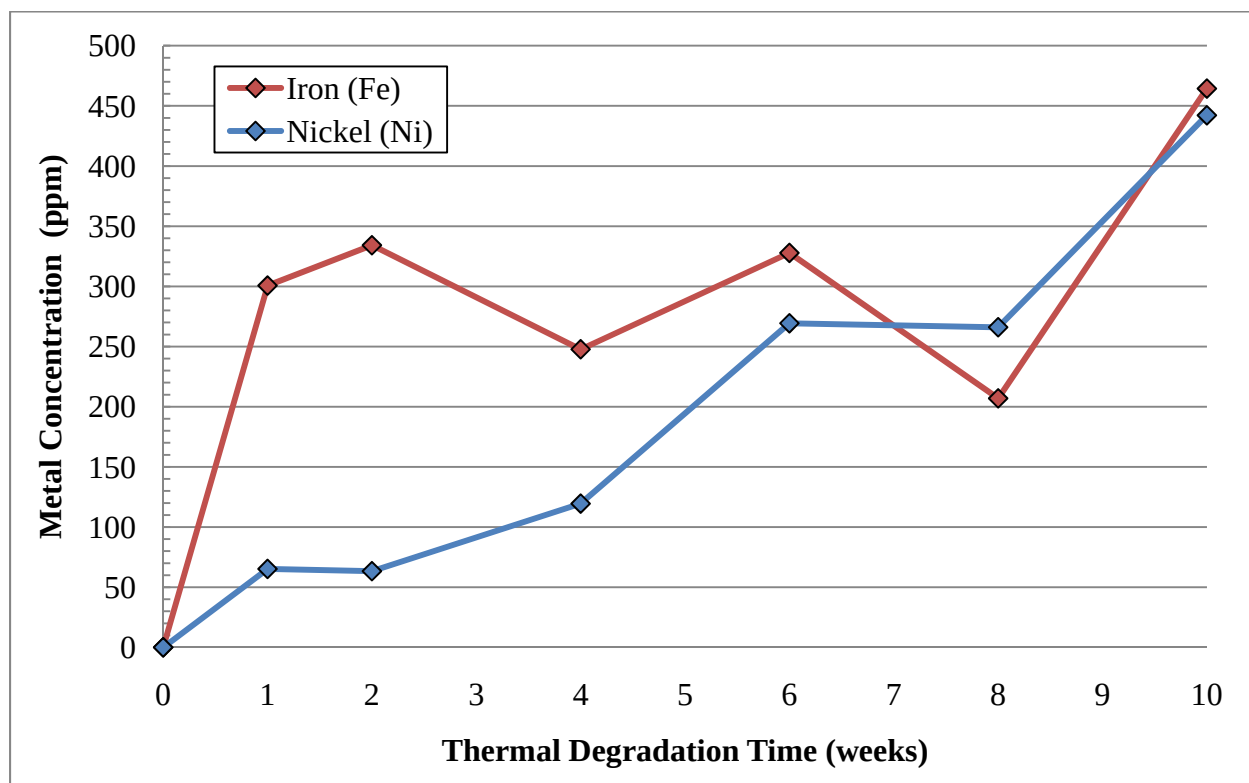


Figure 6: Fe and Ni Concentration Profiles for TDE4 (20 m PZ, 0.1 mol CO₂/mol alkalinity, 175 °C)

Process Modeling

Modeling of thermal reclaimer configurations is necessary to estimate changes in heat duty, chemical make-up rates, and capital cost to an absorption/stripping system. An economic analysis of reclaiming systems and simple “bleed-and-feed” practices for removing process contaminants must be done to justify the use of additional process equipment and potentially higher heat rates.

Modeling of thermal reclaiming systems is difficult for a variety of reasons. First, the range of temperatures and compositions found in thermal reclaiming are at the boundaries of most thermodynamic models. Second, flow rates and heat rates for thermal reclaiming systems are several orders of magnitude smaller than those seen in the absorber/stripper section of the capture process, making integration and convergence difficult. Third, and perhaps most significant, is that reclaiming systems contain non-trivial amounts of a multitude of contaminants, many of which have yet to be identified. Since a variety of contaminants is present in appreciable amounts, adding each component to a thermodynamic model is cumbersome and impractical. Lumped component/pseudo-component methods or other approximations may provide a more practical means of thermodynamic modeling.

Process contaminants for amine-based CO₂ capture systems include heat-stable salts, amides, ureas, metals, and many other non-volatile components. Some contaminants maintain amine functionality. Therefore, any approximation for a collection of contaminants for thermodynamic modeling should include characteristics like amine functionality and non-volatility. Modeling approximations should also be based on thermodynamic measurements and must be extendable to a wide range of possible concentrations and temperatures characteristic of a reclaiming system.

In this work, methyl diethanolamine (MDEA) was used as a “surrogate” for contaminants in PZ reclaimer process modeling. MDEA is a relatively non-volatile component, contains active amine functionality, and is modeled based on numerous thermodynamic measurements using the Fawkes thermodynamic framework for MDEA/PZ blended systems.

Two-Stage Integrated Thermal Reclaimer

The proposed thermal reclaimer design investigated in this work is the “Two-Stage Integrated Thermal Reclaimer,” and is shown in Figure 7 below.

The CO₂ stripping section of the Two-Stage Integrated Thermal Reclaimer consists of a high-pressure heated flash stage and a low-pressure adiabatic flash stage. The reclaiming section consists of an adiabatic flash followed by a heated flash stage. The pressure in the low-pressure flash and both reclaimer flash stages is equal so the heat from the reclaimer vapor can be recovered in the low-pressure flash stage. A heat recovery system for the high-pressure stage vapor is used to recover latent heat associated with water vapor which would otherwise be condensed before the remaining CO₂ is compressed.

The Two-Stage Integrated Thermal Reclaimer was evaluated using a “degraded” 8 m PZ solvent. The concentration of degradation products (MDEA) was specified to be 1 m for every case considered. To maintain total alkalinity, the rich solution was specified as 7.5 m PZ/1 m MDEA. The rich and lean loadings were kept constant at 0.40 and 0.31 for every case considered according to optimization performed by Van Wagener (2010).

The high-pressure (HP) flash tank temperature was kept constant at 150 °C and the heat rate was changed to meet the lean loading specification of 0.31 for every case considered. The low-pressure (LP) flash and both reclaimer pressures were set to be equal. The low-pressure flash and first thermal reclaimer (R-1) were set as adiabatic. The second thermal reclaimer (R-2) was set to operate at 150 °C due to thermal degradation considerations.

All heat exchangers were specified to have approach temperatures of no less than 5 K on either the cold or hot side. Pinch locations for the heat exchangers in the high-pressure vapor heat recovery loop change according to reclaimer flow rates, so specifying an approach side for each exchanger can lead to infeasibilities.

The rich pump outlet pressure was adjusted for each simulation to match the high-pressure flash stage plus an additional 50 kPa to account for frictional loss. The lean pump outlet pressure was kept constant at 275 kPa to account for frictional and gravitational losses in returning the lean stream to the absorber. In cases in which the low-stage pressure exceeded 275 kPa, the lean pump work was neglected in total equivalent work calculations.

Total equivalent work for each case was calculated using Equation 4 shown below:

$$W_{eq} = \sum_{i=1}^{n_{reboilers}} 0.75 Q_i \left(\frac{T_i + 5 \text{ K} - T_{sink}}{T_i + 5 \text{ K}} \right) + W_{pumps} + W_{comps} \quad (4)$$

Total equivalent work includes heat duty (Q_i) of supplied steam at a specified temperature (T_i) plus a driving force of 5 K, the work of pumps (W_{pumps}), and compression work (W_{comps}). The sink temperature was assumed to be 313 K for each case. The compression work for the multistage compressor was approximated using a correlation developed by Van Wagener (2010), and is shown below in Equation 5. The correlation provides an accurate method for estimating compression work by neglecting the effects of small quantities of vaporized amine which can significantly affect convergence. The outlet pressure was held at 150 bar. P_{in} is equal to the highest pressure stage in bar.

$$W_{comp} \left(\frac{\text{kJ}}{\text{gmol CO}_2} \right) = \begin{cases} 4.572 \ln \left(150/P_{in} \right) - 4.096, & P_{in} \leq 4.56 \text{ bar} \\ 4.023 \ln \left(150/P_{in} \right) - 2.181, & P_{in} > 4.56 \text{ bar} \end{cases} \quad (5)$$

Remaining adjustable variables include the reclaimer flow rate and the low-stage pressure. The reclaimer flow rate is specified as a percentage of the lean flow rate and was varied between 0.5 and 3%. The low-stage pressure was varied between 1 and 4 bar.

Figures 8–13 show simulation results for heat work, compression work, total work, HP flash pressure, HP and LP flash vapor rates, purge stream total molality, and the ratio of contaminants (total MDEA) to PZ in the purge stream.

As the reclaimer flow rate increases, vapor production in both reclaimers, and subsequently the LP flash stage increases. Increased vapor production in the low-pressure stage decreases the vapor production in the HP stage, which results in an increased pressure and increased CO₂ selectivity. However, as the low-stage pressure decreases, CO₂ selectivity decreases causing the HP vapor production curve to increase with increasing reclaimer flow rates. At a low-stage pressure of 4 bar, the vapor rate out of the LP flash drops to zero; CO₂ from the reclaiming stages increases the loading in the LP flash, causing the HP flash to remove more CO₂ than necessary. The subtle effect of CO₂ dilution of the LP flash causes the upward curvature of the HP flash

vapor rate for the 4 bar case; Figure 13 illustrates the dilution effect. An increase in the pressure of the HP stage decreases the multi-stage compressor work and the latent heat associated with vaporized water, but the rich pump work, low-pressure CO₂ compression work, and reclaimer heat rate all increase.

An increase in low-stage pressure reduces the pressure in the HP flash causing an increase in the multi-stage compressor work. However, increasing the low-stage pressure significantly decreases the rich pump and low-pressure CO₂ compression work as well as the reclaimer heat rate. The combination of effects causes equivalent work to decrease with increasing low-stage pressure.

The effects of the heat integration network are much more subtle, though the overall effect is to reduce the total heat rate for the process. Increasing the reclaimer flow rate allows more heat recovery from the HP vapor, but increasing the reclaimer flow rate decreases the HP vapor rate. Increasing the reclaimer flow rate also decreases the heat recovery from the rich/lean exchanger, meaning the HP heated flash must provide more sensible heat.

The difference in mass flow rate between the reclaiming flow stream and the HP vapor dictates the distribution of the heat recovery between exchangers HP-1 and HP-2. For reclaimer flow rates above 0.5%, the rate is high enough that the pinch in the heat exchanger network occurs on the cold-side of HP-1. Since the first reclaimer (R-1) is adiabatic, the cold-side pinch on HP-1 necessarily corresponds to the hot-side pinch on HP-2, meaning very little heat is exchanged in HP-2 for reclaimer flow rates above 0.5%. As the reclaimer flow rate decreases, the amount of heat exchange in HP-2 increases causing an increase in R-1 vapor production. The only case in which the temperature pinch did not simultaneously occur on the cold-side of HP-1/hot-side of HP-2 was the 0.5% reclaimer flow rate case in which the temperature pinch was on the hot-side of HP-1. As a consequence of the temperature approach specification for every heat exchanger, the temperature pinched simultaneously on the hot/cold-side of HP-1 and the hot-side of HP-2, meaning very little heat was exchanged in HP-1.

The molality and contaminant (MDEA) to PZ ratio are independent of reclaimer flow rate, though model instability shows deviation at significantly high molality. As the low-stage pressure is reduced the molality and contaminant/PZ ratio increase due to increased vaporization of PZ as expected.

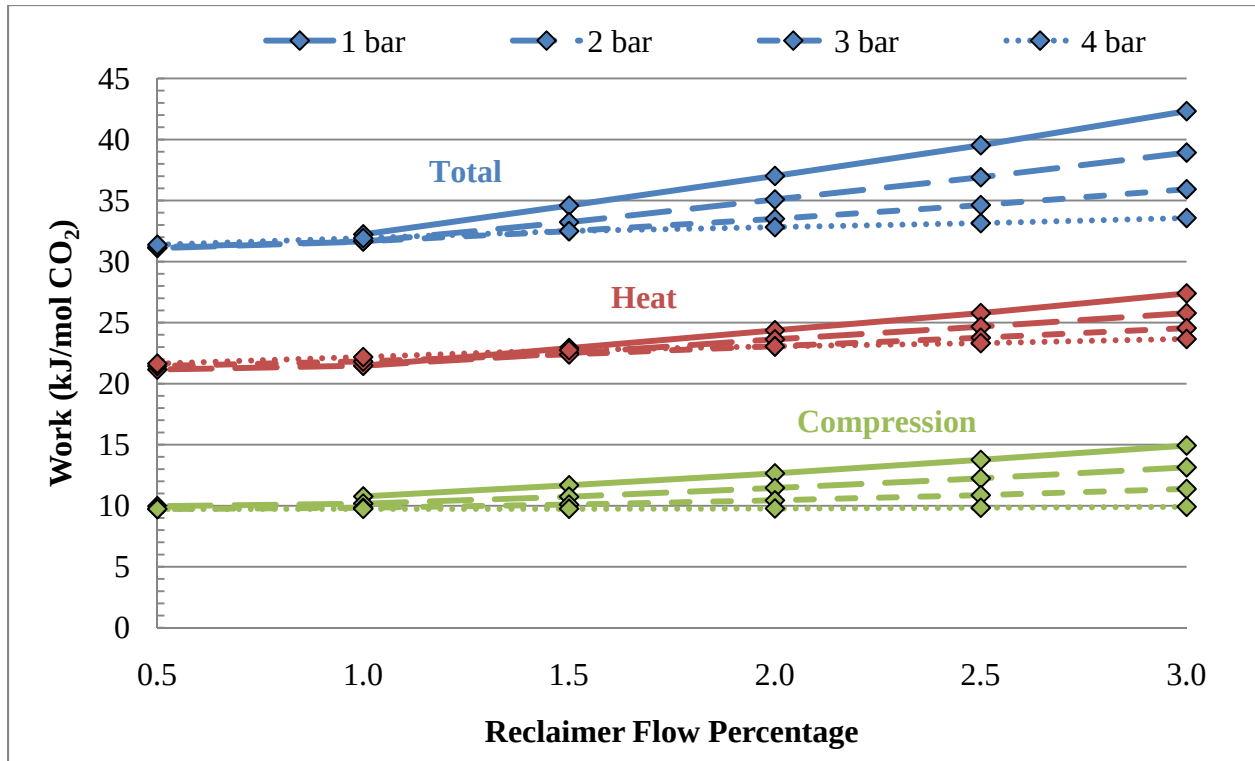


Figure 8: W_{eq} , Q , and W_{comp} for a Two-Stage Integrated Thermal Reclaimer. 7.5 m PZ/1 m MDEA, $\alpha_{lean} = 0.31$, $\alpha_{rich} = 0.40$, $T_{reb} = 150$ °C, and compression to 150 bar.

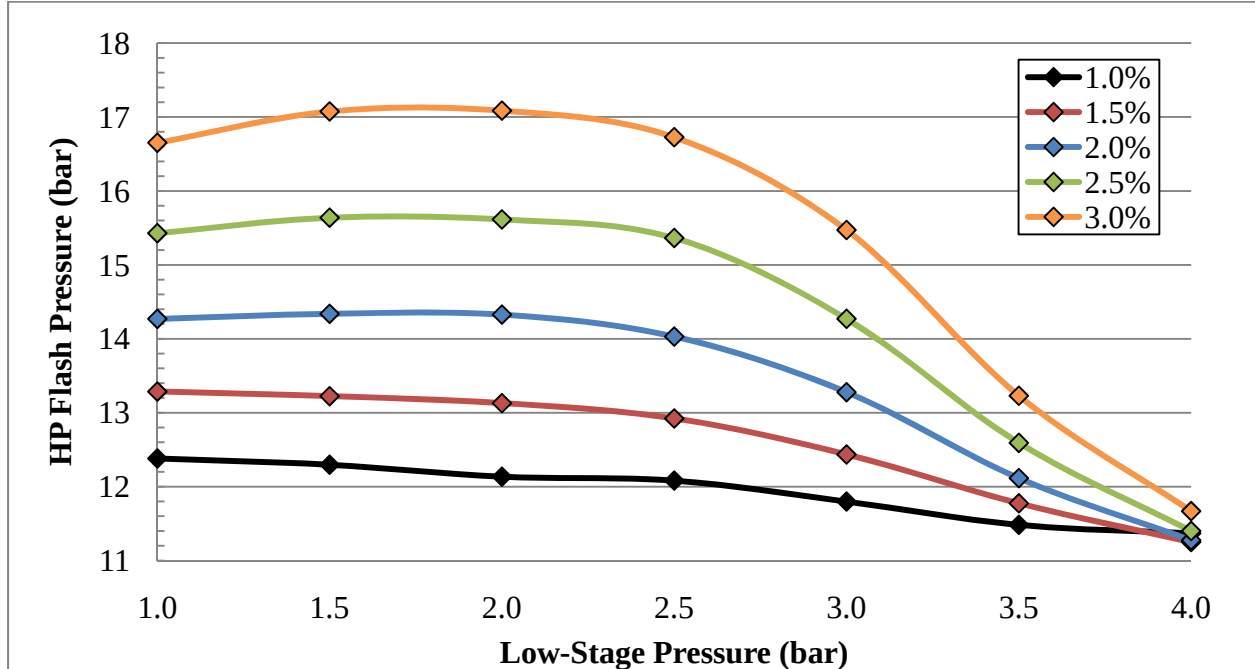


Figure 9: HP Flash P for a Two-Stage Integrated Thermal Reclaimer. 7.5 m PZ/1 m MDEA, $\alpha_{lean} = 0.31$, $\alpha_{rich} = 0.40$, $T_{reb} = 150$ °C, and compression to 150 bar.

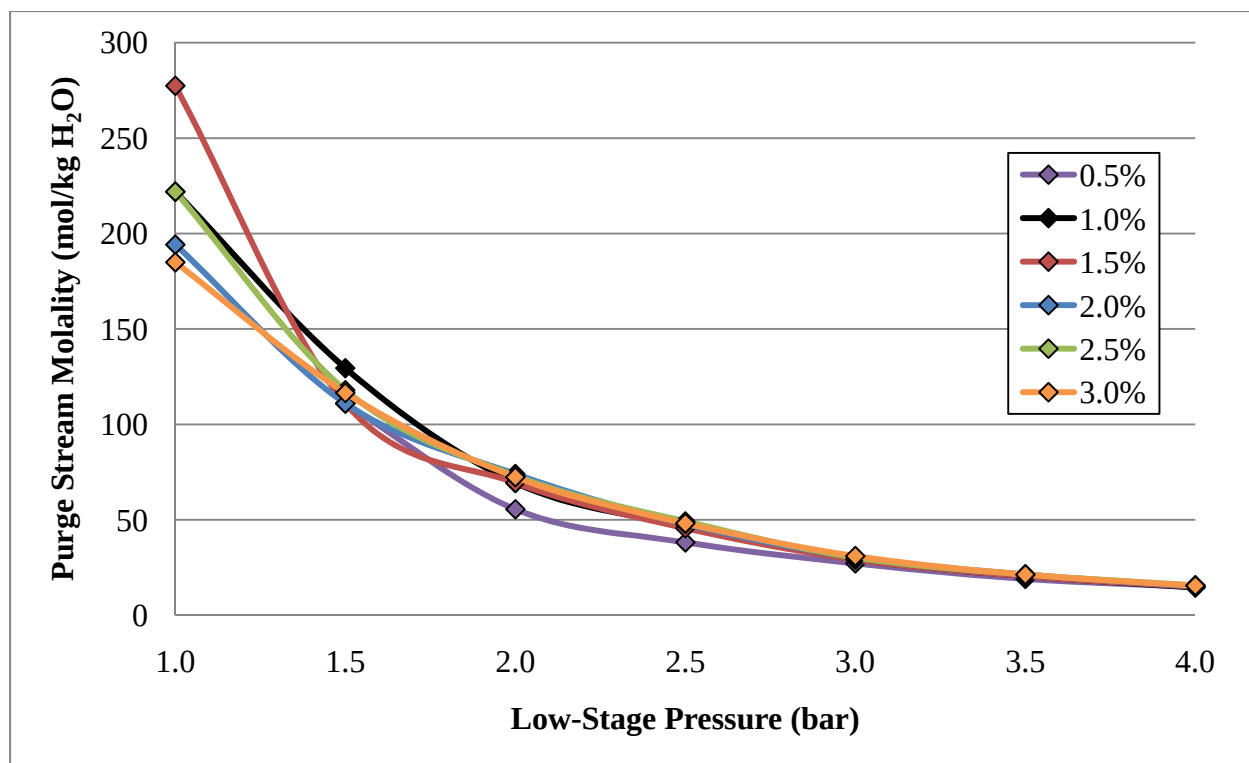


Figure 10: Purge Molality for a Two-Stage Integrated Thermal Reclaimer. 7.5 m PZ/1 m MDEA, $\alpha_{\text{lean}} = 0.31$ lean, $\alpha_{\text{rich}} = 0.40$, $T_{\text{reb}} = 150$ °C, and compression to 150 bar.

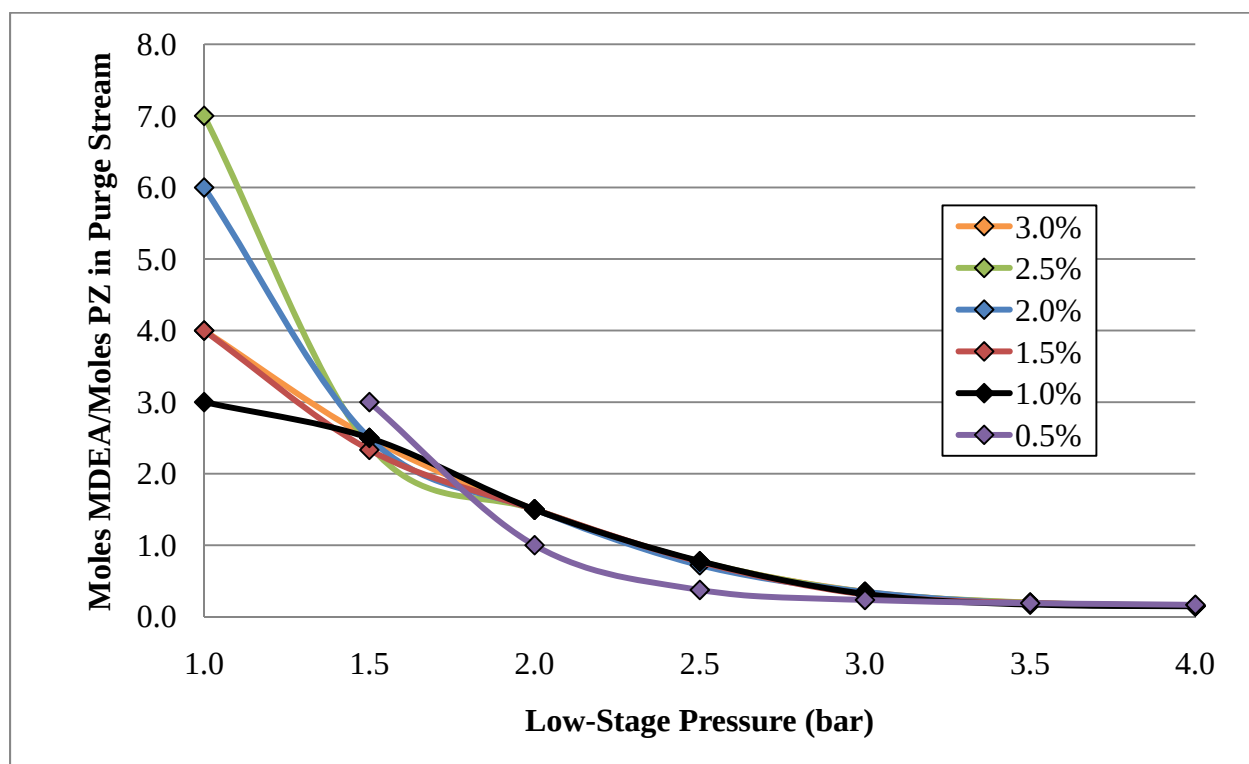


Figure 11: MDEA/PZ Ratio for a Two-Stage Integrated Thermal Reclaimer. 7.5 m PZ/1 m MDEA, $\alpha_{\text{lean}} = 0.31$, $\alpha_{\text{rich}} = 0.40$, $T_{\text{reb}} = 150$ °C, and compression to 150 bar.

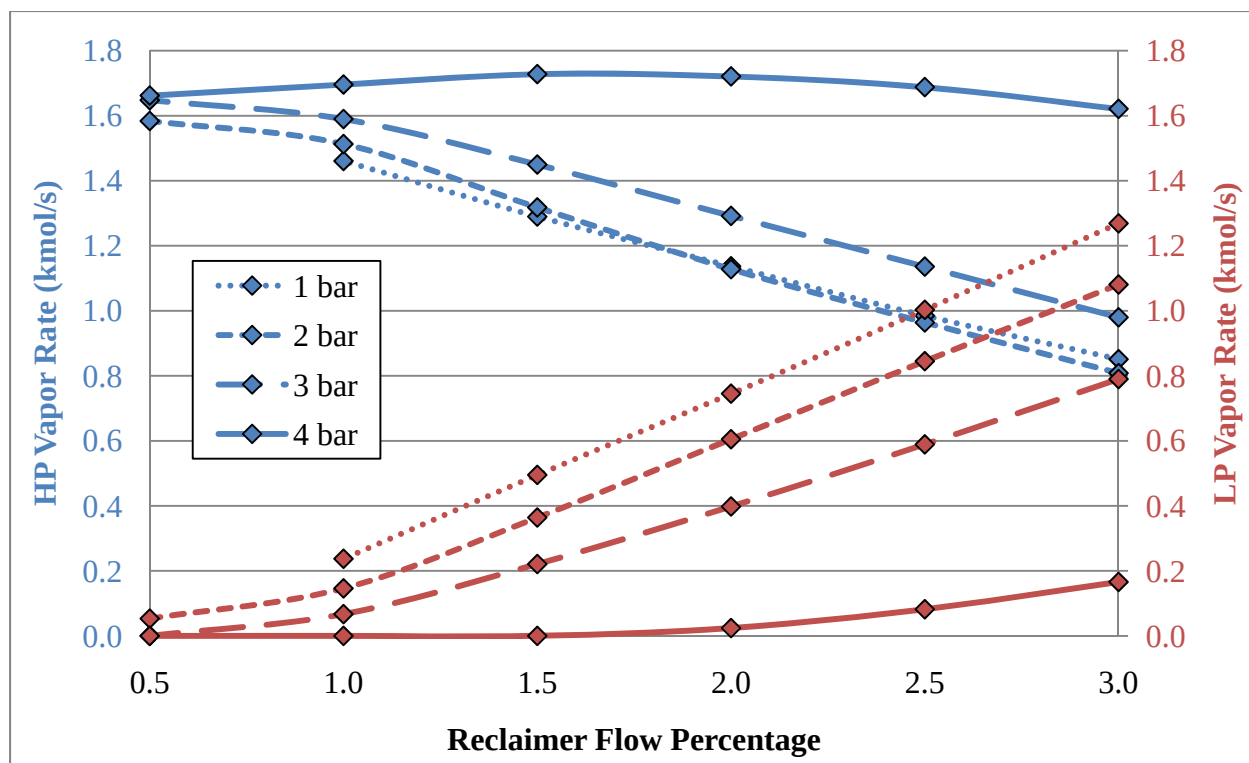


Figure 12: HP and LP Vapor Rates for a Two-Stage Integrated Thermal Reclaimer. 7.5 m PZ/1 m MDEA, $\alpha_{\text{lean}} = 0.31$, $\alpha_{\text{rich}} = 0.40$, $T_{\text{reb}} = 150^\circ\text{C}$, and compression to 150 bar.

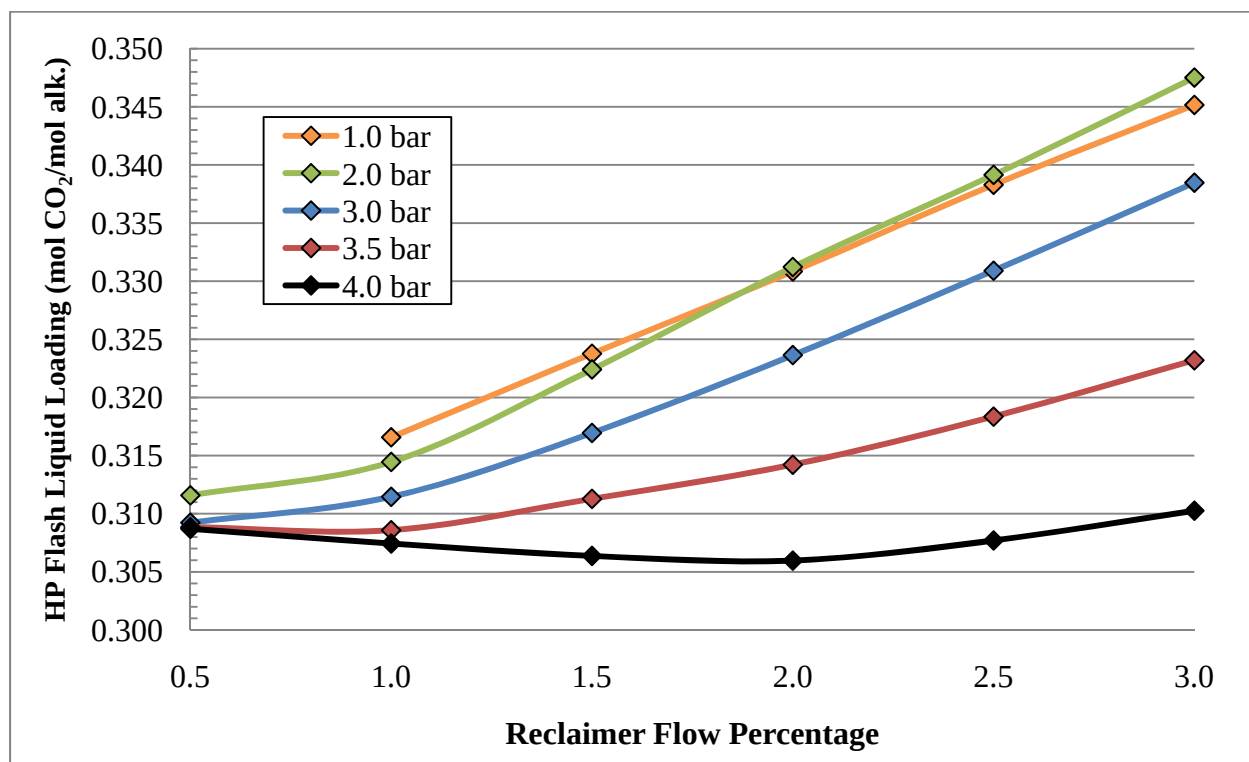


Figure 13: HP Flash Liquid Loading for a Two-Stage Integrated Thermal Reclaimer. 7.5 m PZ/1 m MDEA, $\alpha_{\text{lean}} = 0.31$, $\alpha_{\text{rich}} = 0.40$, $T_{\text{reb}} = 150^\circ\text{C}$, and compression to 150 bar.

Case Study

Using MDEA as a surrogate for degradation products allows for direct estimation of removal rates for a collection of contaminants. If an estimate of contaminant production normalized to removal rate is given, reclaimer flow rates, energy requirements, and amine make-up rates can be extrapolated from previous simulation results.

One case study was considered for this work, the assumptions for which are presented in Table 4. Solvent molality, contaminant molality, lean loading, and rich loading were kept constant and equal to previous simulation values.

Table 4: Parameter Assumptions Used to Estimate Energy, Make-Up, Disposal, and Total Costs for a Two-Stage Integrated Reclaiming System

Parameter (Units)	Value
Contaminant Production Rate (mol MDEA/mol CO ₂ Removed)	1x10 ⁻⁵
CO ₂ Capacity (mol CO ₂ /kg solvent)	0.725
Energy Price (\$/MWh)	100
Fresh PZ Price (\$/kg)	4.84
PZ Disposal Cost (\$/kg)	4.84
MDEA Disposal Cost (\$/kg)	4.84

MDEA and PZ removal rates were found to be linear functions of reclaimer flow percentage, (Figures 14 and 15), and were modeled using linear fits forced through zero, since a reclaimer flow percentage of zero implies no removal. Reclaimer flow percentages were varied for low-stage pressures from 1-4 bar to match the removal rate of MDEA for each respective CO₂ capture rate.

Total equivalent work asymptotes at approximately 31.12 kJ/mol and shows non-linear behavior towards reclaimer flow percentage. A second-order fit for total equivalent work with respect to reclaimer flow percentage forced through 31.12 kJ/mol was used to estimate the total equivalent work for each low-stage pressure.

Fitting both removal rate and total equivalent work using linear and quadratic curve fits can lead to problematic results. Small changes in polynomial coefficients can lead to several orders of magnitude difference in calculated values for such small values of reclaimer flow percentages. Forcing the removal curves through zero and the total equivalent work curves through an asymptotic value show the correct order of magnitude relationship change in relation to the reclaimer flow percentage.

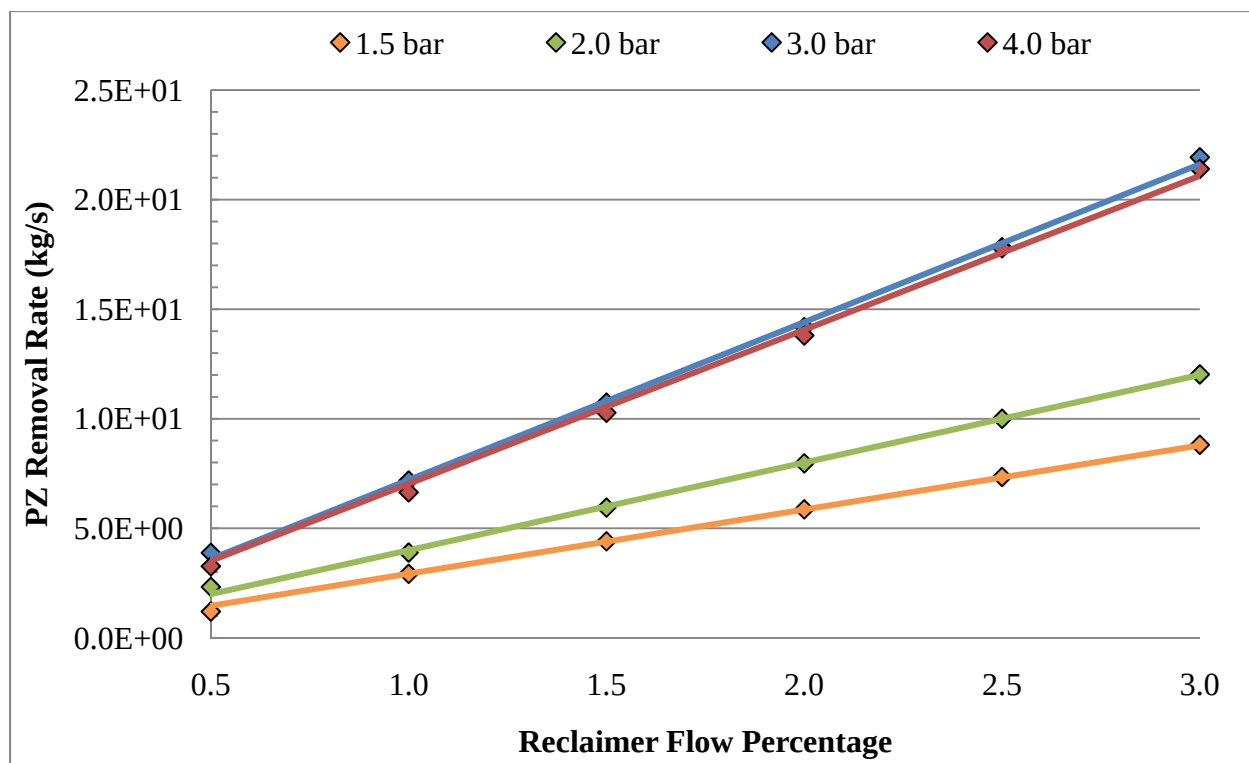


Figure 14: PZ Removal Rate for 1×10^{-5} Mole Contaminant Produced/Mole CO_2 Captured Using a Two-Stage Integrated Thermal Reclaimer

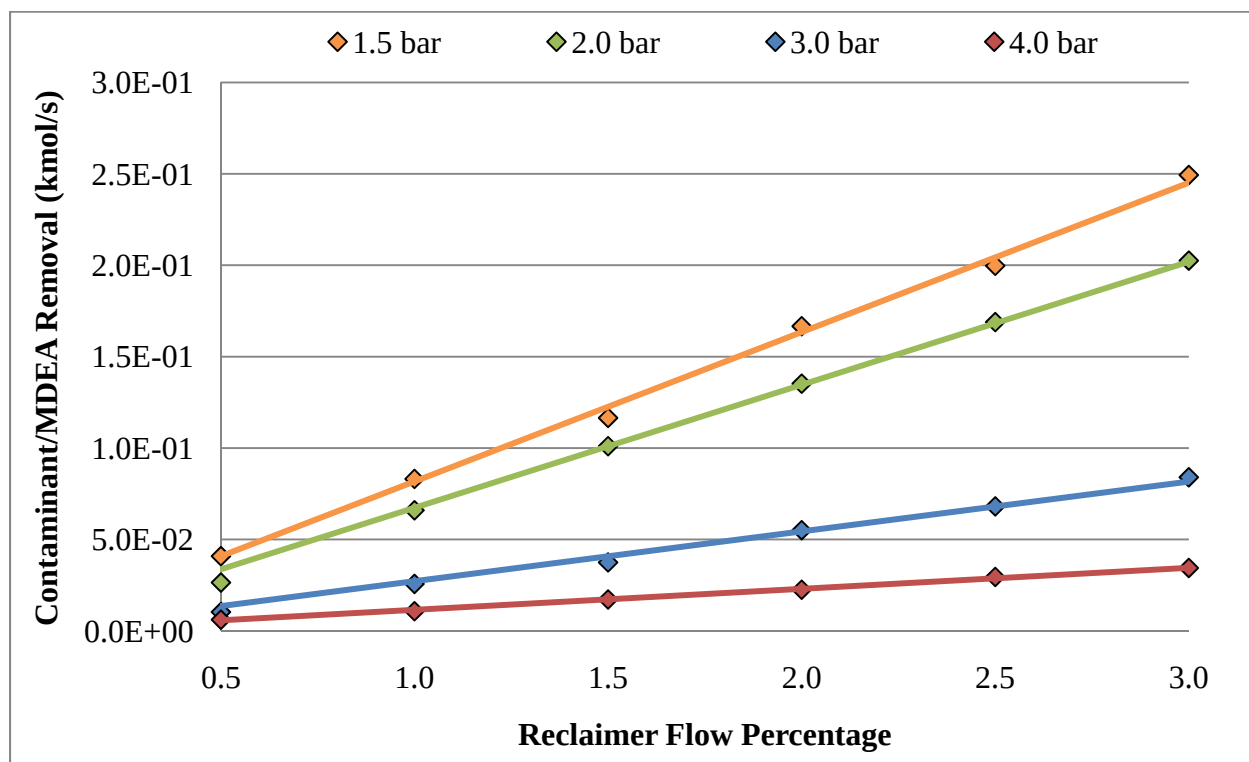


Figure 15: Contaminant/MDEA Removal Rate for 1×10^{-5} Mole Contaminant Produced/Mole CO_2 Captured Using a Two-Stage Integrated Thermal Reclaimer

Applying the assumptions listed above, the reclaimer flow percentage, energy cost, make-up cost, disposal cost, and total cost can be calculated for each low-stage pressure. The results are shown in Figures 16 and 17.

The required reclaimer flow percentage to remove 1×10^{-5} moles of general contaminants produced for every mole of CO_2 captured was between 1×10^{-4} and 1×10^{-3} percent which is several orders of magnitude less than the often quoted value of 1–3%. Davis (2009) found a similar order of magnitude for a reclaimer flow percentage (2×10^{-5} %) for an MEA system by minimizing the overall thermal degradation rate.

The energy cost was shown to be independent of the low-stage pressure. The combination of make-up and disposal costs increased with increasing low-stage pressure due to the increase in required reclaimer flow percentage and the decrease in total MDEA to total PZ ratio found in the purge stream. The make-up and disposal costs are much more important considerations when designing a thermal reclaiming system than energy cost, assuming a consistent contaminant production rate and constant reboiler temperatures.

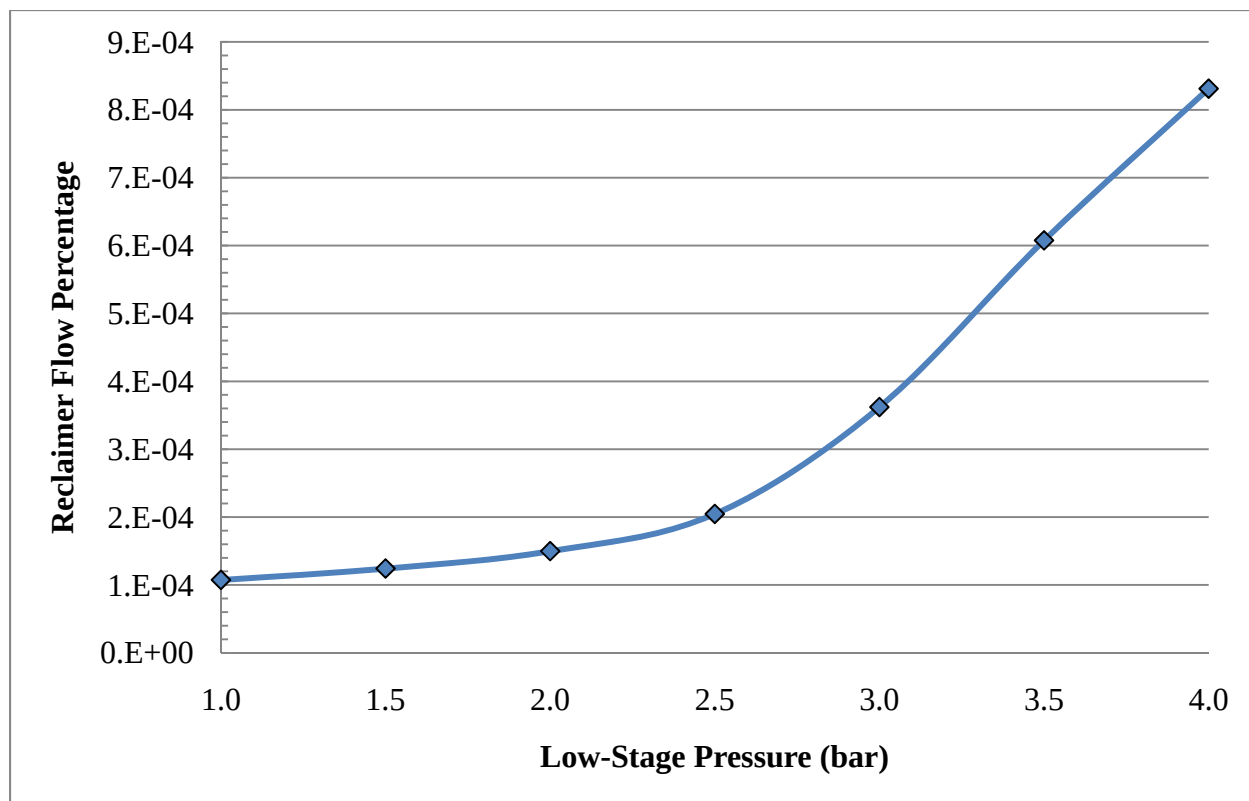


Figure 16: Reclaimer Flow Percentage for 1×10^{-5} Mole Contaminant Produced/Mole CO_2 Captured Using a Two-Stage Integrated Thermal Reclaimer

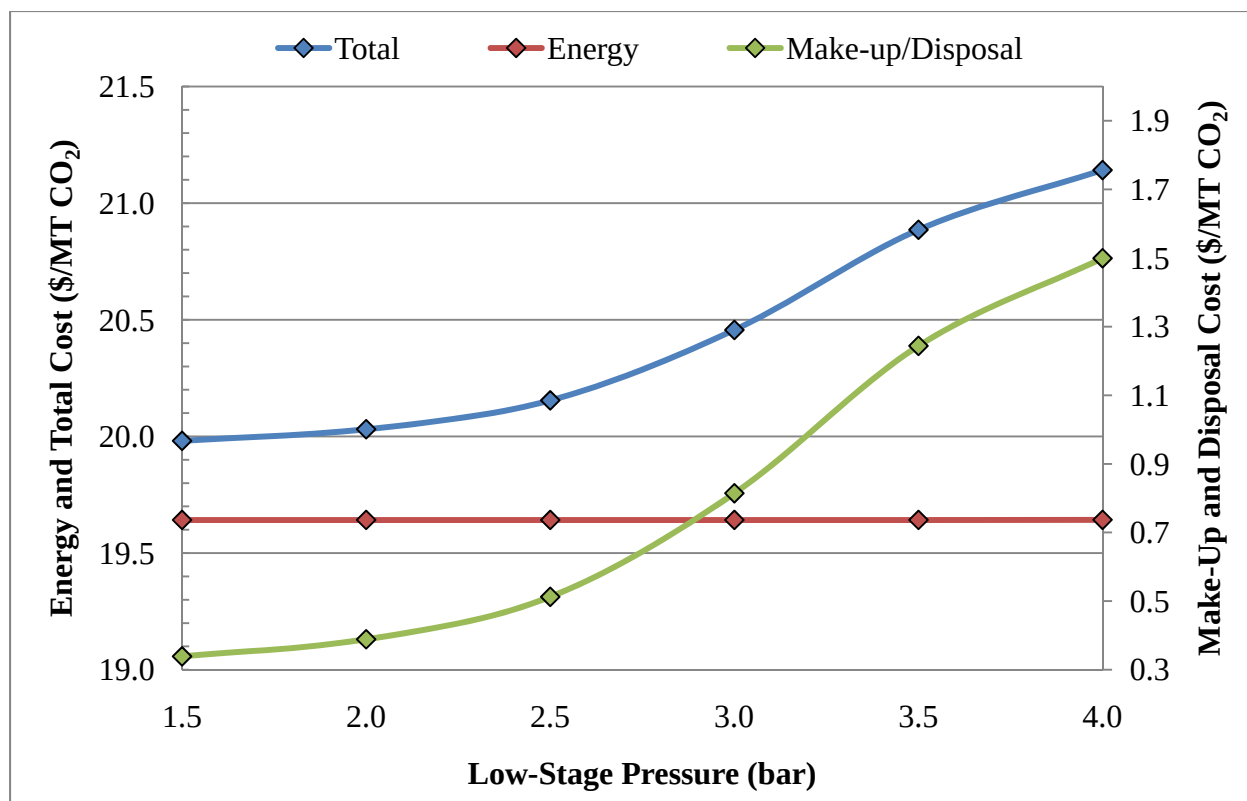


Figure 17: Energy, Make-Up/Disposal, and Total Cost for 1×10^{-5} Mole Contaminant Produced/Mole CO₂ Captured Using a Two-Stage Integrated Thermal Reclaimer

Conclusions

An 8 m PZ, 0.1 mol Inh A per kg H₂O solution formed two liquid phases for $0 \leq \text{loading} \leq 0.375$ by addition of anhydrous K₂CO₃. For a total solution loading of approximately 0.375, K⁺ and CO₂ are 50 and 60 times more concentrated in the bottom, aqueous phase, respectively. PZ was 335 times more concentrated in the top, organic phase. Measureable Inh A was 2 times more concentrated in the top, organic phase.

Adding anhydrous KOH to an 8 m PZ, 0.1 mol Inh A per kg H₂O, 0.3 mole CO₂ per mole alkalinity solution precipitated KHCO₃, preventing liquid-liquid separation.

The pK_a of the free amine functionality group for N-formyl piperazine (FPZ) was measured as 7.807. At high pH conditions in a reclaimer, FPZ will exist primarily as the de-protonated species, reducing potential volatile losses.

A 20 m PZ solution initially loaded to 0.1 moles CO₂ per mole alkalinity was thermally degraded for a period of 10 weeks at 175 °C. The average loss rate of total alkalinity, PZ, and CO₂ was 0.185, 0.212, and 0.093 moles per kg, respectively. The ratio of total alkalinity and PZ loss to CO₂ loss was 1.990 and 2.280, respectively. FPZ was the dominant degradation product followed by formate, ammonium, and EDA. Glycolate and oxalate were determined to be insignificant carboxylate degradation products. Nitrite, nitrate, HEP, and DMPZ were found in negligible concentrations. Dissolved metals, particularly Fe and Ni, increased with thermal degradation time. Cr was found in negligible amounts.

A two-stage integrated thermal reclaimer was designed in Aspen Plus[®] using the Fawkes thermodynamic framework. MDEA was used as a surrogate for a collection of unknown degradation products for thermodynamic modeling. An economic case study was investigated assuming a constant contaminant production rate of 1×10^{-5} moles/mole CO₂ captured.

The energy cost for the reclaiming system was independent of the low-stage pressure. The make-up and disposal costs are much more important considerations when designing a thermal reclaiming system than energy cost, assuming a consistent contaminant production rate and constant reboiler temperatures.

Future Work

Goals for next quarter include continued phase characterization experiments for contaminant and inhibitor separation using liquid-liquid separation. Thermal degradation experiments for solutions containing KOH, KHCO₃, and K₂CO₃, to mimic neutralized reclaiming solutions, will be analyzed.

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Solvent Reclaiming by Solids Precipitation and PZ blend Solubilities

Quarterly Report for January 1 – March 31, 2011

by Humera Abdul Rafique

Supported by the Luminant Carbon Management Program

Department of Chemical Engineering

The University of Texas at Austin

April 30, 2011

Abstract

8 m PZ (40%) exists in liquid form between loadings of 0.32 and 0.43 mol CO₂/ mol alkalinity. The solid phase at the lean end is PZ.6H₂O and that at the rich end is H⁺PZCOO⁻.H₂O. To expand the solubility envelope, solid solubility experiments were carried out for the following blends: 3.75 m PZ/3.75 m 1MPZ/0.5 m 1,4DMPZ; 4 m PZ/4 m 2MPZ; 6 m PZ/2 m 2MPZ. To better understand the properties of the 2MPZ loaded blend, solid solubility for 8 m 2MPZ was also studied. Because of the lower concentration of PZ in the blends, the PZ.6H₂O precipitated at lower loadings (0.23 and 0.15 mol CO₂/mol alkalinity for 3.75 m PZ/3.75 m 1MPZ/0.5 m 1,4DMPZ and 4 m PZ/4 m 2MPZ, respectively). A maximum loading of 0.23 and 0.15 mol CO₂/mol alkalinity was obtained for the 3.75/3.75/0.5 and 4/4, respectively. No solid precipitation was observed as with 8 m PZ. 8 m 2MPZ precipitated out H⁺2MPZCOO⁻.H₂O at a loading of 0.47 mol CO₂/mol alkalinity.

The electrolyte-NRTL model in Aspen Plus[®] can be used for data regression of the sulfate solubility experimental analysis to model a sulfate reclaiming system. The model uses an energy parameter, τ , and a non-randomness factor, α , to calculate the activity coefficient of the ionic species specified in the model. This in turn enables us to calculate the solubility product of the salt in PZ over a wide range of temperatures and amine concentrations.

Introduction

This quarter, CO₂ loading capacities and solubilities of some PZ blends were measured. The blends included 3.75 m PZ/3.75 m 1MPZ/0.5 m 1,4DMPZ, 4 m PZ/4 m 2MPZ, 6 m PZ/2 m 2MPZ and 8 m 2MPZ. A CO₂ loading of approximately 0.25 mole CO₂/ mol alkalinity is required to maintain a liquid solution of 8 m PZ without precipitation at room temperature (20 °C) (Freeman, 2009). Piperazine hexahydrate (PZ.6H₂O) is formed in PZ loaded solutions lower than 0.22 mole CO₂ per mole of alkalinity at 25 °C for 8 m PZ. Because of a lower concentration of PZ in the blends, the PZ.6H₂O precipitates out at lower temperatures, expanding the solubility envelope of the blend.

Aspen Plus[®] modeling for the prediction of electrolyte interaction parameters and K₂SO₄ solubility in loaded PZ solutions was started. This work will allow us to predict the energy

parameter τ in the e-NRTL model in Aspen Plus[®]. The values predicted will be used to calculate the activity coefficients and therefore the solubility product K_{sp} of K_2SO_4 in PZ.

Experimental Methods

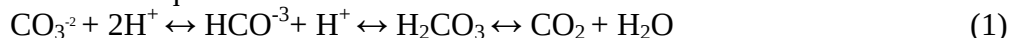
The experimental method for the solid solubility analysis of PZ and PZ blends is detailed in previous quarterly reports (Rochelle et al., 2010a).

Analytical Methods

The concentration of PZ, 1MPZ, and 2MPZ in the samples was analyzed using a cation chromatograph. The total alkalinity of the blends of PZ/2MPZ was measured using titration because the retention time of the PZ and 2MPZ in the cation chromatograph overlap. The CO_2 concentration in solutions was determined using a Total Inorganic Carbon (TIC) Analyzer, and the SO_4^{2-} concentration was analyzed using an anion chromatograph.

Cation Chromatography: A Dionex ICS-2500 with a CS17 IonPac column with 4-mm Cationic Self-Regenerating Suppressor (CSRS) was used as previously described by Sexton (2008) with DDI in the eluent.

Total Inorganic Carbon Analyzer: Quantification of CO_2 loading was performed using a total inorganic carbon analyzer. In this method, a sample is acidified with 30 wt % H_3PO_4 to release the CO_2 present in solution (Hilliard, 2008). The CO_2 is carried in the nitrogen carrier gas stream to the detector. PicoLog software was used to record the peaks produced from each sample. A calibration curve was prepared at the end of each analysis using a TIC standard mixture of K_2CO_3 and $KHCO_3$. The TIC method quantifies the CO_2 , CO_3 , and HCO_3 present in solution. These species are in equilibrium in the reaction below:



Acidification of the sample shifts the equilibrium toward CO_2 which bubbles out of solution and is detected in the analyzer (Rochelle et al., 2010a).

Results and Discussion

Solid Solubility

The structures for 1-methyl-PZ (1-MPZ) and 2-methyl-PZ (2-MPZ) are:

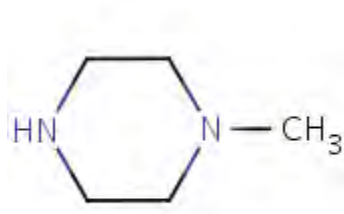


Figure 1: 1-methyl-PZ (1-MPZ)

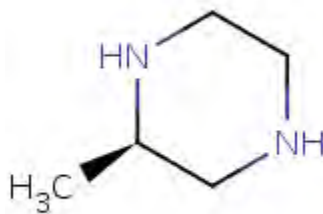


Figure 2: 2-methyl-PZ (2-MPZ)

The blends that were taken into consideration were:

3.75 m PZ/3.75 m 1MPZ/0.5 m 1,4DMPZ

4 m PZ/4 m 2MPZ

6 m PZ/2 m 2MPZ and

8 m 2MPZ

Solid solubility experiments were carried out for the blends as described in previous quarterly reports (Rochelle et al., 2010b). For 3.75 m PZ/3.75 m 1MPZ/0.5 m 1,4DMPZ, a maximum CO₂ loading of 0.39 was obtained at room temperature and 0.43 at 20 °C. No solids were observed at the rich end of the solution. Because of a lower concentration of PZ in the blends, the PZ.6H₂O formed at low loadings precipitates at approximately 33 °C. Per conversations with Xi Chen, the operating range of this blend is between 0.23 and 0.32 moles of CO₂ per mole of alkalinity. The solubility envelope for the blend is shown in black in Figure 3.

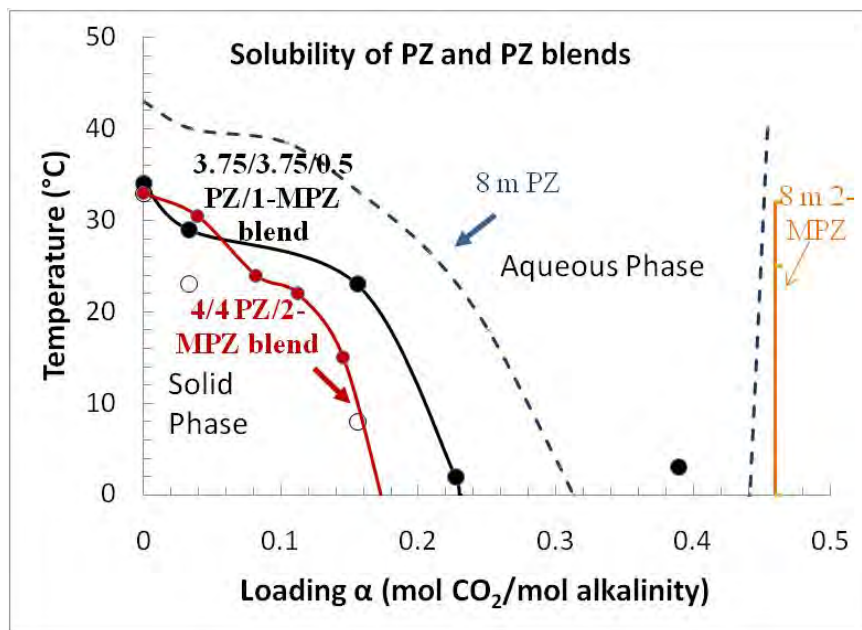


Figure 3: Solubility curves of PZ and PZ blends

For 4 m PZ/4 m 2MPZ, a maximum CO₂ loading of 0.47 was obtained at room temperature without any solid precipitation H⁺PZCOO⁻.H₂O. The PZ.6H₂O precipitates at approximately 33 °C for this blend as well. Per conversations with Xi Chen, the operating range of this blend is

between 0.3 and 0.39 moles of CO₂ per moles of alkalinity. The solubility envelope for the blend is shown in red in Figure 3.

Solid solubility experiments were also carried out on a loaded solution of 8 m 2MPZ to determine any science that would relate the formation of the H⁺PZCOO⁻.H₂O (or H⁺2MPZCOO⁻.H₂O in the case of 8 m 2MPZ) in rich loaded solutions as with PZ. At a loading of 0.46, solids were formed which melted at a temperature of approximately 32 °C. Through this observation it can be deduced that H⁺PZCOO⁻.H₂O may form in blends with concentrations of PZ greater than 4 m. For this reason, solid solubility for 6 m PZ/2 m 2MPZ is now being studied and analyzed.

Regression of interaction parameters in the electrolyte-NRTL model in Aspen Plus[®]

The electrolyte-NRTL model in Aspen Plus[®] was used to start modeling the sulfate reclaiming system. The e-NRTL model calculates the energy parameter, τ , and a non-randomness factor, α , to calculate the activity coefficient of the ionic species specified in the model. The thermodynamic calculations of the model depends on the ionic forces of the individual ionic species. The forces of the species can be long range forces or short range forces.

Chen et al. (1982) proposed an excess Gibbs energy equation for each of the short and long range interactions. Solubility of K₂SO₄ in CO₂-loaded PZ can be considered a high electrolyte concentrated solution. Short range interactions dominate regions of high electrolyte concentrations. The excess Gibbs energy for such interactions is calculated below (Hilliard, 2005):

$$\frac{G_m^{*E,lc}}{RT} \sum_m X_m \frac{\sum_j X_j G_{jm} \tau_{jm}}{\sum_k X_k G_{km}} + \sum_c X_c \sum_{a'} \left(\frac{X_{a'}}{\sum_{a''} X_{a''}} \right) \frac{\sum_j G_{jc,a'c} \tau_{jc,a'c}}{\sum_k X_k G_{kc,a'c}} + \dots + \sum_a X_a \sum_{c'} \left(\frac{X_{c'}}{\sum_{c''} X_{c''}} \right) \frac{\sum_j G_{ja,a'c} \tau_{ja,a'c}}{\sum_k X_k G_{ka,a'c}} \quad (2)$$

Where:

$$G_{cm} = \frac{\sum_a X_a G_{ca,m}}{\sum_{a'} X_{a'}}$$

$$G_{am} = \frac{\sum_c X_c G_{ca,m}}{\sum_{c'} X_{c'}}$$

$$\alpha_{cm} = \frac{\sum_a X_a \alpha_{ca,m}}{\sum_{a'} X_{a'}}$$

$$\alpha_{am} = \frac{\sum_c X_c \alpha_{ca,m}}{\sum_{c'} X_{c'}}$$

$$G_{jc,a'c} = \exp(-\alpha_{jc,a'c} \tau_{jc,a'c})$$

$$G_{jc,c'a} = \exp(-\alpha_{jc,c'a} \tau_{jc,c'a})$$

$$G_{im} = \exp(-\alpha_{im} \tau_{im})$$

$$G_{ca,m} = \exp(-\alpha_{ca,m} \tau_{ca,m})$$

$$\tau_{ma,ca} = \tau_{am} - \tau_{ca,m} + \tau_{m,ca'}$$

$$\tau_{mc,ac} = \tau_{cm} - \tau_{ca,m} + \tau_{m,ca'}$$

$X_j = x_j C_j$ ($C_j = Z_j$ for ions and $C_j =$ unity for molecules);

α is the non randomness parameter;

τ is the binary energy interaction parameter.

The τ parameter has default values in Aspen Plus[®] for the molecule-electrolyte and electrolyte-water pairs as shown in Table 1 below:

Table 1: Aspen default binary interaction parameters

Binary Interaction Pairs	τ value
Molecule – Electrolyte	10 (sometimes 15 is used)
Electrolyte – Molecule	-2
Electrolyte – Water	8
Water – Electrolyte	-4

The τ parameters are temperature dependent and are adjusted to fit the experimental data input into Aspen Plus[®]. The τ parameters are fitted using the following equation:

$$\tau_{m,ca} = A_{m,ca} + \frac{B_{m,ca}}{T} + C_{m,ca} \left[\frac{(T_{ref}-T)}{T} + \ln \left(\frac{T}{T_{ref}} \right) \right] \quad (3)$$

$$\tau_{ca,m} = A_{ca,m} + \frac{B_{ca,m}}{T} + C_{ca,m} \left[\frac{(T_{ref}-T)}{T} + \ln \left(\frac{T}{T_{ref}} \right) \right] \quad (4)$$

A, B, and C are given as GMELCC, GMELCD, and GMELCE, respectively in Aspen Plus[®] and will be called the C, D, and E parameters in this report. These interaction parameters are then used to calculate the activity coefficients, which in turn are used to calculate the Ksp of K₂SO₄ in PZ.

The solubility product, Ksp, of a salt is calculated using activity coefficients using the following equation:

$$K_{sp} = x^2(K^+) \cdot \gamma^2(K^+) \cdot x(SO_4^{-2}) \cdot \gamma(SO_4^{-2}) \quad (5)$$

Where x is the mole fraction and γ is the activity coefficient of the ionic species.

The expression for the chemical equilibrium of the dissociation of the salt is given by Hilliard (2005):

$$\ln K = A + \frac{B}{T(K)} + C \ln T(K) \quad (6)$$

The values for A, B, and C for K₂SO₄ are input into Aspen Plus[®] as K-salt values as follows (Sohnel, 1984; Xu, 2008):

Table 2: K-salt values for K₂SO₄

K-SALT/1 (A)	265.7
K-SALT/1 (B)	-14954
K-SALT/1 (C)	-40.7

The following molecules, cations, and anions are assumed to be present in the sulfate reclaiming system:

Molecules: H₂O, PZ, H⁺PZCOO⁻

Anions: SO₄⁻², PZCOO⁻

Cations: H⁺PZ, K⁺

While a number of combinations of electrolyte-molecule pairs can be regressed, this work focuses on those including K^+ and SO_4^{-2} . The combinations will include:

Table 3: Electrolyte-molecule pairs to be regressed

Component i	Component j
K^+ , SO_4^{-2}	H^+PZCOO^-
H^+PZCOO^-	K^+ , SO_4^{-2}
$PZCOO^-$, K^+	H_2O
H_2O	$PZCOO^-$, K^+
H_2O	H^+PZ , SO_4^{-2}
H^+PZ , SO_4^{-2}	H_2O
K^+ , SO_4^{-2}	PZ
PZ	K^+ , SO_4^{-2}

The values for the H_2O , K^+ , SO_4^{-2} pair are given in Chen et al. (1982) as:

Table 4: τ parameters for H_2O , $K^+SO_4^{-2}$ system (Chen et al., 1982)

Component i	Component j	τ
H_2O	K^+ , SO_4^{-2}	9.247
K^+ , SO_4^{-2}	H_2O	-4.964

Future Work

Experiments are being carried out to understand the precipitation of $H^+PZCOO^- \cdot H_2O$ in rich loaded PZ solutions.

The Aspen Plus[®] model for the sulfate reclaiming system using KOH is currently being developed. Since experiments were carried out in the last quarter of 2010 to determine the solubility of Na_2SO_4 in PZ, the model developed may also be modified for using NaOH and precipitating Na_2SO_4 in PZ for sulfate reclaiming. Once the model is developed, an economic analysis of the reclaimer can be performed.

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Oxidation of Monoethanolamine and Other Amine-Based Solvents used for Post-Combustion CO₂ Capture

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1.0 Introduction

Introduction to CO₂ Capture

Carbon capture technology is used worldwide for natural gas treating and other applications. These technologies have more recently been proposed for the application of carbon dioxide removal from power plant flue gas and other sources. Carbon dioxide captured from these sources is subsequently stored underground—in the effort to mitigate anthropogenic CO₂ emissions that are precipitating global climate change. Amine scrubbing is the cheapest and most well-known carbon capture technology for post combustion CO₂ capture from existing coal and natural gas fired power plants. However, the current amine scrubbing systems cost approximately \$50-70/MtCO₂, compared with \$5-10/MtCO₂ for transportation and storage (IPCC 2005, 2005). Given that the price of CO₂ in proposed climate change legislation in the US is only \$10-25/MtCO₂, reducing this cost will be necessary to facilitate the widespread adaptation of carbon capture technology.

Introduction to Amine Oxidation

Amine oxidation can represent a significant part of the cost of operating amine scrubbing system for CO₂ removal if the solvent is prone to oxidation. Solvent oxidation was found to cost ~\$2/MtCO₂ for a carbon capture plant using 9 m monoethanolamine (MEA) (Sexton, 2008). Oxidation reduces the CO₂ carrying capacity of the solvent and requires that makeup solution be added on a continuous basis. Further costs are incurred from reclaiming oxidized MEA to remove degradation products and from reduced equipment lifetime due to the increased corrosivity of degraded solutions. Concerns have also been raised about the environmental impacts of some oxidation products, which include aldehydes, amides, and ammonia (Attalla, 2010). All of these costs are estimated to add up to 10% of the cost of operating a CO₂ capture process (Rao, 2002); however, if left completely unmanaged, the cost of degradation could be much greater.

Although MEA has many desirable properties, such as its low cost, fast reaction rate with CO₂ and high heat of absorption, its susceptibility to oxidation has motivated the search for more stable solvents (Kindrick, 1950a; Kindrick 1950b). Since many other solvents lack the low cost and superior thermodynamic properties of MEA, this is not necessarily the cheapest solution. An alternative is to develop solutions that manage and minimize solvent oxidation and reduce the overall cost of the process.

A thorough understanding of the degradation process of MEA is required it to be used as a solvent for carbon capture in a real system. Although some previous works have studied MEA oxidation, the overall understanding of this process still has contains many holes.

2.0 Previous Work

Previous studies have determined the rate of MEA oxidation at various conditions (temperature being the notable exception), the types of oxidation products formed, as well as catalysts and inhibitors of oxidation. However, this previous work is incomplete for several reasons:

- Not all catalysts were screened, particularly gas phase contaminants (NO_2 , NO , and SO_2). Previous work also left out or showed conflicting results for transition metals, many of which are known to catalyze MEA oxidation. Transition metals enter the system from fly ash, corrosion, or other sources.
- The mechanism of oxidation and pathway to products is not well understood. Thus it has been hard to predict which compounds would inhibit the oxidation process. Many traditional anti-oxidants are pro-oxidants in aqueous MEA; the action of known inhibitors is often not understood.
- The pathway to final products (and indeed the identity of these products) is not known. Thus the material balance has never been closed 100%. Many very unlikely products have also been proposed (such as 18-crown-6), although their existence has not been completely disproven.

This is to name only a handful of the knowledge gaps around MEA oxidation. To make matters worse, previous works have too often exhibited fundamental experimental flaws. Partially as a result, these findings were often incomplete, contradictory, or both. A summary of flawed experimental conditions is shown below (Table 1), the consequence in each case being that the findings do not reflect what happens in a real system.

Table 1 – Experimental Flaws in Previous Works

<u>Experimental Condition</u>	<u>Flaw</u>
Pressurized, batch, oxidation reactor	Oxygen partial pressure is not constant and is unknown. As oxygen is consumed, the pressure goes down. Production of volatile degradation products also changes the oxygen partial pressure.
No agitation	For systems with high oxygen partial pressure, agitation is required to ensure sufficient oxygen mass transfer
No CO_2 present	Oxidation proceeds much more slowly when no CO_2 is present. A real system would have CO_2 .
No metals (esp. iron) present	A real system as metals contamination from corrosion, additives and fly ash. Oxidation is much faster in the presence of such metals.
Low amine concentration	Oxidation proceeds significantly faster in more concentrated solutions. Oxidation experiments should use only the “practical” concentration for CO_2 capture (typically 7 – 12 molal)
High oxygen partial pressure	Oxygen partial pressure in the absorber is 5 kPa to

High temperature (esp. with high oxygen partial pressure)

15 kPa. Higher pressures, especially those in excess of 1 atm give unrealistic results.

The amine solution only sees a small amount of oxygen (dissolved oxygen in the cross exchanger) at high temperature. Temperatures should reflect those encountered in the absorber (40 – 80°C)

In some cases the experimental conditions (high oxygen pressure and high temperature) are chosen to allow for accelerated oxidation. The tradeoff is that the results are less meaningful for a real system. Other conditions, such as the presence of CO₂ and metals were simply ignored. All oxidation experiments should be conducted with the practical amine concentration (typically 7 – 12 molal, or 30 – 50 wt%), in the presence of 0.1 – 10 mM iron, and in the presence of CO₂.

The goal of this work is to design an experiment that better represents the conditions of a real system, and thus fill the major gaps in the state-of-knowledge of MEA oxidation in a real system. A more thorough discussion of what previous research has to offer is provided in Appendix A.

3.0 Problem Statement

Research Goal

The key to managing oxidation is identifying the most potent catalysts and inhibitors in an industrial amine scrubber. Mitigating MEA oxidation (by identifying inhibitors that are highly effective in an industrial system) would significantly reduce the need for further study on this topic. It is therefore the primary objective of this research to screen all of the potential catalysts in an industrial system. Catalysts come from a variety of sources, including equipment corrosion (Hall, 1981), flue gas contaminants (SO₂, NO_x, and fly ash), and additives (such as corrosion inhibitors). In particular, fly ash is known to contain a cornucopia of heavy metals, which can leach into aqueous solutions (Sushil, 2006; Fytianos, 1998).

A second objective is to find an inhibitor that can practically be used to minimize oxidation in an industrial plant, in the presence of the most problematic catalysts. This inhibitor should be either stable and very potent at low concentrations, or cheap enough that it can be added to the process in significant quantities on a regular basis. It should also have low toxicity and not significantly alter the chemistry of the process (for example by changing the vapor-liquid equilibrium with CO₂ detrimentally, being highly corrosive, or accelerating thermal degradation). Identification of potent catalysts and inhibitors will be used to develop a broader understanding of the oxidation mechanism and various modes of inhibition.

A secondary objective of this research will be to develop a better understanding of the oxidation process, primarily by identifying oxidation products, studying the relationship between process

conditions (namely temperature) and oxidation rate, and identifying amines which are resistant to oxidation.

The following objectives are proposed to address the most critical aspects of amine oxidation.

Primary Objectives

1. Assess the relative potency of various catalysts and inhibitors of MEA and PZ oxidation at conditions similar to those encountered in an industrial CO₂ capture system by analysis of gas phase ammonia production from the solution.
2. Verify the effect of the most important additives on MEA oxidation using long-term oxidation experiments including liquid phase analysis of MEA concentration and oxidation products, as well as using thermal degradation cycling experiments with liquid phase analysis

Secondary Objectives

1. To determine the temperature dependence of MEA oxidation under a set of representative conditions for an industrial system and in the presence of the most relevant catalysts and inhibitors
2. To determine the concentrations of all known, quantifiable oxidation products of MEA over the course of a multi-day oxidation experiment.
3. To determine the temperature stability of known, quantifiable oxidation products, and to determine the oxidative stability of other known, quantifiable degradation products
4. To estimate the oxidation rate of MEA in a pilot-scale carbon-capture system through quantification of an oxidation product, such as NH₃ or formate.
5. To analyze pilot plant samples using MEA in the presence of oxygen for known degradation products.
6. To screen current and future amine solutions for carbon capture for oxidative stability

4.0 Proposed Methods

The methods for completing the above objectives involve conducting experiments (experimental methods) and analyzing samples (analytical methods). There are three types of experimental apparatuses that will be used to study MEA oxidation. These are oxidation reactors, thermal degradation reactors, and pilot plants or industrial systems. Many analytical methods are available for sample analysis. The most important methods are gas phase fourier-transform infrared analysis, liquid chromatography, and ion chromatography. These methods have been described in great detail in previous literature (Goff 2005; Sexton 2008). Other methods which are available include total inorganic carbon analysis, total carbon analysis, total nitrogen analysis, total alkalinity (titration), gas chromatography coupled with mass spectrometry, liquid chromatography coupled with mass spectrometry and high-resolution mass spectrometry.

Experimental apparatuses for MEA oxidation

Oxidation reactors proposed for this research will resemble those used in previous studies, with some minor modifications. Two types of semi-batch oxidation reactors are proposed: the high gas flow (HGF) system and the low gas flow (LGF) system (Figure 1). These apparatuses are very similar to those used by Goff (2005) and Sexton (2008) in their studies on MEA oxidation.

The advantage of the LGF reactor is that it can achieve greater oxidation rates due to the use of pure oxygen rather than air. The water balance in this system is also easier to control because the gas rate is much lower. One significant drawback of this system is that volatile species (namely ammonia and MEA) are not accounted for, therefore the mass balance cannot be fully closed. The HGF system analyzes the gas leaving the reactor, therefore ammonia and MEA losses can be accounted for. The drawback to this system is that volatile amine losses become significant over multi-day experiments. The apparatus also requires more daily maintenance, and the water balance can be more difficult to control.

In the LGF apparatus, the gas composition is set by two mass flow controllers fed by high purity oxygen and CO₂. The blended gas is fed to a saturator before entering the headspace of the reactor, which is heated by a water-heated jacket. The liquid in the reactor is vigorously agitated; the gas exits from the headspace from a gap surrounding the agitator. The reactor is open to the atmosphere, and any degradation products in the gas leaving the reactor are unaccounted for. The saturator and reactor are set to the same temperature, thus the reactor slowly loses water at a rate of approximately 5-10mL/day.

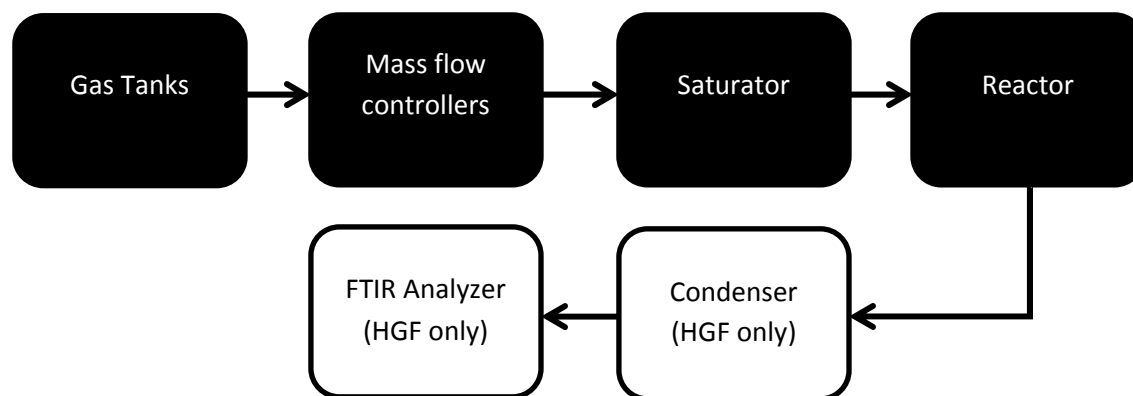


Figure 1 – Flow Diagram for the HGF and LGF apparatuses

The HGF apparatus is somewhat more complicated than the LGF apparatus. In particular, the water balance is much more problematic due to the higher gas rate. In the HGF apparatus, house air and high-purity CO₂ are fed to a saturator via two mass flow controllers. Two positive displacement pumps are used to maintain a constant level of water in the saturator. Gas exiting the saturator is sparged into the bottom of the reactor, which is heated by recirculating oil that flows between the jacket and a heated reservoir. Gas exits through the top of the reactor into a condenser. The condenser is tuned to the correct temperature to prevent any net water loss from the reactor. After the condenser, the gas enters a heated line and is pumped to a hot gas fourier transform infrared (FTIR) analyzer. The analyzer can analyze the oxidation gas leaving the reactor for up to 30 individual components simultaneously, including water, CO₂, volatile amine, NH₃, NO, NO₂, and others. A summary of the analysis regions used

by the instrument for some components is shown in Table 2. If the condenser is not used, agitation can be provided via a port in the center of the reactor. A photograph of the apparatus is shown in Figure 2 below.

Table 2 – Summary of Analysis Areas used for FTIR Gas Analysis

Compound	Range 1 (cm^{-1})	Range 2 (cm^{-1})	Range 3 (cm^{-1})
Water	3157 – 3477		
CO ₂	910 – 1003	3425–3616	2165–2251
MEA	2416 – 3150		
NH ₃	915 – 988	2423–2560	
NO ₂	2760 – 2995		
NO	1875 – 2150	2448 – 2593	
N ₂ O	2123 – 2224	2505 – 2628	

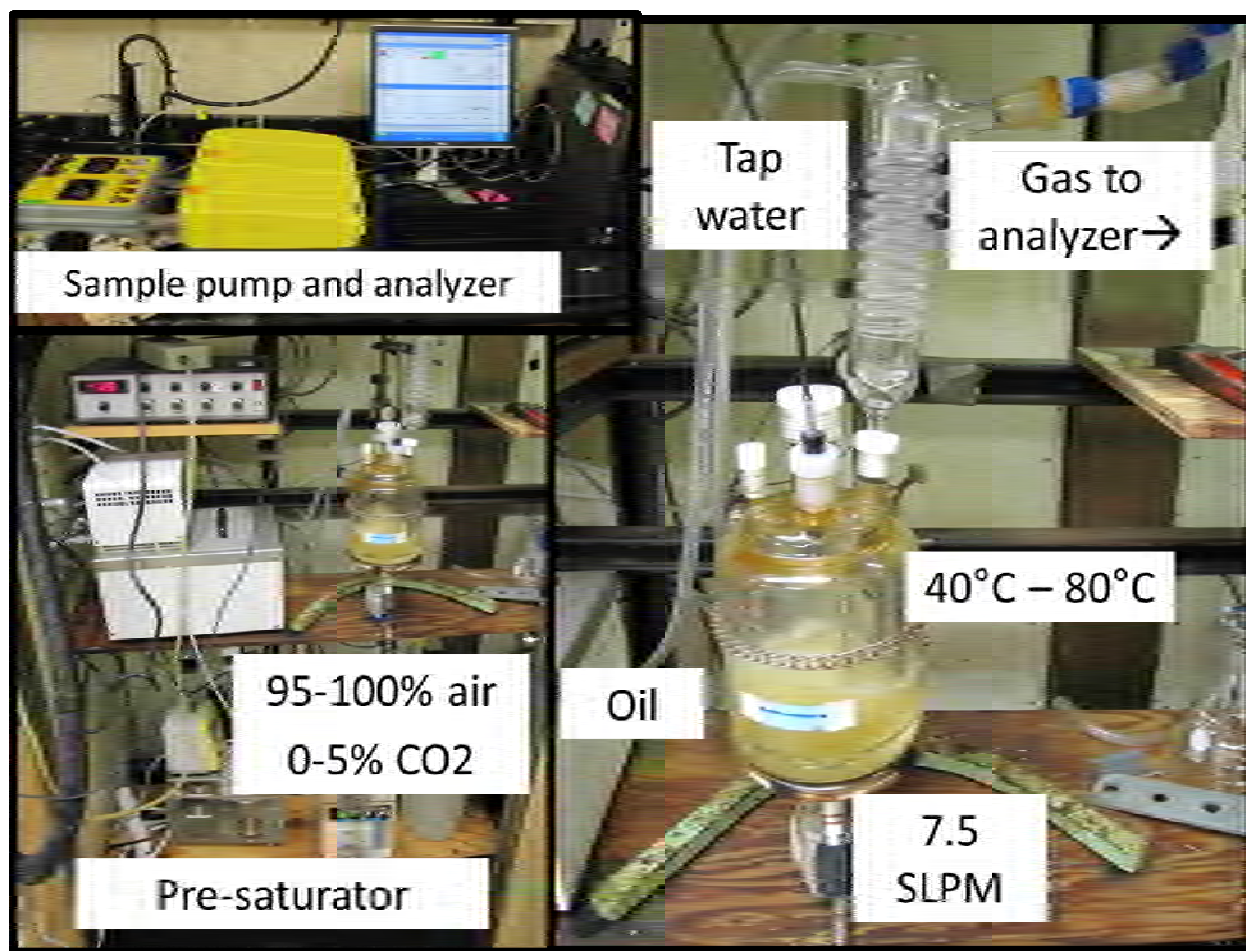


Figure 2 – High Gas Flow Apparatus

The primary purpose of the condenser is to reduce volatile amine emissions at high temperatures, which would significantly alter the total liquid phase concentration over time. The experimental conditions are

selected to accurately represent the conditions encountered in a real system as much as possible. The absorber would operate at atmospheric pressure with CO₂ entering at 12 kPa and exiting at 1.2 kPa. The oxygen partial pressure would range from 5% (for coal-fired boilers) to 15% (for natural gas fired boilers). The temperature range was selected to encompass the range of the temperature bulge in a real system (Plaza, 2009). A comparison of the two reactor types is shown in table 3.

Table 3 – Comparison of Experimental Conditions for the HGF and LGF Oxidation Systems

	LGF	HGF
Dry gas rate (SLM)	0.100	7.65
Oxygen partial pressure (kPa)	98	21-50
CO ₂ partial pressure (kPa)	2	2
Temperature (°C)	55	40 – 80
Solution volume (mL)	350	350
Catalysts	Liquid phase only	Liquid and gas phase (NO _x)
Gas analysis	None	FTIR
Agitation	1400 RPM	1400 RPM (w/o condenser)

A pilot plant at the Pickle Research Campus will be used to assess amine oxidation by installing an FTIR analyzer at the absorber outlet. Ammonia production from the top of the absorber column will be measured over the course of several days at various conditions. Liquid samples from the pilot plant will also be analyzed for degradation products, as will liquid samples from other industrial amine scrubbing systems.

Thermal degradation reactors are proposed for use in this work, because they will be used to assess the effect of thermal degradation products on the oxidation rate. Thermal degradation is carried out in 3/8" stainless steel pipes sealed with Swagelok end caps. The Swagelok seal can withstand high pressure and thus prevent any CO₂ from escaping during the experiment. A thermal degradation experiment will utilize 10-20 separate cylinders, which are placed in an oven and removed sequentially over the course of several weeks or months. Larger quantities of thermally degraded MEA will be produced by using a 2" pipe with welded endcaps fitted with 1/4" Swagelok connectors. The connector can be capped while the reactor is in the oven, and uncapped to take a sample after the reactor has been removed and cooled.

Analytical methods for degraded samples

The primary analytical methods are used to determine the amount of MEA, which has been oxidized, and the amounts of known oxidation products formed. Methods for quantification will be cation and anion chromatography, HPLC with UV and ELS detection, and FTIR. Other methods for identifying unknown products include GCMS, LCMS, ICMS, and high-resolution MS. Finally, total inorganic carbon analysis will be used for determining the CO₂ loading; total nitrogen and total organic carbon will be used for checking the material balance of oxidized samples. The various analytical methods are summarized in table 4.

Table 4 – Summary of Proposed Analytical Methods

Instrument	Method	Analytes	Application

Primary Analytical Methods (for quantification of substrate and products)

Cation chromatograph	MSA elution	MEA	Quantify MEA loss by oxidation
Anion chromatograph	Sodium hydroxide elution	Organic acids and amides	Quantify anionic oxidation products
HPLC	Reverse-phase, UV and ELS detection	HEI, HEPO	Quantify major condensation products
FTIR	Gas-phase analysis, multi-component analysis	NH ₃	Fast screening of catalysts and inhibitors

Identification of unknown oxidation products

GC-MS	Polar and non-polar columns	Oxazolidone	Identify volatile oxidation products
IC-MS	MSA elution, ESI	--	Identify unknown cationic degradation products
LC-MS	HILIC mode, ESI	--	Identify unknown condensation products
High Res MS	Chemical ionization	--	Determine formula for unknown compounds
MS-MS	ESI with triple quadrupole	--	Determination of mass-spectra for unknown products

Total Material Methods

Total inorganic carbon	Phosphoric acid evolution	Carbon dioxide	Determine solution loading
Total organic carbon	HCl evolution, combustion	Carbon containing organic molecules	Carbon material balance
Total nitrogen	Combustion, NO ₂ detection	--	Nitrogen material balance

Data Analysis

Initial screening work will attempt to establish the potency and stability of successful inhibitors. This will be accomplished by adding a small amount of inhibitor (0.1%wt.) and observing the time for the NH₃

rate to reach the midpoint between the initial rate and the inhibited rate (t_{50}). In a separate set of experiments, the concentration of inhibitor required to reduce the ammonia rate by 50% will be calculated by successive additions (C_{50}). A table will be compiled specifying the t_{50} , C_{50} , and bulk price of all successful inhibitors. A higher t_{50} will reduce inhibitor loss from oxidation, whereas a lower C_{50} will reduce reclaimer losses (for non-volatile inhibitors). Process modeling and simple economic analysis will be used to calculate an overall figure of merit for each inhibitor, and select the cheapest option.

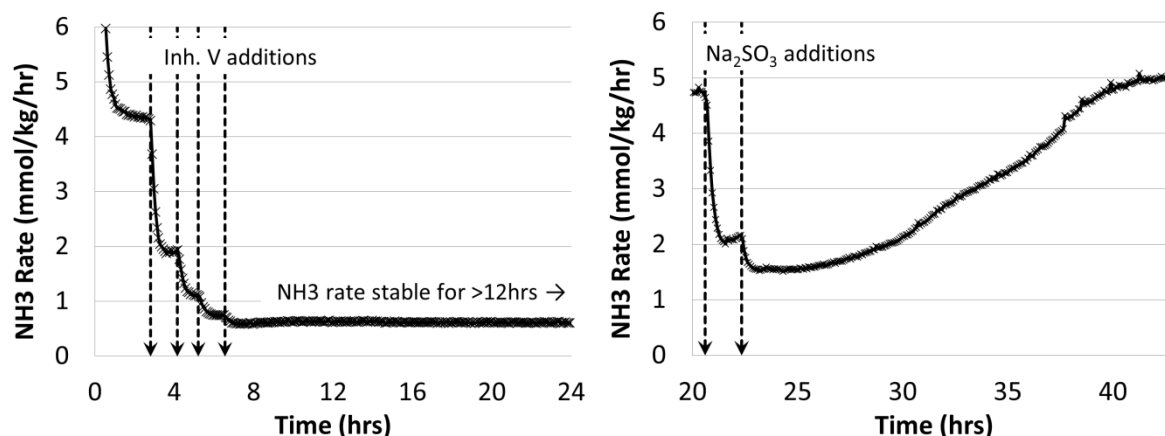
5.0 Preliminary Results

MEA Oxidation Catalysts

Many transition metals and NO_2 have been screened for their effect on the steady state NH_3 rate from aqueous MEA (Table 3). The catalysts and inhibitors that had a significant effect on the NH_3 rate are shown below. Manganese, which was previously shown to be an inhibitor, was found to switch oxidation states and behave as a potent catalyst. Vanadium, which is used as a corrosion inhibitor, was found to mildly inhibit oxidation—therefore it is recommended for use as a corrosion inhibitor instead of copper.

MEA Oxidation Inhibitors

Inhibitors were screened by adding a small quantity (0.01 – 1.5wt%) of each material to a solution of 9 m MEA received from a pilot plant. The pilot plant solution was analyzed and found to contain 0.56 mM Fe, 0.02 mM Cr, and 0.03 mM Ni. Ammonia production from the solution was monitored before, during and after the addition of each inhibitor. Successful inhibitors resulted in an immediate and substantial drop in NH_3 production from the solution. Stable inhibitors maintained a lower level of NH_3 production for an extended period of time (>12 hours) (Figure 3), whereas less stable inhibitors showed a visible increase in the NH_3 rate (Figure 4).



Figures 3 and 4 – Oxidation of 9 m pilot plant MEA with Inhibitor V (0.066, 0.134, 0.355, 1.45wt%) and sodium sulfite (0.654, 1.540wt%) in the HGF apparatus. Conditions 70°C, 98 kPa air, 2 kPa CO_2 , 0.56 mM Fe, 0.02 mM Cr, 0.03 mM Ni, saturator (30.0°C), condenser (17.5°C), no agitation

Inhibitors discovered in this work (namely V, Z, and X) represent a substantial improvement on the state of the art. These inhibitors were more potent and more stable than any known inhibitors (Table 5), and are part of a pending patent application—they will be revealed after the patent has been filed.

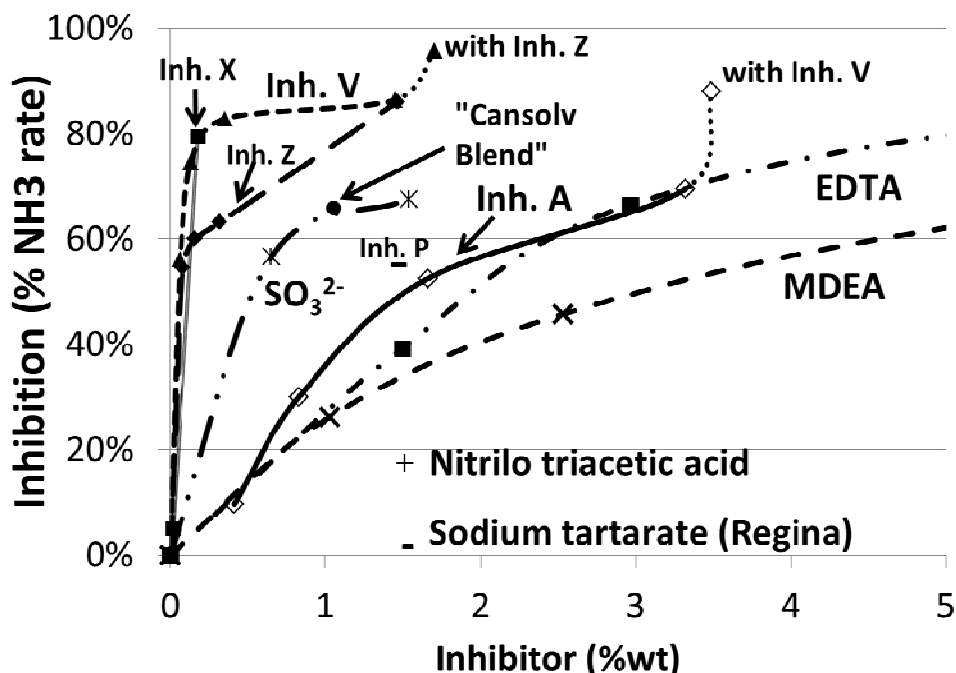


Figure 5 – Summary of state-of-the-art inhibitors, compared with inhibitors discovered in this work.
Conditions: 9 m MEA, 70°C, 98 kPa air, 2 kPa CO₂

Table 5 – Summary of Catalysts and Inhibitors Studied for MEA Oxidation. Conditions: 98kPa air, 2kPa CO₂, 55 – 70°C

Catalyst	Effect on NH ₃ Rate (mmol/kg/hr)	Inhibitor	NH ₃ Inhibition (1.5%wt Inh.)	NH ₃ Rate (%) / Inh. (%wt)	Stability at 70°C
Cr ³⁺	↑ NH ₃ 0.06	V	86	56 / 0.06	Good
Fe ²⁺	↑ NH ₃ 1.17	Z	91	55 / 0.08	Good
Cu ²⁺	↑ NH ₃ 5.70	X	--	80 / 0.2	Moderate
Mn	↑ NH ₃ 4.96	Y	77	45 / 0.04	Poor
VO ⁴⁻	↓ NH ₃ rate 40%	O	67	56 / 0.65	Poor
		P	55		
Mn ²⁺	↓ NH ₃ rate 80–90%	Others	<55	--	--

Temperature Dependence of NH₃ Production During MEA Oxidation

The temperature dependence of a previously known trade secret inhibitor (“Inhibitor A”) was studied in this work. The results of the temperature dependence of ammonia production from oxidized MEA are shown in table 6 below

Table 6 – Effect of Inhibitor A on Oxidation of MEA at Various Concentrations. Conditions: 7 m MEA, 40 – 70°C, 98 kPa air, 2 kPa CO₂

Conc. Inh. A (mM)	Activation Energy NH ₃ Rate (kJ/mol)	Change in NH ₃ Rate at 55°C (%)
0	86	--
10	75	35
50	102	-74
100	113	-93
200	133	-99

Cycling Effects and Product Stability

The stability of thermal degradation products in an oxidative environment, as well as oxidative products in a thermal degradation environment has been studied. Organic acids and amides are primarily expected to be oxidation products, while HEIA and HEEDA are known thermal degradation products (Davis, 2009; Polderman, 1955). The results of this work are summarized below in table 7.

Table 7 – Stability of various products during cycling between oxidation and thermal degradation. Conditions: 7 m MEA; Oxidation – 55°C, 98kPa air, 2kPa CO₂; Thermal degradation – 0.4ldg, 135°C

Compound	Type of Product	Stability in cycling
Hydroxyethyl imidazolidinone (HEIA)	Thermal	Oxidatively stable
Hydroxyethyl ethylenediamine (HEEDA)	Thermal	Oxidizes rapidly
Hydroxyethyl imidazole (HEI)	Oxidative	Moderately stable
Formate	Oxidative	Equilibrates with formamide
Formamide	Oxidative	Equilibrates with formate
Oxalate	Oxidative	Converted to formate
Mono-oxalamide	Oxidative	Converted to oxalate
Di-oxalamide	Oxidative	Converted to oxalate
Nitrate	Oxidative	Thermally stable
Nitrite	Oxidative	Reacts rapidly

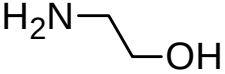
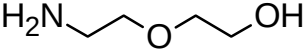
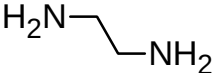
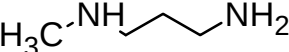
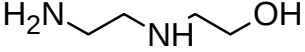
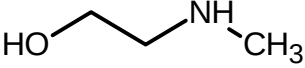
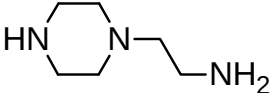
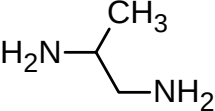
Amine Screening

One solution to mitigating oxidative degradation is to choose an amine that is resistant to oxidation. Significant work has been conducted to determine which amines are oxidative stable by carrying out oxidation experiments in the HGF apparatus and observing the production (or lack thereof) of volatile oxidation products (namely NH₃, H₃CNH₂, NO, NO₂, and N₂O). In all experiments, 98kPa O₂ with 2 kPa CO₂ was used as the oxidant. NH₃ was the only product observed, except for potassium sarcosine and

methyl-amino-ethanol, where methylamine was also observed. In most cases, the effect of metal (Fe^{2+} only, or $\text{Fe}^{2+} + \text{Cr}^{3+} + \text{Ni}^{2+}$) and inhibitor A was also assessed (Table 8).

The results for each amine are not directly comparable for all experiments because the conditions (namely temperature) were not constant. However, these results offer a general idea of which solutions are prone to oxidation. Except for AMP, all primary amines were susceptible to degradation. Tertiary amines and PZ derivatives (except AEP, which is also a primary amine) were found to be stable (Table 9).

Table 8 – Amines Which Produced Volatile Oxidation Products in the HGF Apparatus. Conditions: 98 kPa air, 2 kPa CO_2 , gas rate 5 – 7.5SLPM (dry)

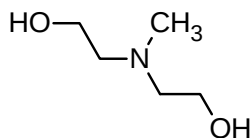
<u>Amine Solution</u>	<u>Structure</u>	<u>Temp (°C)</u>	<u>NH_3 Rate with Fe^{2+} present (mmol/kg)</u>	<u>Effect of Fe^{2+}</u>	<u>Inh. A Effect</u>
Oxidized Amines					
Monoethanolamine (MEA) – 7 m		55°C	1.55	Catalyst	Inhibitor
Diglycolamine (DGA) – 17 m		70°C	6.13	No effect	Catalyst
Ethylenediamine (EDA) – 8 m		55°C	0.78	Inhibitor	Inhibitor
Methyl-amino propylamine (MAPA) – 8 m		55°C	0.47	Inhibitor	Inhibitor
Hydroxyethyl ethylenediamine (HEEDA) – 7 m		70°C	0.99	Inhibitor	Inhibitor
Methyl aminoethanol (MAE) – 7 m		80°C	1.90 (NH_3) 1.29 (H_3CNH_2)	Catalyst	Inhibitor
Aminoethyl piperazine (AEP) – 8 m		70°C	2.73	Inhibitor	Inhibitor
1,2-diamino propane (DAP) – 8 m		55°C	2.68	Not tested	No effect

Oxidized Amino Acid Salts						
Potassium glycine (KGLY) – 6 m		80°C	6.25	Catalyst	Catalyst	
Potassium taurine (KTAU) – 5 m		80°C	0.62	Catalyst	Inhibitor	
Potassium homotaurine + taurine (KHTAU) – 5/3 m		80°C	0.43	No effect	No effect	
Potassium sarcosine (KSAR) – 6 m		80°C	0.05 (H ₃ CNH ₂)	--	--	

Table 9 – Amines that did not produce volatile oxidation products in the HGF apparatus

<u>Amine Solution</u>	<u>Structure</u>	<u>Temperature</u>
Diethanolamine (DEA)		70°C
Piperazine (PZ)		70°C
1-methyl-piperazine (1MPZ)		55°C
2-piperadine ethanol (2PE)		55°C
2-amino-2-methyl-propanol (AMP)		55°C

Methyl
diethanolamine
(MDEA)



55°C

6.0 Future Work and Experiment Timeline

Overall significant progress has been made in the study of oxidation of MEA. However much more work remains to be done to understand, manage, and minimize MEA oxidation as it applies to an industrial CO₂ capture system.

Many previous works conducted oxidation experiments at conditions that do not represent an industrial process. In addition, there is little understanding of the oxidation mechanism, which types of compounds are catalysts and inhibitors (and why), and how the oxidation products are formed.

The goal of this work is to fill in the biggest gaps in the state of knowledge on this topic and develop recommendations for reducing the cost of amine oxidation in an industrial system. The following experimental research activities will be completed by March 2013. The dissertation will be submitted by August 2013.

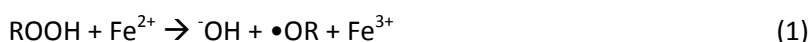
- Continue to screen inhibitors for MEA in the HGF apparatus
- Continue to stress-test inhibitors for MEA in the LGF and batch cycling experiments
- Install FTIR analyzer at the Pickle Pilot Plant; analyze for NH₃ from neat and inhibited solutions
- Oxidize inhibited MEA solutions using gas phase contaminants SO₂, NO₂, and NO in the HGF apparatus
- Measure temperature dependence of additional inhibitors and catalysts in the HGF apparatus
- Screen catalysts and inhibitors for activity in PZ solutions (using findings from MEA oxidation)
- Screen additional amines and amino acids as needed for oxidative stability
- Construct a nitrogen material balance for one MEA oxidation experiment using the following analytical methods: cation chromatography, anion chromatography, HPLC-UV-ELS, HPLC-ECD (amino acids method), ICMS, GCMS, LCMS, and total nitrogen
- Reconfigure the integrated solvent degradation apparatus (ISDA) to use FTIR analysis
- Screen catalysts and inhibitors of MEA, PZ and other amines in the ISDA with FTIR analysis

Appendix A: Detailed Findings of Previous Work

Oxidation Mechanism

MEA oxidation is a very complex process: the reaction may be dependent on oxygen mass transfer in a given apparatus, and has a non-linear dependence on MEA concentration, CO₂ loading, and temperature. Furthermore, the reaction is catalyzed by small (<5ppm) amounts of dissolved iron and other metals. In this work, one possible mechanism is described based on previous studies.

The process of oxidation may be initiated by classic Fenton-type chemistry, in which the reaction of peroxides with ferrous forms a free radical (Stumm, 1961; Dennis, 1967; Kovtun, 1973; Kovtun, 1974; Petryaev, 1984; Denisov, 1996).



Free radicals produced by this mechanism in an MEA solution with CO₂ are likely contained in an iron-coordinated “cage,” wherein they go on to react directly with MEA, rather than being released into the bulk solution. Initially the iron is coordinated with three molecules of bicarbonate, or with two molecules of bicarbonate and one molecule of MEA (Stadtman, 1993; Berlett, 1990). MEA-carbamate is may also participate in this complex. Oxidation proceeds by abstraction of a hydrogen on the carbon alpha to the amino group in the presence of oxygen. The MEA radical undergoes a series of reactions (3 – 8 below), which result in formation of iminoethanol (in equilibrium with alpha-hydroxy-aminoethanol). This molecule is unstable and decomposes to form ammonia and aldehydes.

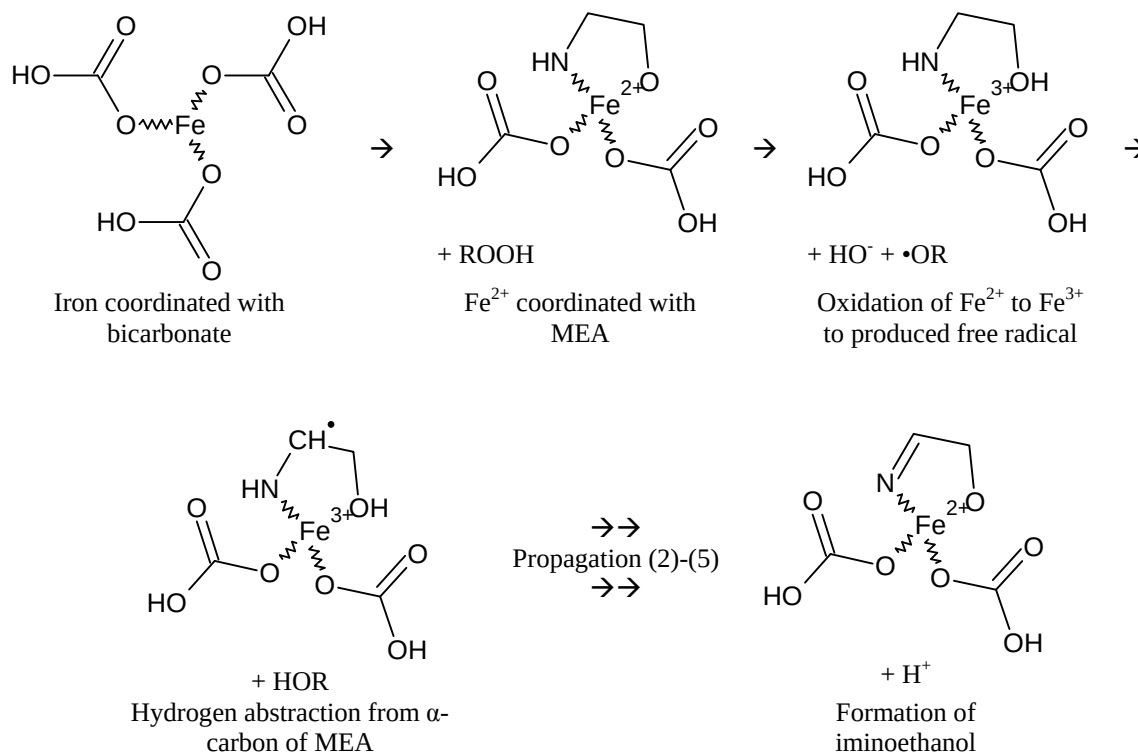
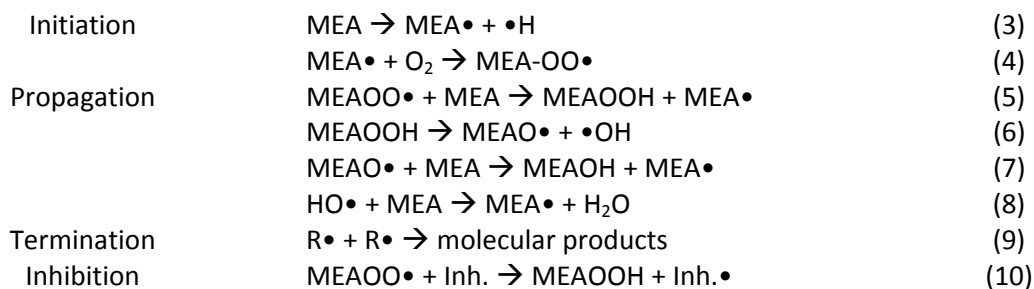


Figure 6 – Iron-coordinated bicarbonate-dependent oxidation of MEA by proton abstraction

An overview of the entire free-radical chain reaction is listed in reactions (3) – (10). Initiation of the oxidation process occurs when a hydrogen atom is abstracted from the α -carbon to the amino group of MEA forming an MEA radical (1). Initiation can be caused by UV light or the presence of a transition metal catalyst. The MEA radical can react with oxygen to form the MEA-peroxide radical (2). The MEA-peroxide radical can abstract a hydrogen atom from another MEA molecule to form MEA-peroxide (3). The MEA-peroxide is unstable and can split forming an MEA oxide radical and hydroxyl radical, which propagates the radical cascade (4). These new radicals can each react with an MEA molecule (5) and (6). Termination occurs when two radical species react with each other to form a stable molecule (7).



Alpha-hydroxyl-MEA formed in equation (5) is unstable and will decompose to form ammonia and hydroxyl-acetaldehyde. It has also been suggested that ammonia and two molecules of formaldehyde may also be formed as primary oxidation species (Petryaev, 1984). This final fragmentation step is assumed to be completely irreversible.



NH_3 Production and Mass Transfer Effects in Oxidation of MEA

Ammonia has been used as an indicator of oxidation of MEA solutions in numerous works (Chi, 2000; Chi, 2002; Goff, 2005; Goff, 2006; Sexton, 2008; Blachly, 1963; Blachly, 1964; Blachly, 1966; Blachly, 1965). The presence of the primary nitrogen in MEA causes it to be susceptible to oxidation (similar molecules, such as ethylene glycol and ethanol oxidize less readily than MEA, whereas ethylene diamine also oxidizes rapidly [Zhou, 2010; Sexton, 2008]). Furthermore, deamination is probably the first step in the oxidation process. Although ammonia production is not necessarily matched 1:1 by NH_3 production (equation 13), relative rates of NH_3 loss match relative rates of MEA loss (Sexton, 2008). This is shown in equation 14, where a fixed number of mols of MEA always produce a fixed number of mols of NH_3 , under many conditions. In other words, catalysts and inhibitors of NH_3 production should always be catalysts or inhibitors of MEA loss. In comparing Goff's work (Goff, 2005) (which relied on NH_3 rates) to Sexton's work (Sexton, 2008) (which measured only MEA loss and liquid phase products), this was mostly found to be the case: Copper is a stronger catalyst than iron, inhibitor A and EDTA were both found to be effective.





Oxygen mass transfer plays an important role in oxidation of MEA. Goff observed that higher agitation rates resulted in increased ammonia production from MEA solutions. There are several possible explanations for this phenomenon –

- Higher agitation rates lead to increased oxygen mass transfer to the solution, which increases the oxidation rate. Increased oxidation results in increased ammonia production.
- Higher agitation rates lead to increased metals concentration in solution. Higher agitation rates result in more metals entering the solution
- Oxidation rate increases slowly over time, as a the reaction rate slowly increases. Rates observed are not at steady state, but are changing over the course of the experiment as a result of changing reaction kinetics
- Liquid entrainment in the heated line occurs at higher agitation rates. Entrained liquid oxidizes rapidly in the line (at 180°C) to produce ammonia
- Ammonia is not an inert species in the solution. Rather than accumulating over time until the removal rate equals the production rate, ammonia reacts in the liquid phase. Increased agitation results in greater stripping rates, giving the NH_3 less time to react in the liquid.
- Shearing of $\text{Fe}(\text{OH})_2$ catalytic particles at higher agitation rates creates greater surface area for oxidation to take place. Greater oxidation increases NH_3 production.

In this work, we will assume that the oxygen mass-transfer ability of the apparatus is sufficiently large that the kinetics of ammonia production can be measured. It will also be assumed that relative rates of ammonia production are representative of relative rates of MEA oxidation. This second assumption will be verified by analyzing the liquid phase MEA concentration for some experiments.

Catalysts and Inhibitors of Oxidation

The discovery by Blachly and Ravner (Blachly, 1963; Blachly, 1964; Blachly, 1965; Blachly, 1966) that the presence of metals, especially copper, exacerbated MEA oxidation laid the groundwork for much of the future work on this problem. This finding was verified by Goff (2005, 2006) and Sexton (2008) using several different experimental and analytical techniques. A summary of catalysts studied in literature is shown in table 9 below; the findings are compared with this work. Most findings agree, however one key exception is manganese, which was found to switch oxidation states and become a potent catalyst in this work.

Table A1 – Summary of Previous work on Catalysts of MEA Oxidation

Catalyst	Effect (Previous)	Effect (This work)	Sources
Iron	Moderate catalyst	Moderate catalyst	Chi, 2000; Chi, 2002; Goff, 2005; Goff, 2006; Sexton, 2008; Blachly, 1963; Blachly, 1964; Blachly, 1966; Blachly,

Nickel	Mixed findings	No effect	1965 Sexton, 2008; Blachly, 1963; Blachly, 1964; Blachly, 1966; Blachly, 1965
Chromium	Mild/Mixed findings	Mild catalyst	Sexton, 2008; Blachly, 1963; Blachly, 1964; Blachly, 1966; Blachly, 1965
Copper	Potent catalyst	Potent catalyst	Goff, 2005; Goff, 2006; Sexton, 2008; Blachly, 1963; Blachly, 1964; Blachly, 1966; Blachly, 1965
Vanadium	Mild catalyst	Mild inhibitor/mild catalyst	Sexton, 2008
Manganese	Inhibitor	Potent inhibitor/potent catalyst	Sexton, 2008

The discovery that some transition metals enhance oxidation of MEA lead to the invention of EDTA as an inhibitor for MEA oxidation—ostensibly by sequestering metals in solution—although some studies indicate another mechanism may be at play (Li, 2007). Numerous other inhibitors have been tested in previous works, a summary of which is provided in table A2. These inhibitors have been categorized by the inhibition mechanism, although it is not well-understood in most cases.

Table A2 – Summary of Successful Inhibitors from Previous Studies. Conditions for this work: 98 kPa air, 2 kPa CO₂, 70°C, 0.56 Fe,

Inhibitor	Inhibitor Type	Effect (Previous)	Effect (This work)	Source
Sulfite	Oxygen scavenger	Moderate inhibitor/mixed findings	Moderate inhibitor	Goff, 2005; Sexton, 2008; Hakka, 2006; Idem, 2009; Supap, 2010
Ascorbic acid	Oxygen scavenger	Adverse	Not tested	Goff, 2005; Delfort, 2010
Formate	Oxygen scavenger	No effect	Not tested	Goff, 2005
Formaldehyde	Oxygen scavenger	Adverse/mixed findings	Not tested	Goff, 2005; Sexton, 2008
Hydroxylamine	Oxygen scavenger	Inhibitor	Adverse	Idem, 2009; Supap, 2010
Manganese		Potent/mixed findings	Inhibitor, adverse	Goff, 2005; Sexton, 2008
Hydroquinone	Hydroxyl radical	Adverse	Not tested	Goff, 2005;

Methyl diethanolamine	scavenger Free-radical scavenger	Mild inhibitor	Mild inhibitor	Delfort, 2010 Faucher, 1989; McCullough, 1990; Lawal, 2006 Singh, 1970
Triethanolamine	Free-radical scavenger	Mild inhibitor	Mild inhibitor	
Inhibitor A	Free radical scavenger	Moderate inhibitor	Moderate inhibitor	Goff, 2005; Goff, 2006; Sexton, 2008
Thiosulfate	Free radical scavenger	Moderate inhibitor	Mild inhibitor	Hakka, 2006
2,2'-thiodiacetate	Free radical scavenger	Strong inhibitor	No effect	Carrette, 2009a
3,3'-thiodipropionate	Free radical scavenger	Strong inhibitor	No effect	Carrette, 2009a
2-mercaptoethyl ether	Free radical scavenger	Strong inhibitor	No effect	Carrette, 2009b
1-thioglycerol	Free radical scavenger	Strong inhibitor	No effect	Carrette, 2009b
2,2-thiodiethanol	Free radical scavenger	Strong inhibitor	No effect	Carrette, 2009b
2,2'-dithiodiethanol	Free radical scavenger	Strong inhibitor	No effect	Carrette, 2009b
Cystamine	Free radical scavenger	Strong inhibitor	Pro-oxidant	Carrette, 2009b
Various thiadiazoles	Free radical scavenger	Strong inhibitor	No effect	Carrette, 2009c
Cystine	Free radical scavenger	Strong inhibitor	Pro-oxidant	Carrette, 2010
Cysteine	Free radical scavenger	Strong inhibitor	Pro-oxidant	Carrette, 2010
Various triazoles	Free radical scavenger	Strong inhibitor	Not tested	Carrette, 2011
Diethyl dithiophosphate	Chelating agent	Strong inhibitor	No effect	Delfort, 2010
Various dithiocarbamates	Chelating agent	Strong inhibitor	Moderate inhibitor	Delfort, 2009
EDTA	Chelating agent	Moderate inhibitor	Moderate inhibitor	Chi, 2000; Chi, 2002; Goff, 2005; Goff, 2006; Sexton, 2008; Blachly, 1963; Blachly, 1964; Blachly, 1966; Blachly, 1965; Ravner, 1964; Johnson,

Gluconate	Chelating agent	Mild inhibitor	Mild inhibitor	1964; Idem,
Bicine	Chelating agent	Mild inhibitor	Mild inhibitor	2009
				Singh, 1970
				Chi, 2000; Chi,
				2008; Blachly,
				1963; Blachly,
				1964; Blachly,
				1966; Blachly,
				1965; Ravner;
				Johnson, 1964
Tartaric acid	Chelating agent	Mild inhibitor	No effect	Idem, 2009;
				Supap, 2010
Phosphate	Chelating agent	Mild inhibitor	Mild inhibitor	Goff, 2005

Findings from various literature studies and this work showed conflicting conclusions as to the effect (catalyst or inhibitor) and potency of various additives. Sexton (2008) showed that Mn was an inhibitor using MEA loss and formate production, whereas Goff (2005) had observed more complex behavior using only ammonia production, but evaluated continuously during an experiment. The key difference between these studies was the amount of Mn initially added, which in Sexton's case was several thousand times more than what Goff had tested. This work shows that Mn is indeed an inhibitor—at first. However, at low concentrations, higher temperatures, and after a sufficient amount of time, Mn switches oxidation states and becomes a catalyst. In other works, experimental conditions may have affected the results. This work was conducted in a semi-batch system using 98 kPa air and 2 kPa CO₂, which is fairly representative of an industrial system. The temperature of 70°C was selected on the basis that it allows for faster steady-states and higher rates of oxidation, while still being within the temperature range expected in an industrial system.

Delfort and Carrette identified numerous antioxidants that substantially reduced heat stable salt production in oxidized MEA solutions. The experiments were conducted at 80°C with 0.5% CO₂ in air at 1 atmosphere. The gas was bubbled through the solution at ~100mL/min; oxygen mass transfer was enhanced by vigorous agitation. However, the experiment was conducted in glass and no metals were added to the solution. When these inhibitors were tested in the HGF apparatus with metals present, most had no effect and several were observed to be pro-oxidants. Only diethyldithiocarbamate, a chelating agent, was observed to inhibit oxidation in the presence of metals. Metals, especially iron, are always expected to be present in an industrial system.

Another important set of findings is related to the material balance and products for oxidation of MEA. Early studies predicted the formation of oxidation fragments—namely NH₃, formaldehyde, and hydroxyacetaldehyde (Dennis, 1967; Kovtun, 1973; Petryaev, 1984). NH₃ was observed in a number of experiments that mimicked industrial systems (Chi, 2000; Chi, 2002; Goff, 2005; Goff, 2006; Sexton, 2008; Blachly, 1963; Blachly, 1964; Blachly, 1966; Blachly, 1965; Epp, 2010). Formaldehyde was also reported in one of these experiments (Epp, 2010). Rooney (1998) showed that many amine systems produced organic acids (namely formate, acetate, glycolate) during oxidation. Koike (1987) first recognized that the amides of these acids were also present (namely N-formyl-diethanolamine). Sexton (2008, 2011) expanded on this work showing that N-formyl-ethanolamine was a major product for MEA oxidation, and in fact was present in much higher concentrations than the formate alone. Sexton also identified another product in MEA oxidation, hydroxyethylimidazole (HEI), and showed that higher

molecular weight condensation products accounted for a majority of the material balance of lost MEA, whereas the organic acids were a minority product (Table A3 and Figure 9). Table A4 summarizes the major products of MEA oxidation that have been identified.

Table A3 – Material Balance for Oxidation of 7 m MEA at 55°C with 98 kPa O₂ and 2 kPa CO₂. Produced from data reported by Sexton (2008)

Compound	Conc. (mmol/kg)	Nitrogen (mmol/kg)	Carbon (mmol/kg)
MEA (loss)	1676	1676	3352
Condensation Products			
HEI	287	574	1435
HEF	383	383	1149
diHEO	44	88	264
Organic Acids			
Glycolate	<1	0	<1
Acetate	<1	0	<1
Formate	144	0	144
Oxalate	10	0	20
Nitrogen-Containing Fragments			
NO ₃ ⁻	42	42	0
NO ₂ ⁻	89	89	0
NH ₃	50	50	0

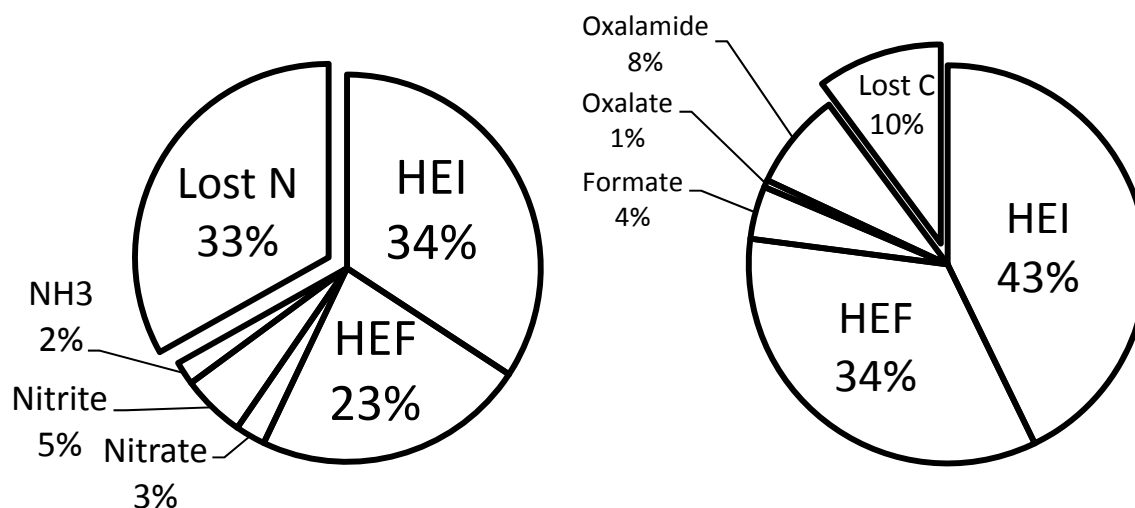


Figure 9 – Material Balance for Oxidation of MEA in the presence of 98 kPa O₂ and 2 kPa CO₂ at 55°C. Data from Sexton (2008).

Strazisar (2003) and LePaumier (2009) both identified a number of other products, but neither was able to complete the material balance for MEA. Various studies have reported synthesizing some of these

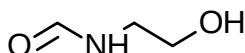
products from reacting amines and ammonia with aldehydes (such as hydroxyl acetaldehyde, formaldehyde, and glyoxal) (Treybig, 1989; Arduengo, 2001). These studies lend significant credibility to the presence of some higher molecular weight condensation products in oxidized MEA solutions

Table A4 – Known and Suspected Oxidation Products of MEA

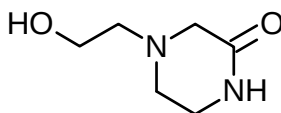
Known Fragmentation Products

Formate, oxalate, nitrate, nitrite, ammonia

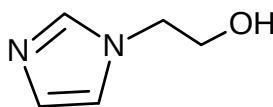
Likely Condensation Products



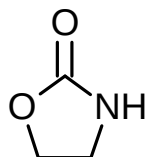
N-(2-hydroxyethyl)-formamide (HEF)



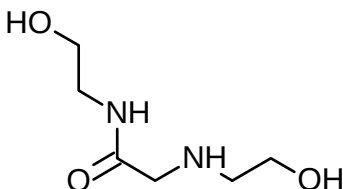
1-(2-hydroxyethyl)-4-piperazinone (HEPO)



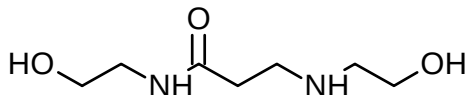
1-(2-hydroxyethyl)-imidazole (HEI)



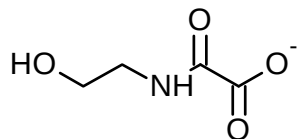
2-oxazolidinone



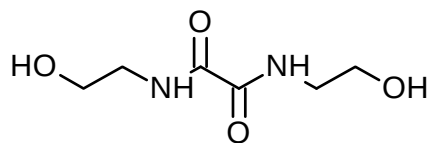
N-[(2-hydroxyethyl)-2-hydroxyethyl-amino]acetamide (HEHEAA)



N-(2-hydroxyethyl)-3-[(2-hydroxyethyl)amino]propanamide (HEHEAP)



N-(2-Hydroxyethyl) oxalamide



N,N'-di(2-hydroxyethyl)-oxal-diamide (diHEO)

7.0 References

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Oxidation of MEA and Other Amines for CO₂ Capture

Alexander Voice

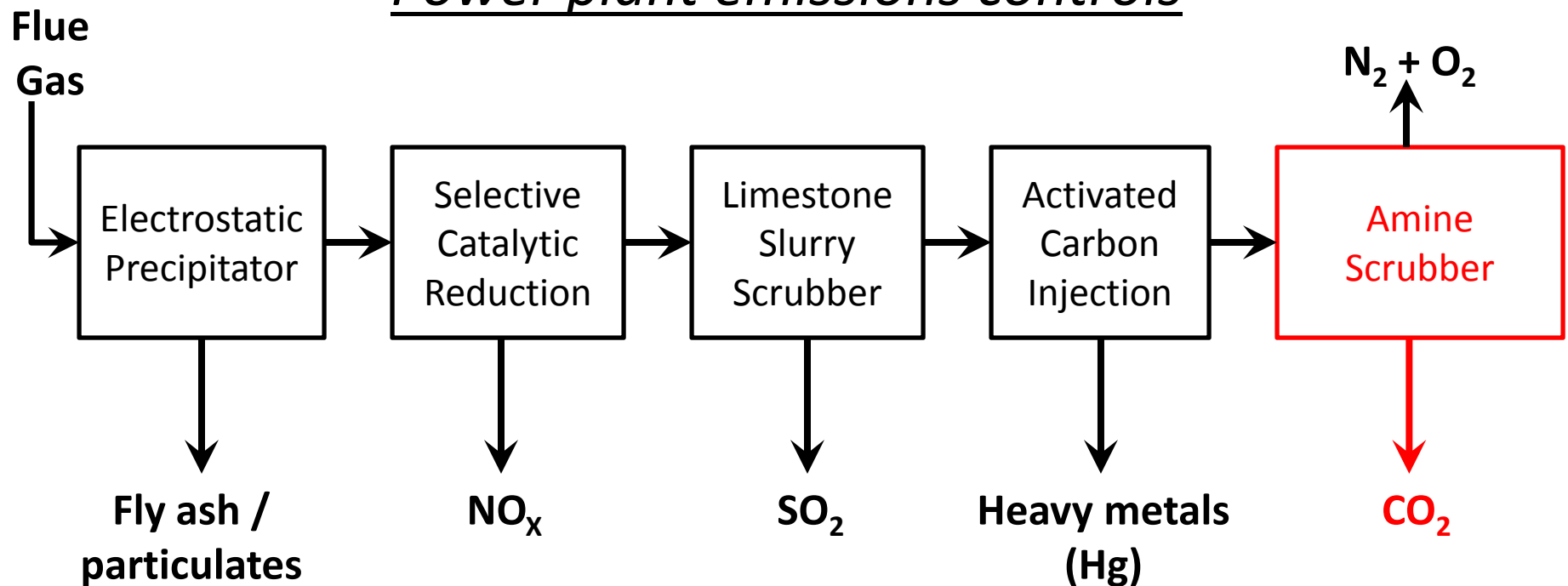
15.Apr.2011

*Oral preliminary examination for
Doctoral candidacy*

Post-combustion CO₂ capture will be used to reduce power plant emissions

- CCS can provide 15-55% of cumulative emissions reductions by 2100 (\$10-100 trillion) @ \$50/tCO₂
- Amine scrubbing is the state-of-the-art technology

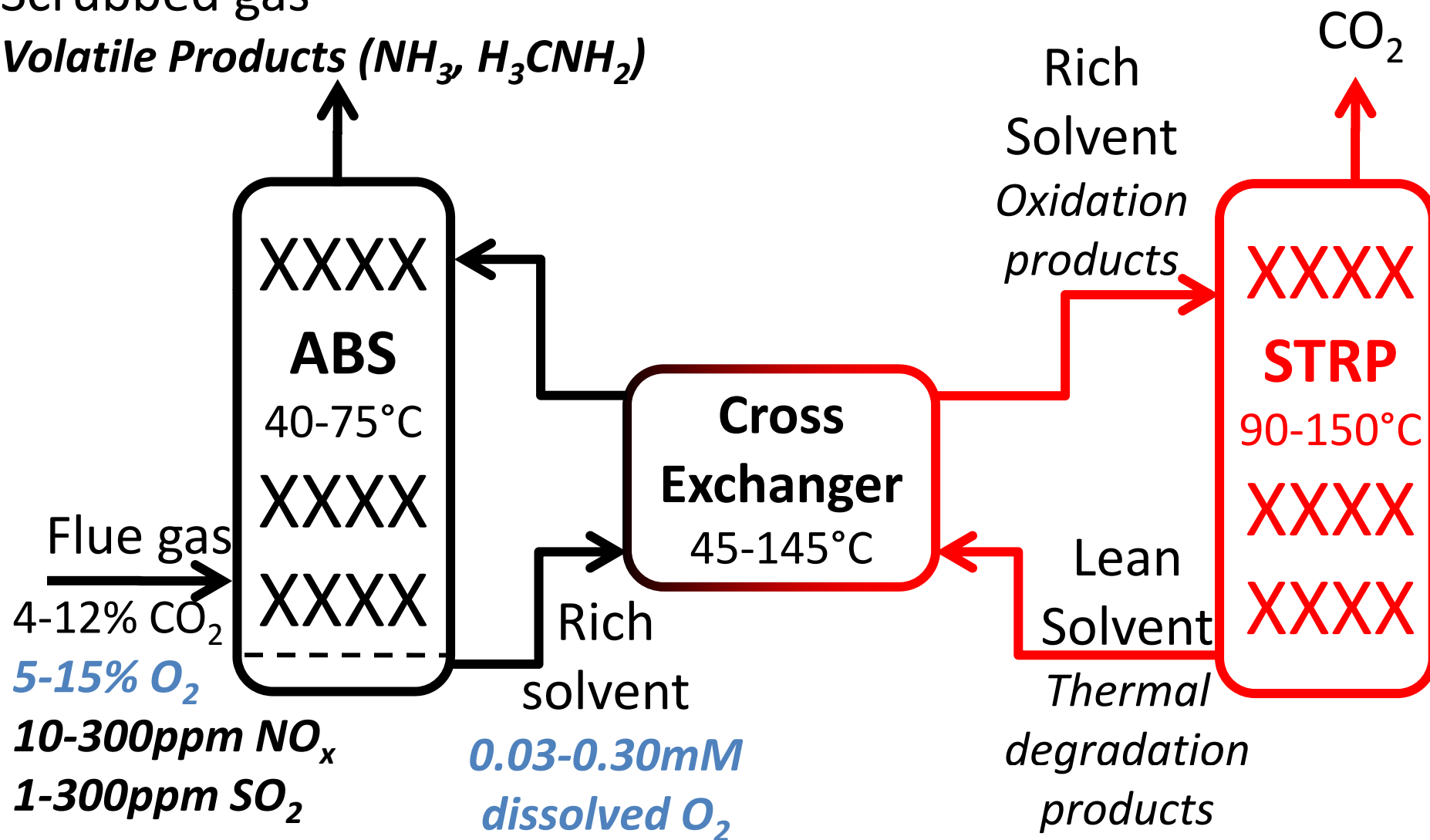
Power plant emissions controls



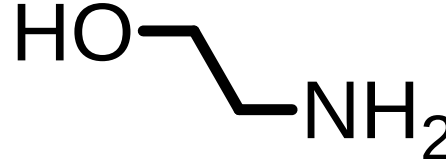
Amine Oxidation in CO₂ Capture

Scrubbed gas

Volatile Products (NH₃, H₃CNH₂)



MEA is an acceptable solvent for CO₂ capture



- Fast reaction rate with CO₂ (low partial pressure)
- High heat of absorption (15% > PZ, 30% > MDEA)
→ reduced steam and compression cost
- Low solvent makeup cost (2-5x cheaper than PZ)
- Physical and chemical properties are
- MEA systems have been optimized to energy demand



Solvent degradation can contribute ~10% of costs for CO₂ capture

Cost of Degradation

- Solvent makeup cost
- Removal of products
- Treatment of waste streams
- Reduce rates/capacity
- Volatile product emissions
- Reduced equipment lifetime

Research Opportunities

- Determine how process conditions affect oxidation
- Identify oxidation catalysts and inhibitors
- Identify degradation products and rates

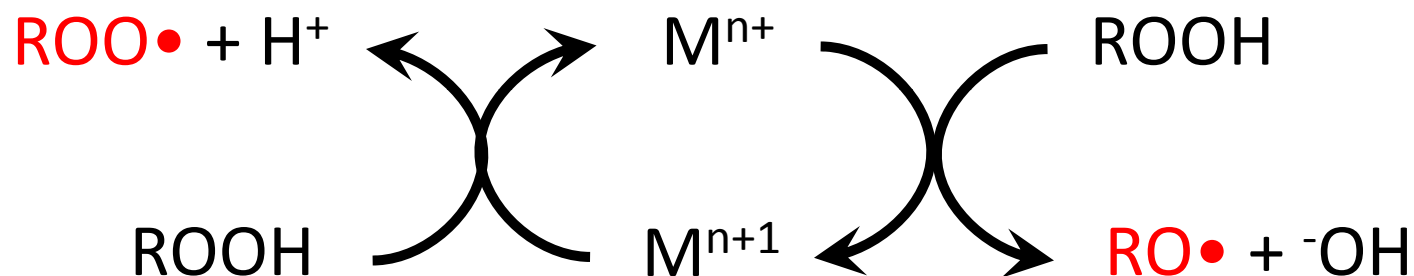
**Manage and minimize
solvent degradation in an
industrial capture system**

Mechanism of MEA Oxidation by Molecular Oxygen

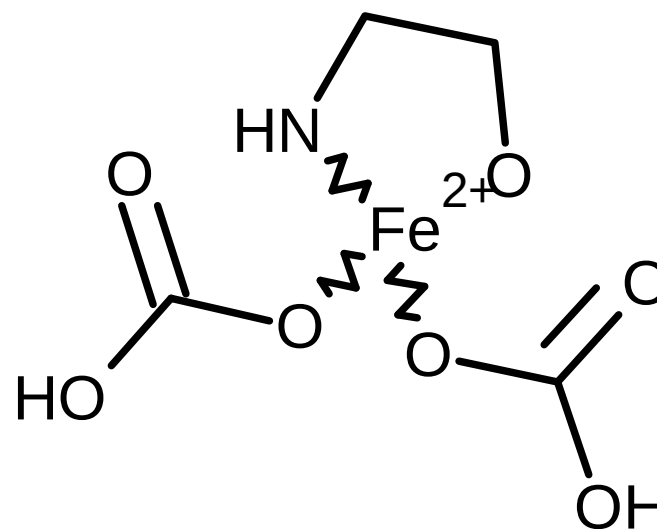
Initiation	$\text{MEA} \rightarrow \text{MEA}\bullet + \bullet\text{H}$ $\text{MEA}\bullet + \text{O}_2 \rightarrow \text{MEA-OO}\bullet$
Propagation	$\text{MEA-OO}\bullet + \text{MEA} \rightarrow \text{MEA-OOH} + \text{MEA}\bullet$ $\text{MEA-OOH} \rightarrow \text{MEAO}\bullet + \bullet\text{OH}$ $\text{MEAO}\bullet + \text{MEA} \rightarrow \text{MEAOH} + \text{MEA}\bullet$ $\text{HO}\bullet + \text{MEA} \rightarrow \text{MEA}\bullet + \text{H}_2\text{O}$
Termination	$\text{R}\bullet + \text{R}\bullet \rightarrow \text{mol. Prod.}$
Inhibition	$\text{MEA}\bullet + \text{Inh.} \rightarrow \text{MEA} + \text{Inh.}\bullet$

Metals are important in amine oxidation

- Metals catalyze the decomposition of peroxides
 - Mn, Cu, Fe, Co, Ce are well known catalysts
 - Corrosion: Fe, Cr, Ni; Inh.: Cu, V; Fly ash: many

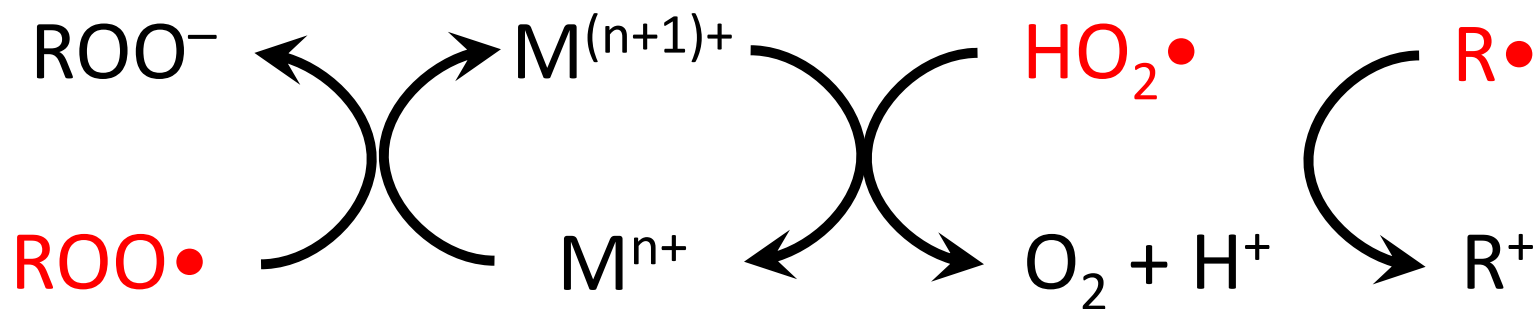


- Ligands form complexes with dissolved metals $\rightarrow \rightarrow$ changes redox potential



Metals are important in amine oxidation

- Metals are involved in termination reactions
 - Cu and Mn are known to be very reactive
 - React with $R\bullet$, $ROO\bullet$, and $HO_2\bullet$



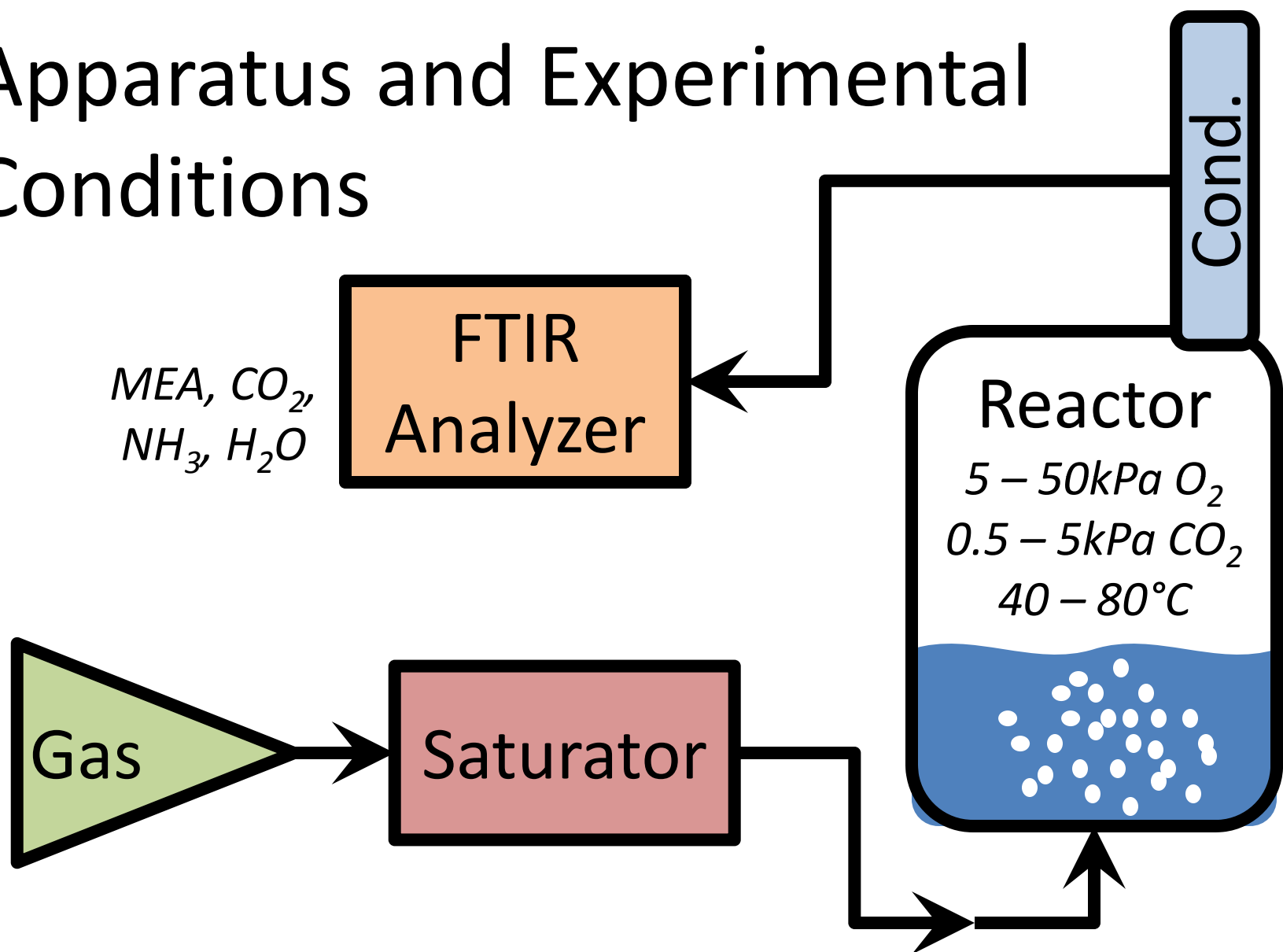
- Metals react with each other (redox cycling)



A much better understanding of MEA oxidation is required

- Experimental design → rates, products, catalysts, inhibitors **comparable to a real plant**
- Product identification → demonstrate plausible **pathway to products**
- Material balance → **account** for all degraded nitrogen and carbon
- Oxidation mechanism → **Understand and predict** the effects of relevant variables
- Catalysts and inhibitors → **screen** all possible candidates in a representative apparatus

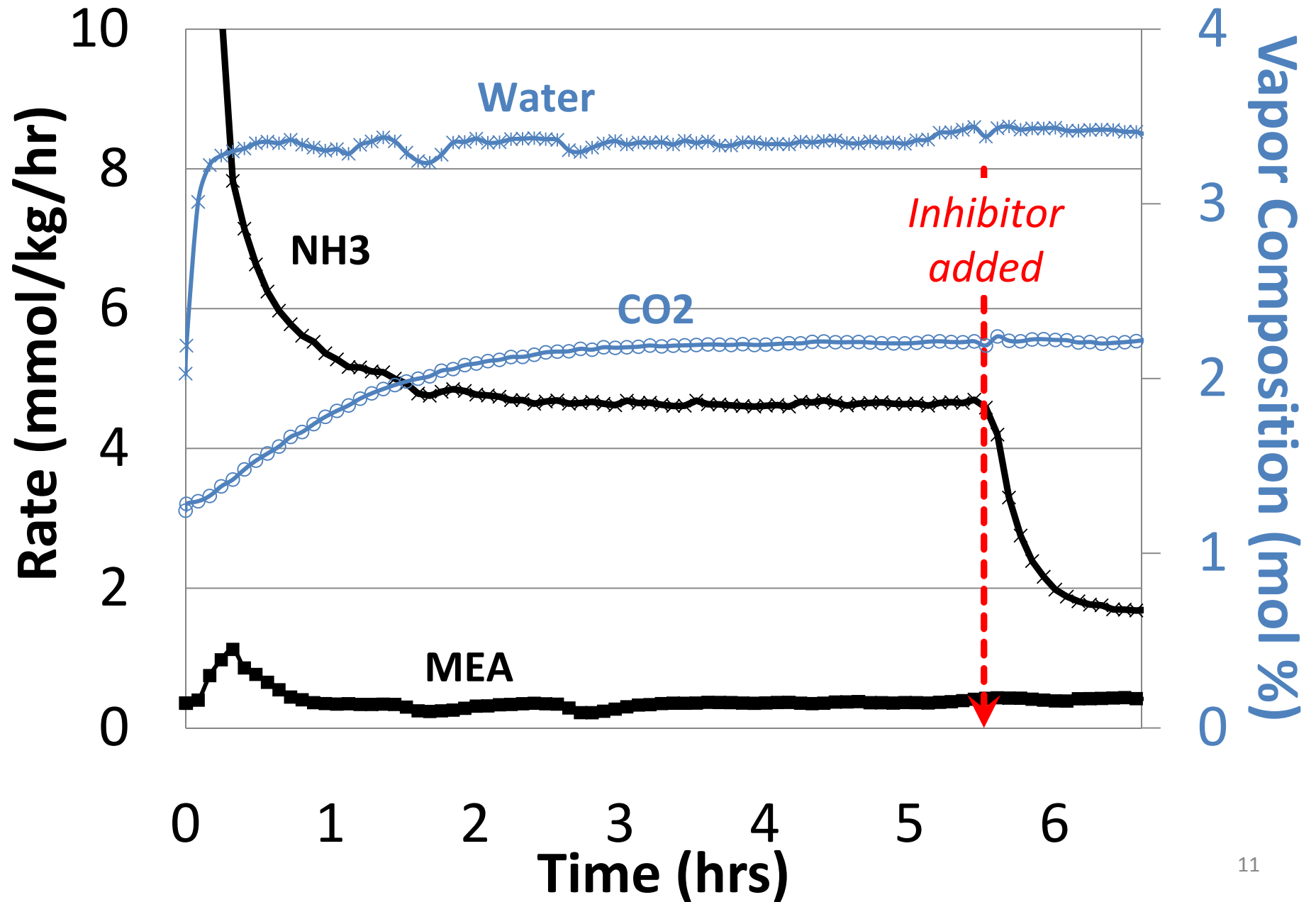
Apparatus and Experimental Conditions



Advantages: representative, see volatiles, continuous analysis

Disadvantages: slow oxidation, no HT cycling, water balance

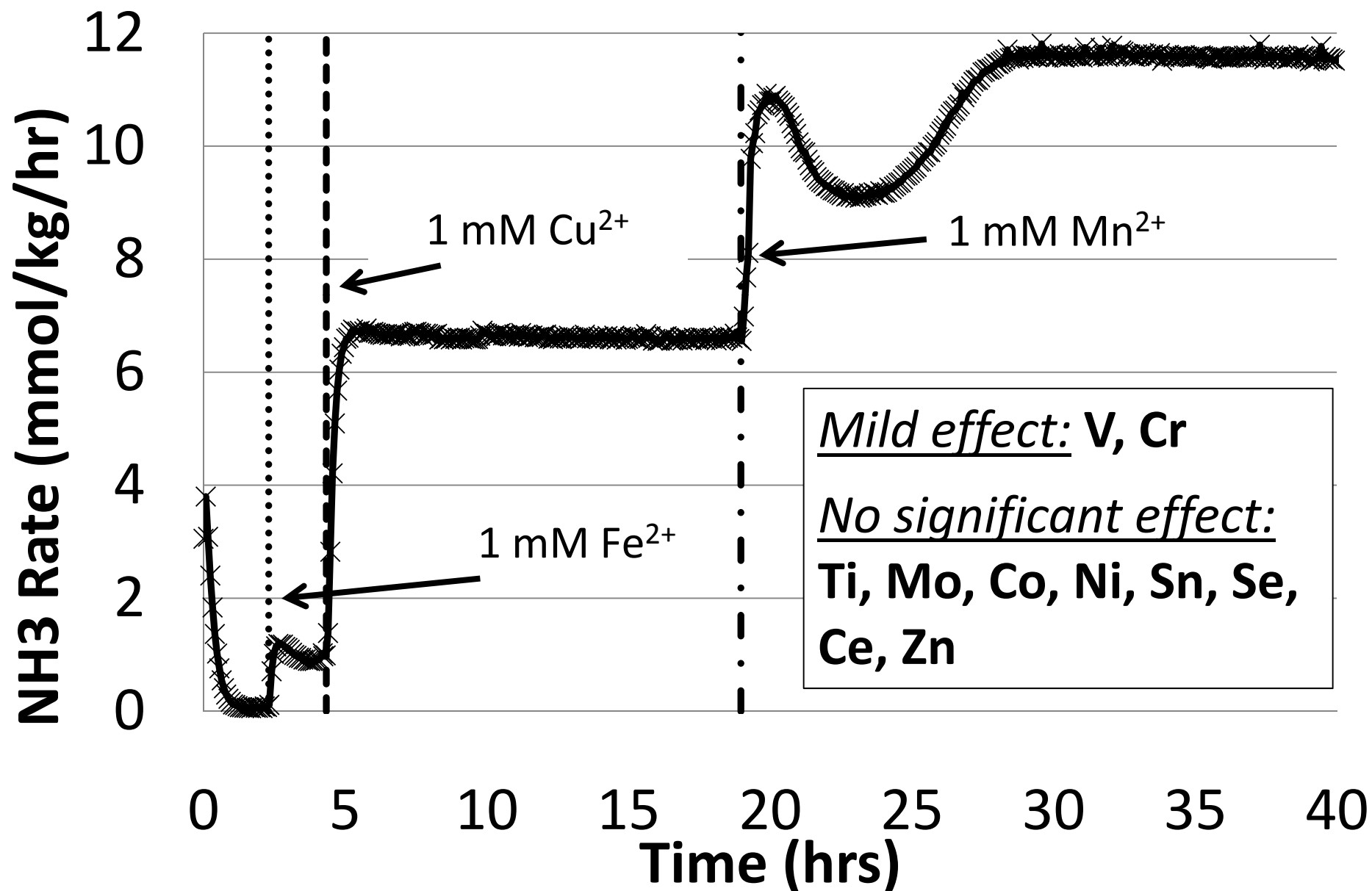
Vapor Composition Analysis with Hot-Gas FTIR



Analytical Instruments

- Primary methods
 - **FTIR**: continuous analysis of volatile oxidation products (NH_3 , methylamine, NO_2 , NO , N_2O)
 - **Anion chromatography**: oxidation fragments (formate, oxalate, nitrate, nitrite, amides)
 - **Cation chromatography**: Liquid-phase amine loss
- Secondary methods
 - **HPLC-MS, GC-MS, MS-MS**:
Identification/quantification of high molecular weight condensation products
 - **Total material methods**: total (in)organic carbon, nitrogen, alkalinity

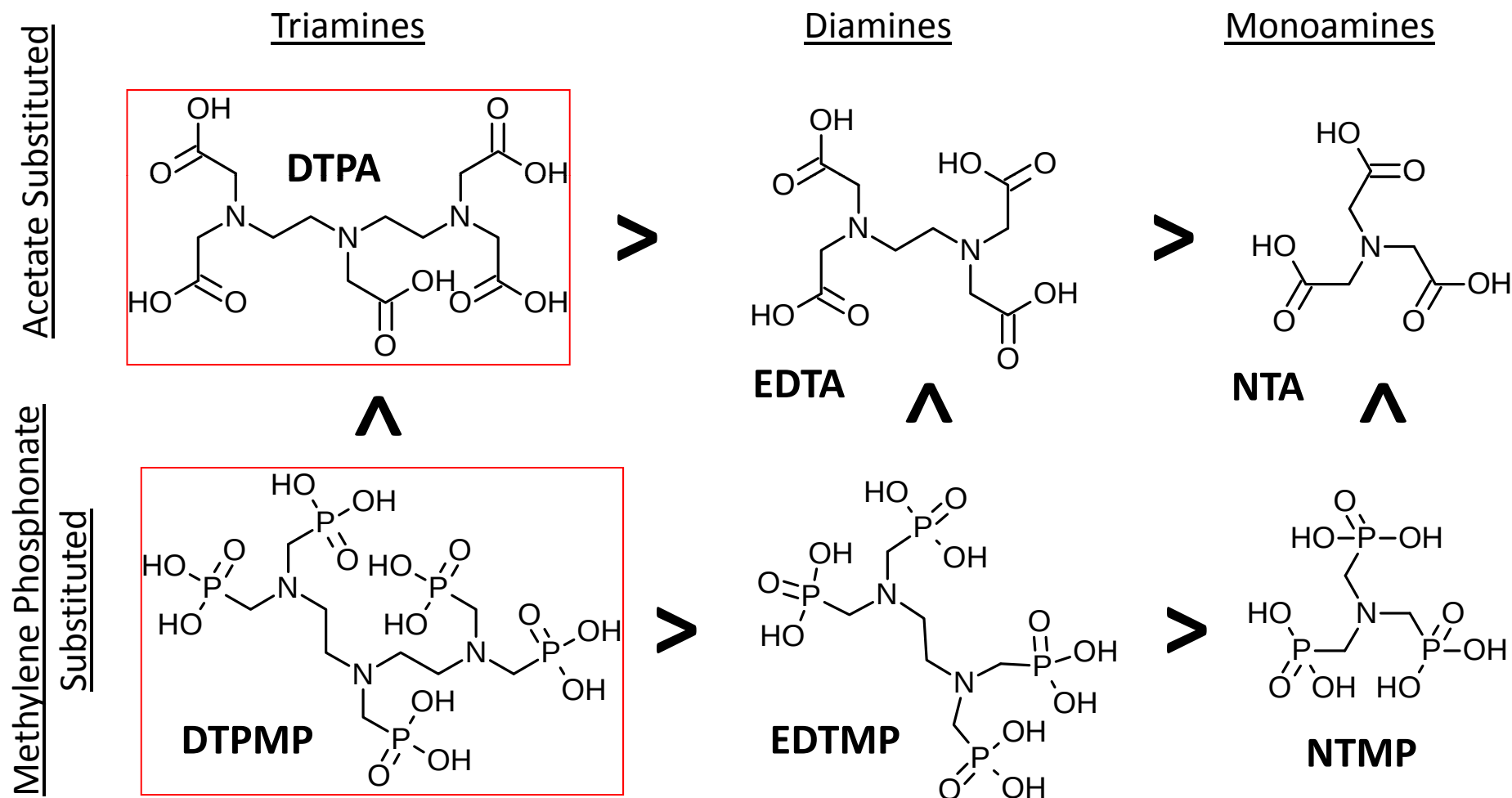
7 m MEA with Fe^{2+} , Cu^{2+} , Mn^{2+}
Conditions: 70°C, 98kPa air, 2kPa CO_2



Inhibitor Screening

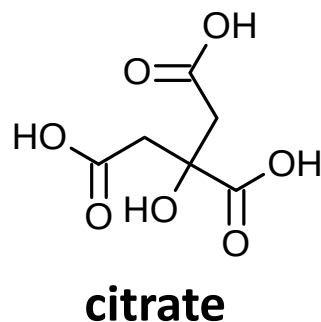
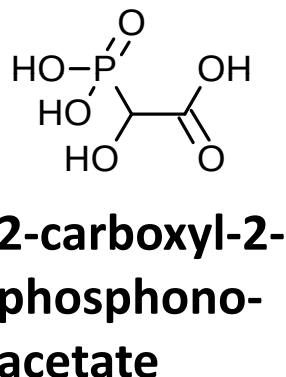
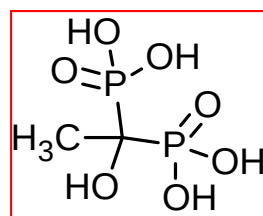
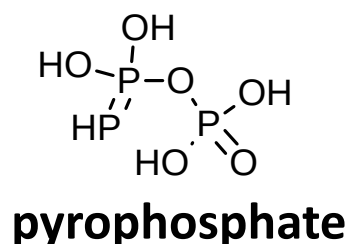
- Conditions: 9 m pilot plant MEA containing 0.5mM Fe, 98 kPa air, 2 kPa CO₂, 70°C, 7.65LPM
- Observed steady-state change in ammonia rate
- Screened 70+ inhibitors using this method
- Literature inhibitors: sulfite, EDTA, inhibitor A
- New inhibitors: more potent than any known inhibitors

Some acetate- and methylene phosphonate-substituted tertiary amines inhibit oxidation

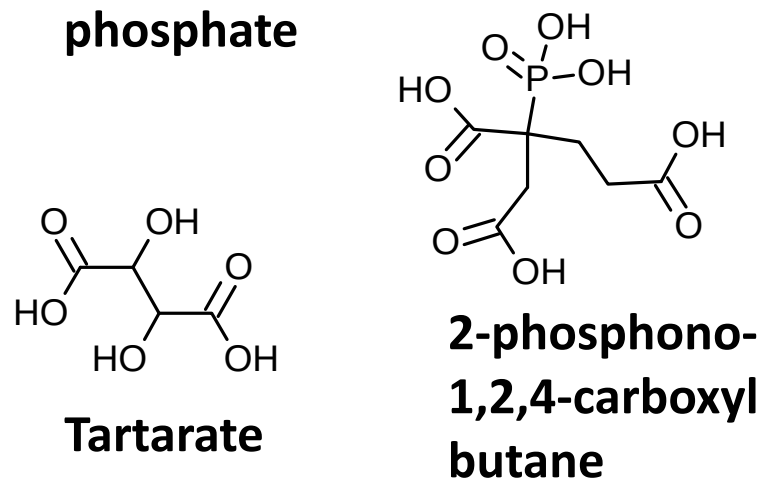
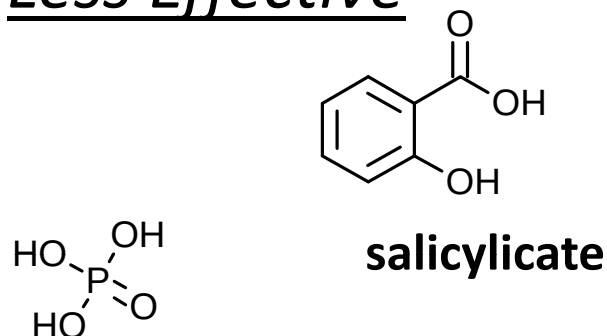


Some carboxylate and phosphonate-containing organics are also inhibitors

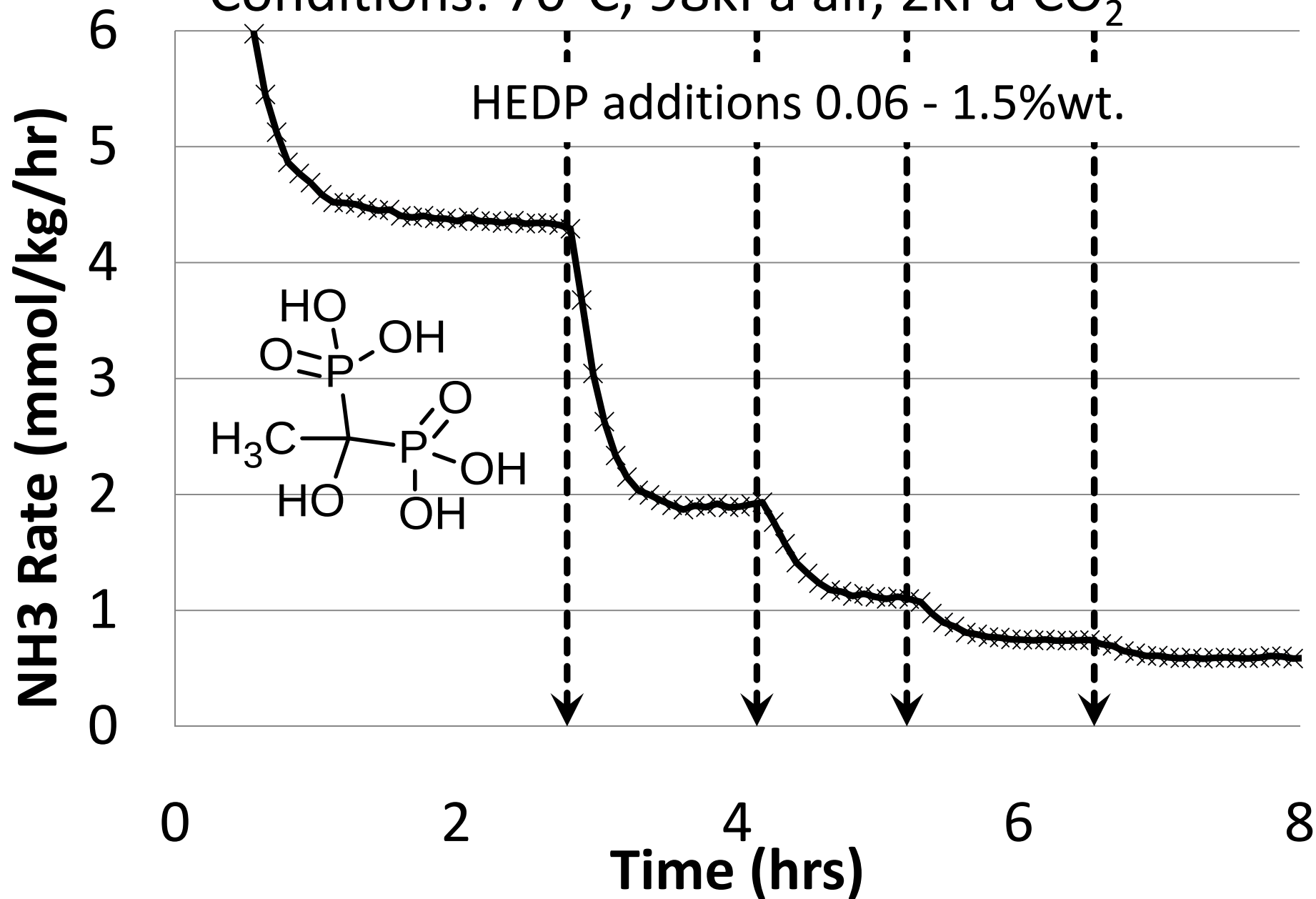
More Effective



Less Effective

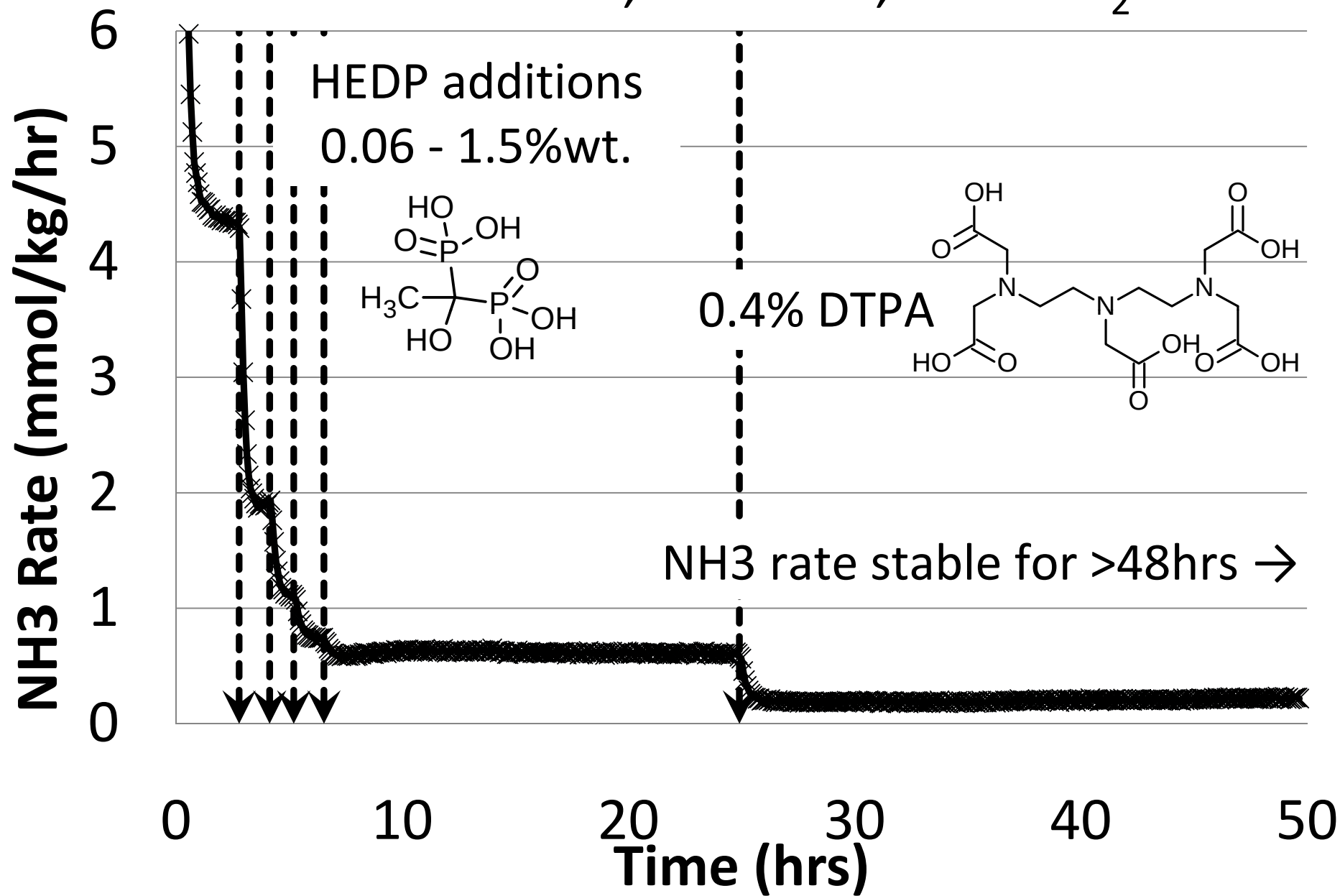


9 m pilot plant MEA with HEDP
Conditions: 70°C, 98kPa air, 2kPa CO₂

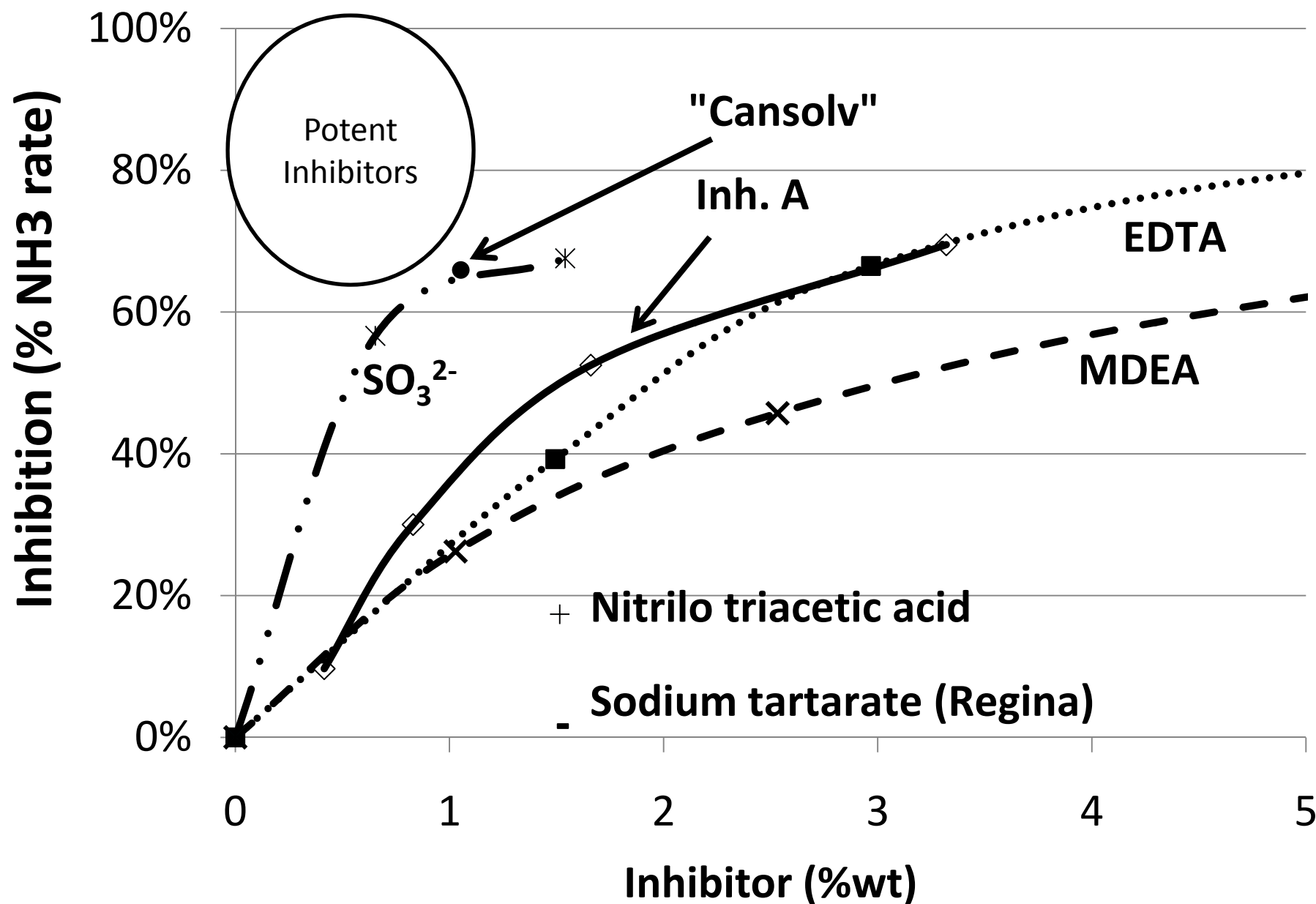


9 m pilot plant MEA with HEDP

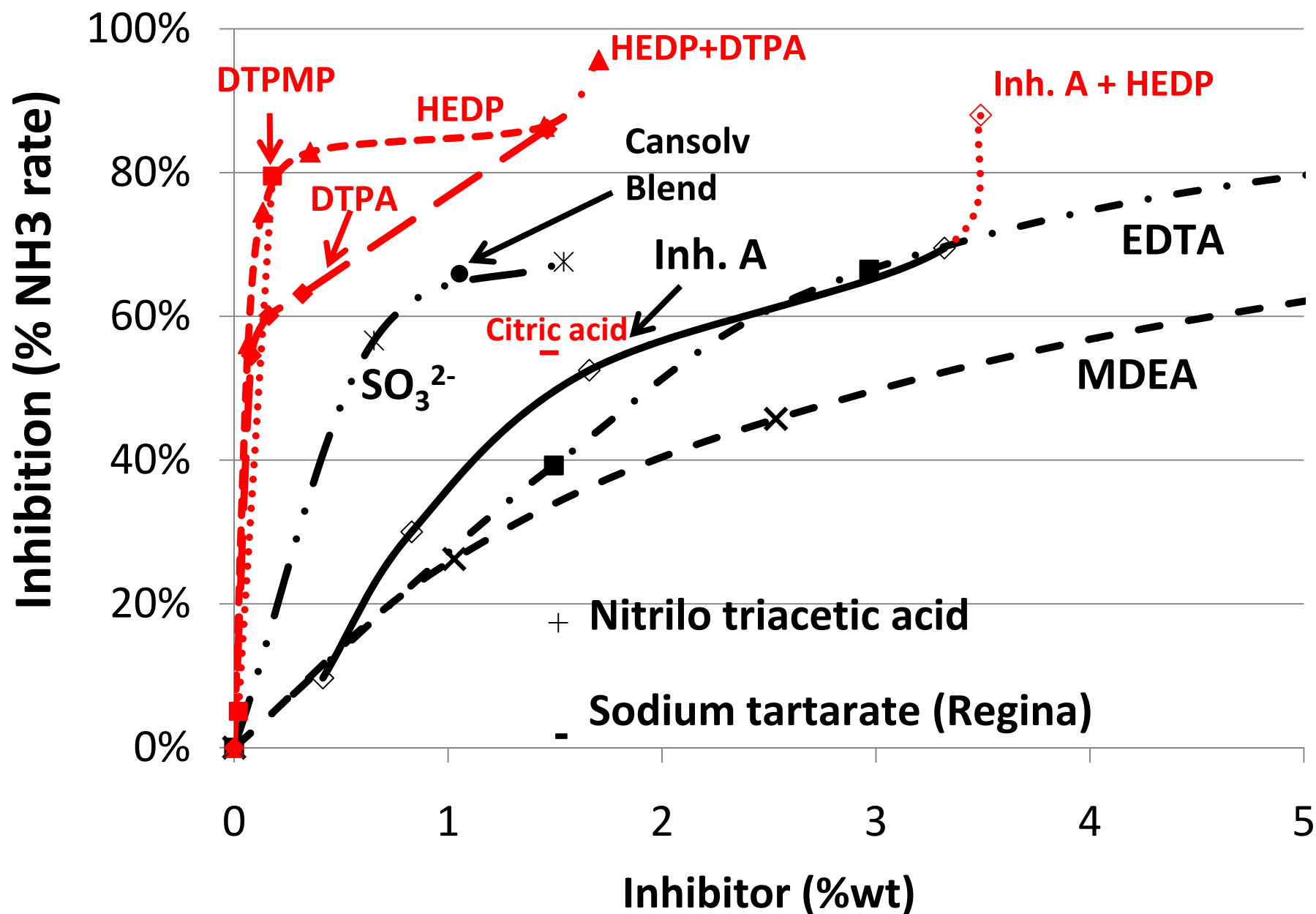
Conditions: 70°C, 98kPa air, 2kPa CO₂



Comparison of inhibitors at 70°C, 98kPa air, 2kPa CO₂



Comparison of inhibitors at 70°C, 98kPa air, 2kPa CO₂



MEA Oxidation – Where did the N go??

98 kPa O₂, 2 kPa CO₂, 55°C, 7 days (LGF)

Methods

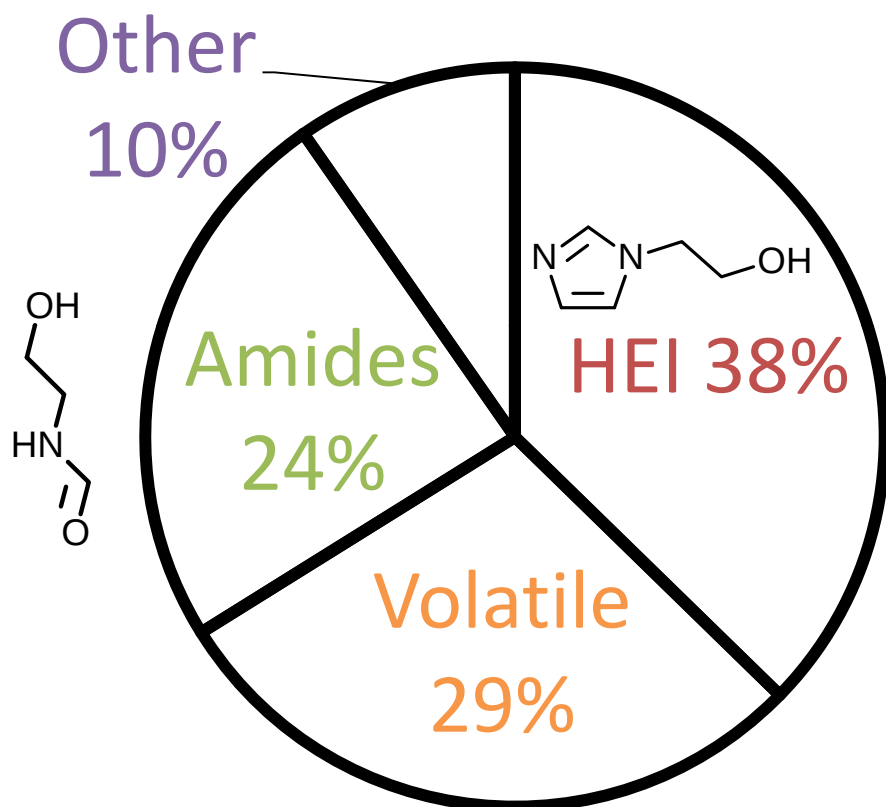
MEA loss – cat. chrom.
(~2mol/kg)

HEI – HPLC-UV

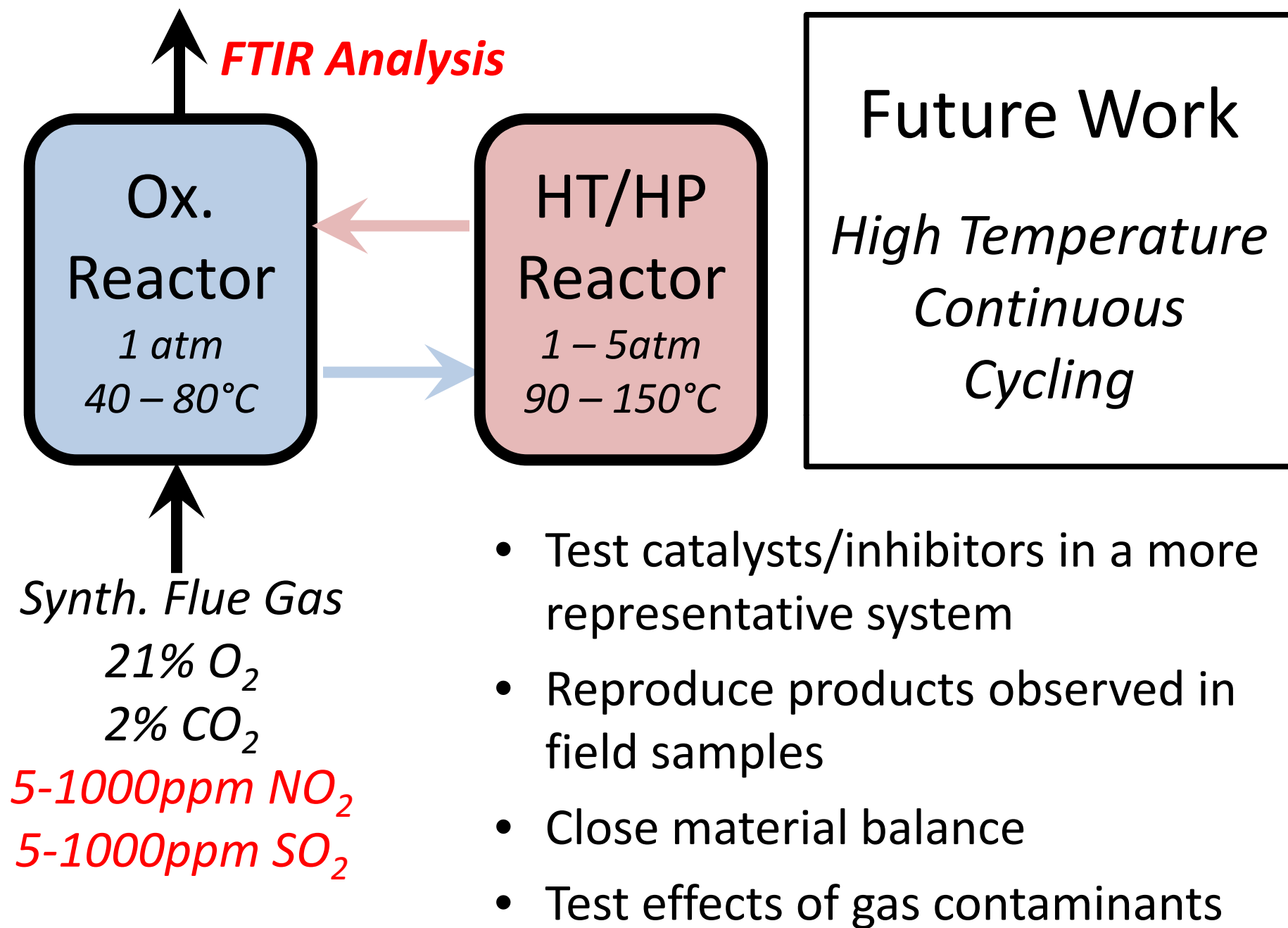
Volatile – total nitrogen

Amides – NaOH, anion
chrom.

Other – Σ nitrate, nitrite,
NH₃(l), HEG



$$\frac{\sum \text{amides, HEI, volatile losses, other N species}}{MEA_i - MEA_f} = 101\%$$



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Luminant Carbon Management Program

Advisor: Dr. Gary T. Rochelle

UG Assistant: Ashley Hill

Lab Colleagues: Fred, Stephanie, Thu, Qing, Xi, Humera, Steven, Lynn

Overview

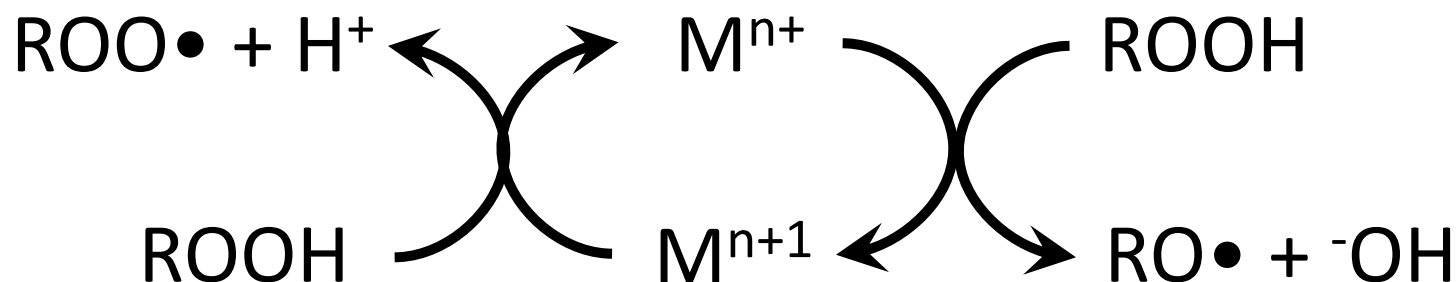
- **Motivation** for research on MEA oxidation
- **Mechanism** of MEA oxidation and anti-oxidation
- **Previous works** on MEA oxidation and inhibition
- **Proposed methods:** experimental apparatuses and analytical instruments
- **Preliminary results** for MEA catalysts, inhibitors, and products
- **Conclusions / Future Work**

Inhibitor Screening Study

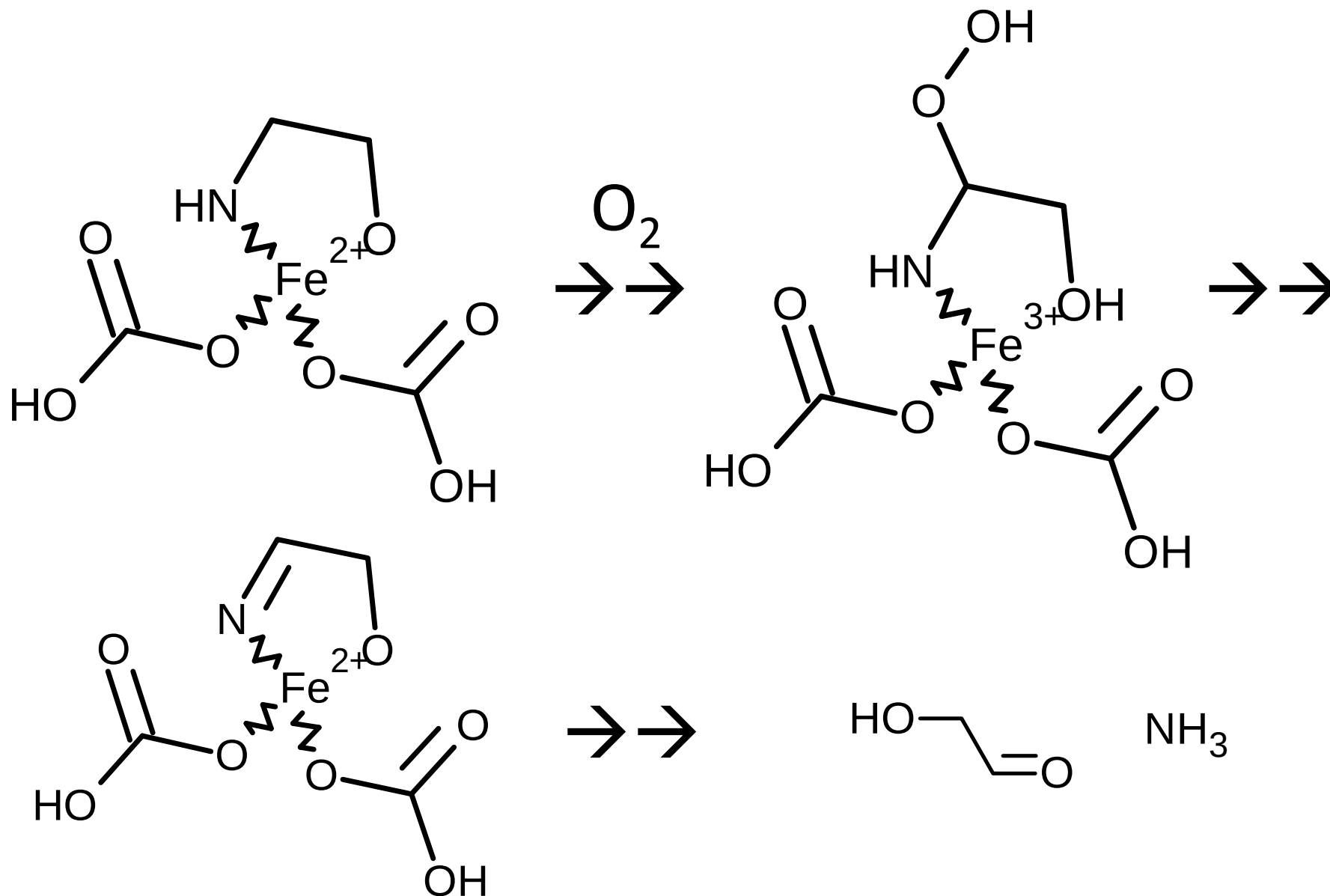
- **Potent**: small amount of inhibitor substantially inhibits oxidation
- **Robust**: Thermally stable up to 150°C, resistant to oxidation
- **Practical**: Works at 40 – 120°C, does not enhance thermal degradation, corrosion
- Screened 68 inhibitors belonging to various chemical classes (potency/robustness)
- “Stress-testing” in progress (practicality)

Rate Constants for Reaction of H_2O_2 with Transition Metal Ions in Aq. Soln.

Metal Ion	k (298) ($\text{M}^{-1}\text{s}^{-1}$)
Cu^+	1.35 e3
Fe^{2+}	63.0 e0
MnO_4^-	3.02 e3
Mn^{3+}	7.24 e4
MnOH^{2+}	3.16 e4
Fe^{2+} -DTPA	1.37 e3



Iron-initiated oxidation of MEA



Basics on Amine Oxidation

- **Where** does oxidation occur?
 - Fast kinetics: absorber, sump and cross exchanger
 - Slow kinetics: cross exchanger
- **What** products are formed?
 - C-N bond is broken, $R_2N-C-R \rightarrow R-C=O + N-R_2$
 - Tertiary $\rightarrow$ secondary $\rightarrow$ primary $\rightarrow$ ammonia

Free radical mediated process – influenced by presence of **metals, CO₂, impurities**

Past Experiments

- **Material balance**
- **Catalysts and inhibitors**
- Other amines (catalysts/inhibitors)
- Thermal/oxidative cycling effects
- Degradation products: stabilities and pathways
- Product identification (field samples) and method development
- Temperature dependence of oxidation
- Gas phase contaminants

Timetable of Future Experiments

- Spring 2011
 - Finish inhibitor screening (HGF)
 - GCMS/LCMS method development
- Summer 2011
 - Finish inhibitor stress testing (batch cycling)
 - Pilot plant NH_3 analysis and inhibitor testing
 - **Construct cycling apparatus with FTIR analysis**
- Fall 2011
 - Degradation with flue gas at TNO (tentative)

Timetable of Future Experiments

- Spring 2012
 - Test inhibitor with continuous cycling/apparatus
- Summer 2012
 - Match products observed in field samples
 - Close cycling material balance
- Fall 2012
 - Solvent screening (cycling apparatus)
 - Last experiments
- Spring 2013
 - Dissertation writing

Backup Slides

Methods of Inhibition

- Cyclic chain-termination reactions

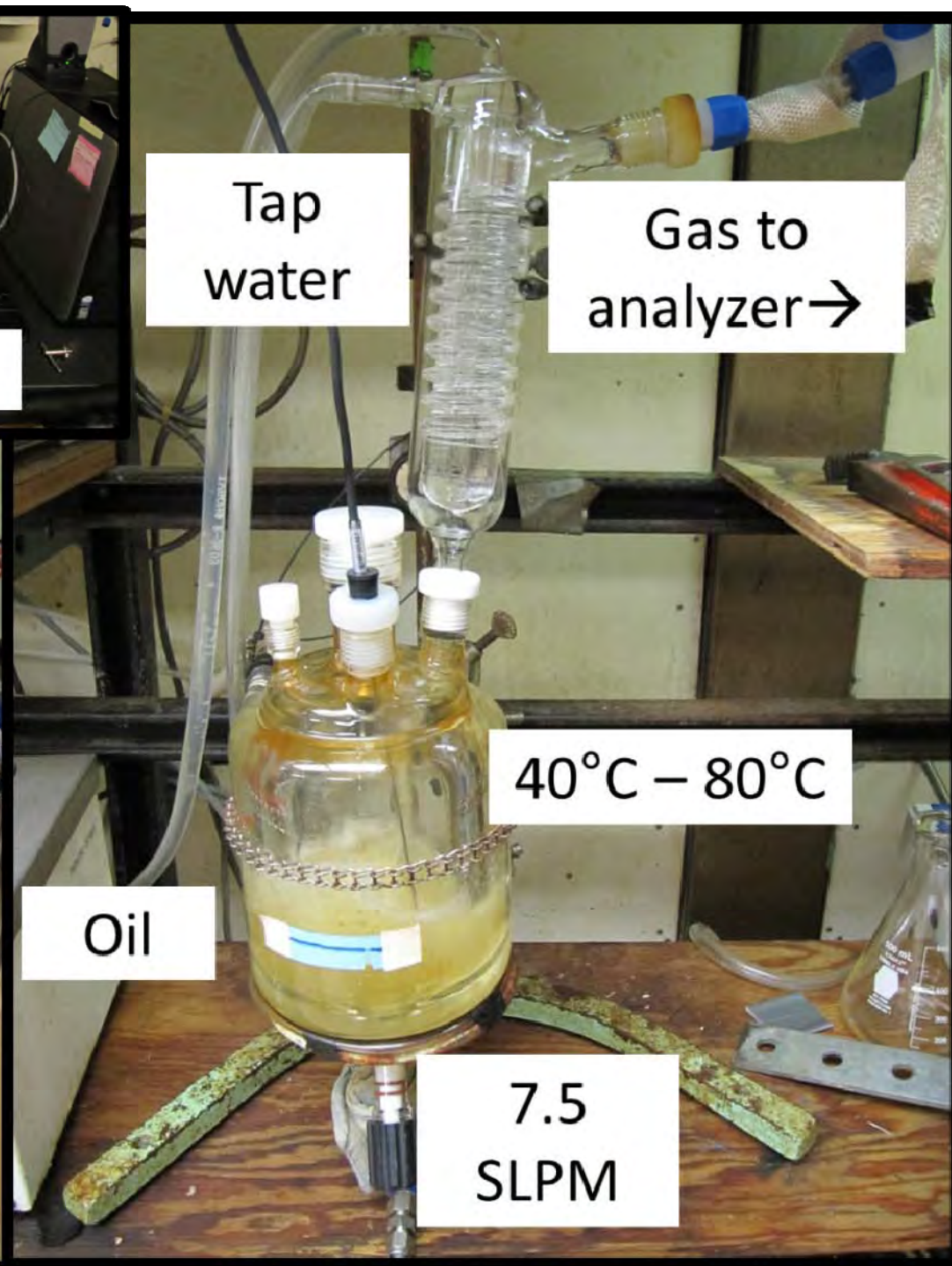
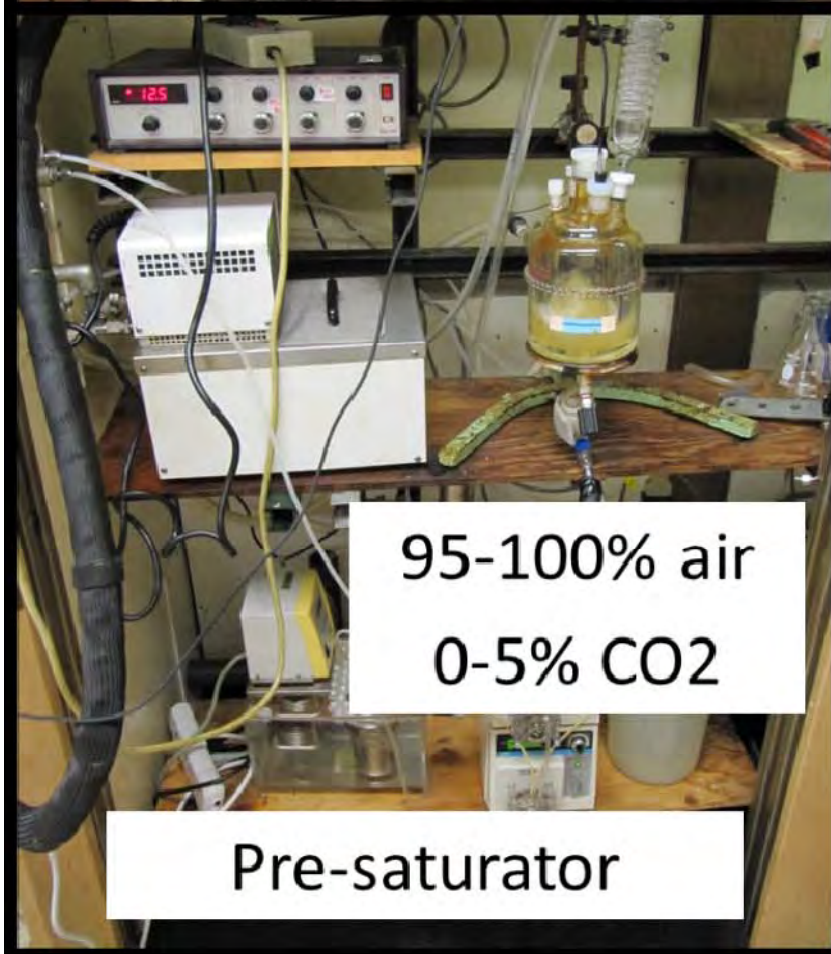
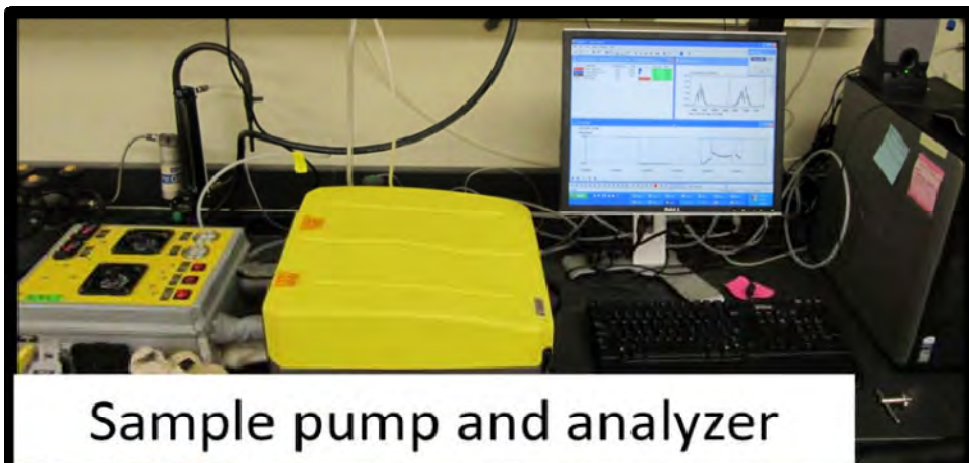


- Peroxide decomposition



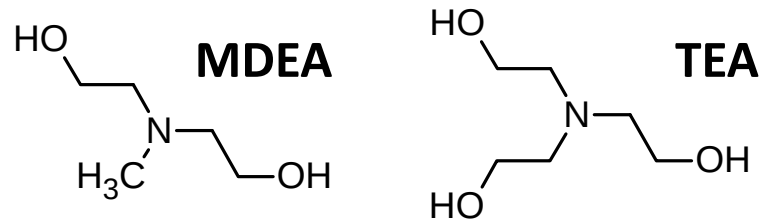
– Ligands change the relative rates of peroxide decomposition; different for different metal-ligand combinations

- Metal sequestration/deactivation

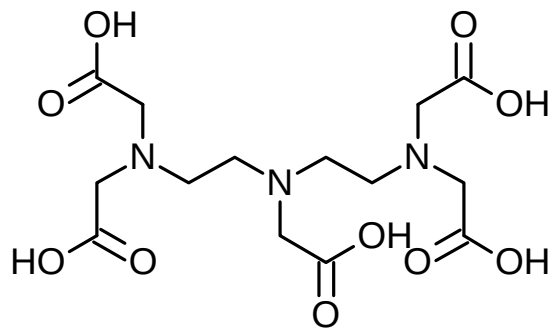


Summary of Inhibitors

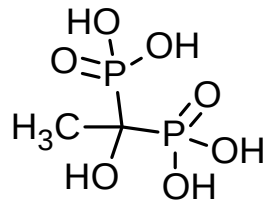
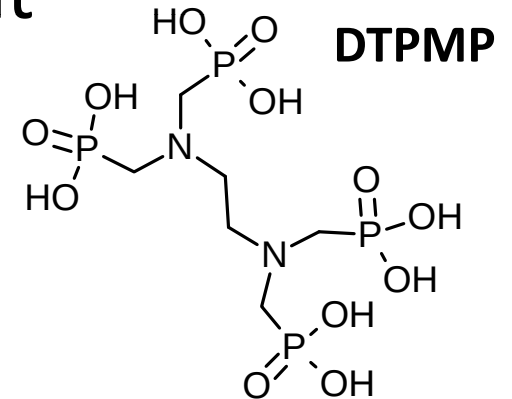
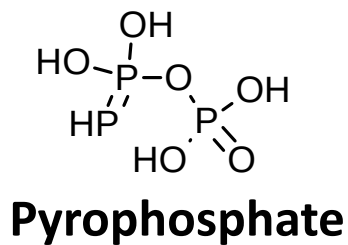
- Tertiary amines – weak, but have CO₂ capacity



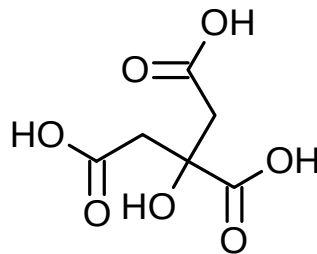
- Certain chelating agents are potent inhibitors...



DTPA

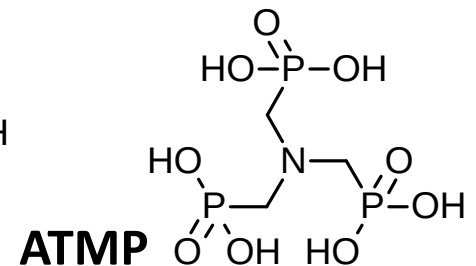
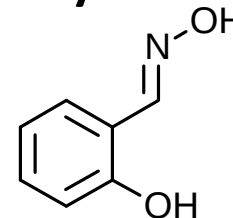


HEDP



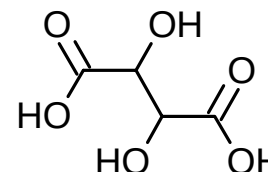
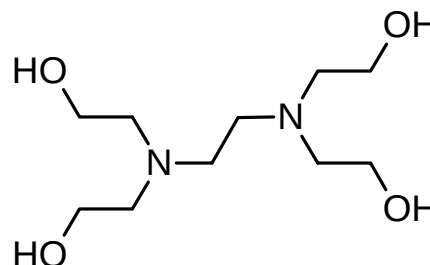
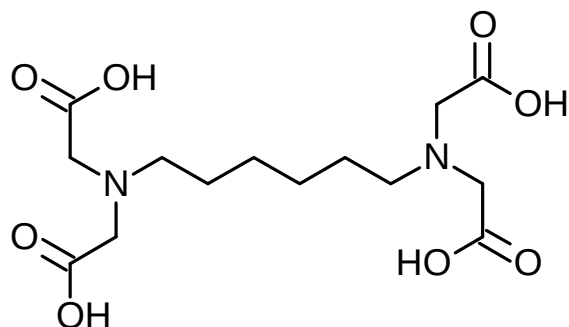
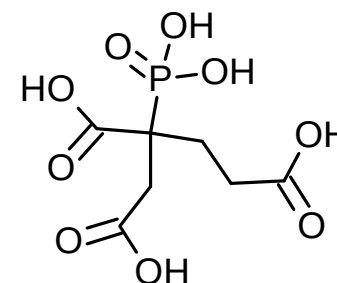
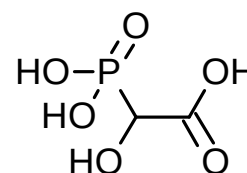
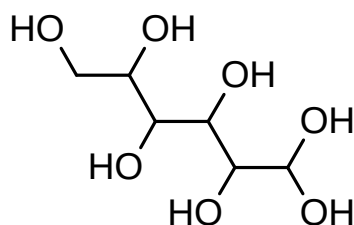
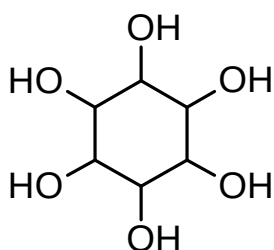
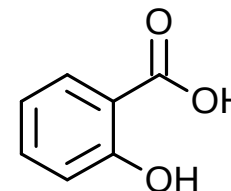
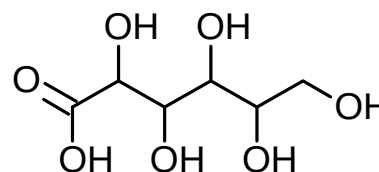
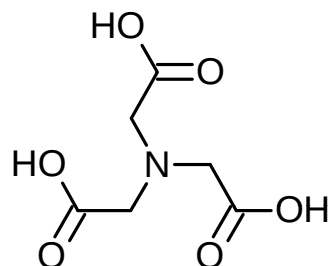
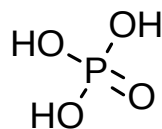
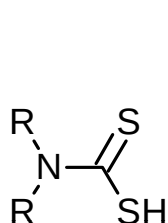
Citric acid

Salicylaldoxime



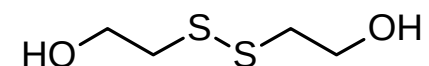
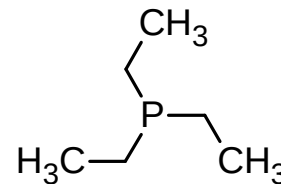
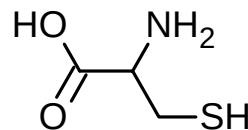
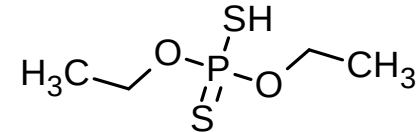
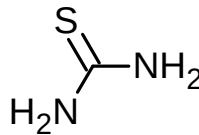
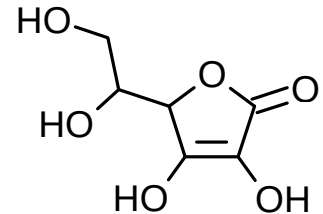
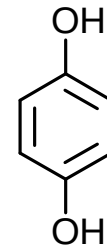
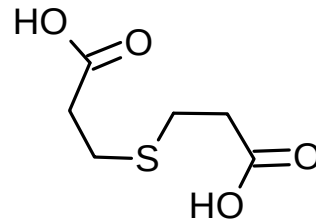
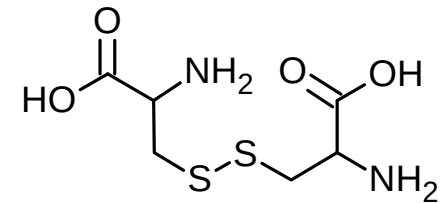
Summary of Inhibitors (cont.)

- Other chelating agents are less potent...



Summary of Inhibitors (cont.)

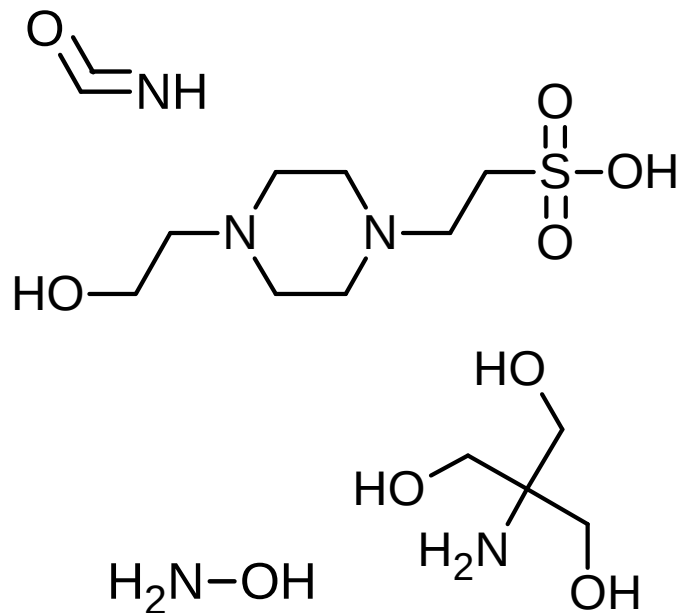
- Most chain-breaking antioxidants are not effective
 - traditional AOs (tannic acid)
 - phosphites (volatile)
 - disulfides
 - sulfides
 - sulfur
 - thiophosphates
 - thioureas
 - Cu, Mn



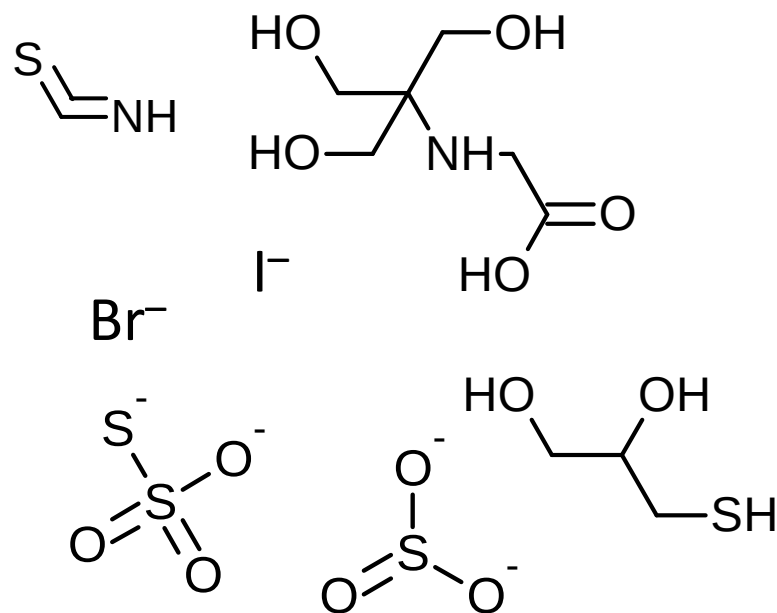
Summary of Inhibitors (cont.)

- Some miscellaneous oxygen scavengers, radical scavengers, and reducing agents are weak or moderate inhibitors

Not Effective

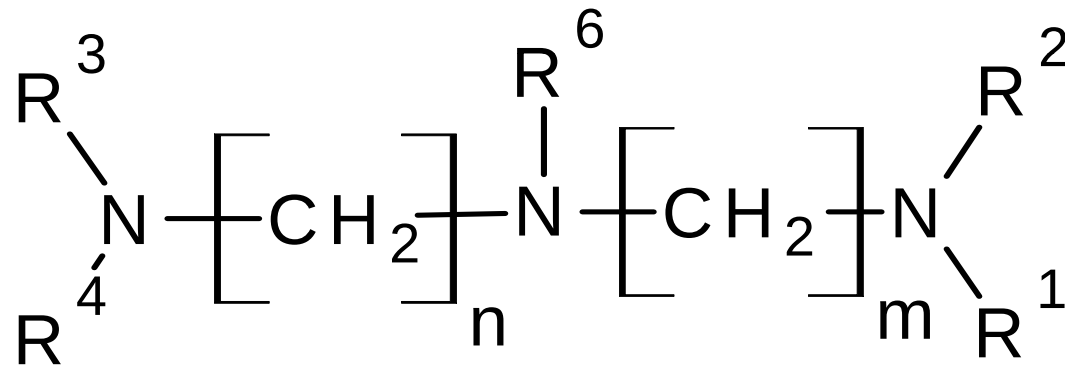


Effective

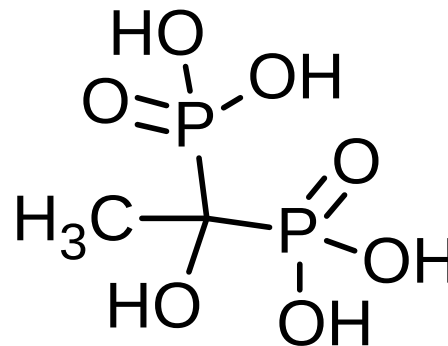


Best Inhibitors Identified

- Acetate- and methylene phosphonate-substituted tertiary polyamines are effective inhibitors; DPTA >> EDTA >> NTA; NTMP>>NTA



- HEDP was the most potent and the most oxidatively stable inhibitor



- Chelating agents were the best inhibitors
 - Previously known: Gluconate, bicine, EDTA, phosphate
 - Novel: imino diacetic acid, salicyl aldoxime, DDTC
- Tertiary amines could also be useful
 - MDEA, TEA

Timetable of Past Experiments

- Spring – summer 2009: Screening amines for oxidative stability (HGF)
- Fall 2009: Thermal/oxidative cycling, product stability
- Spring – Summer 2010: LC, GC method development, product identification, temperature dependence
- Fall 2010: catalyst screening inhibitor screening, amino acid oxidation
- Spring 2010: inhibitor stress testing, material balance and pathways, standard synthesis, apparatus design

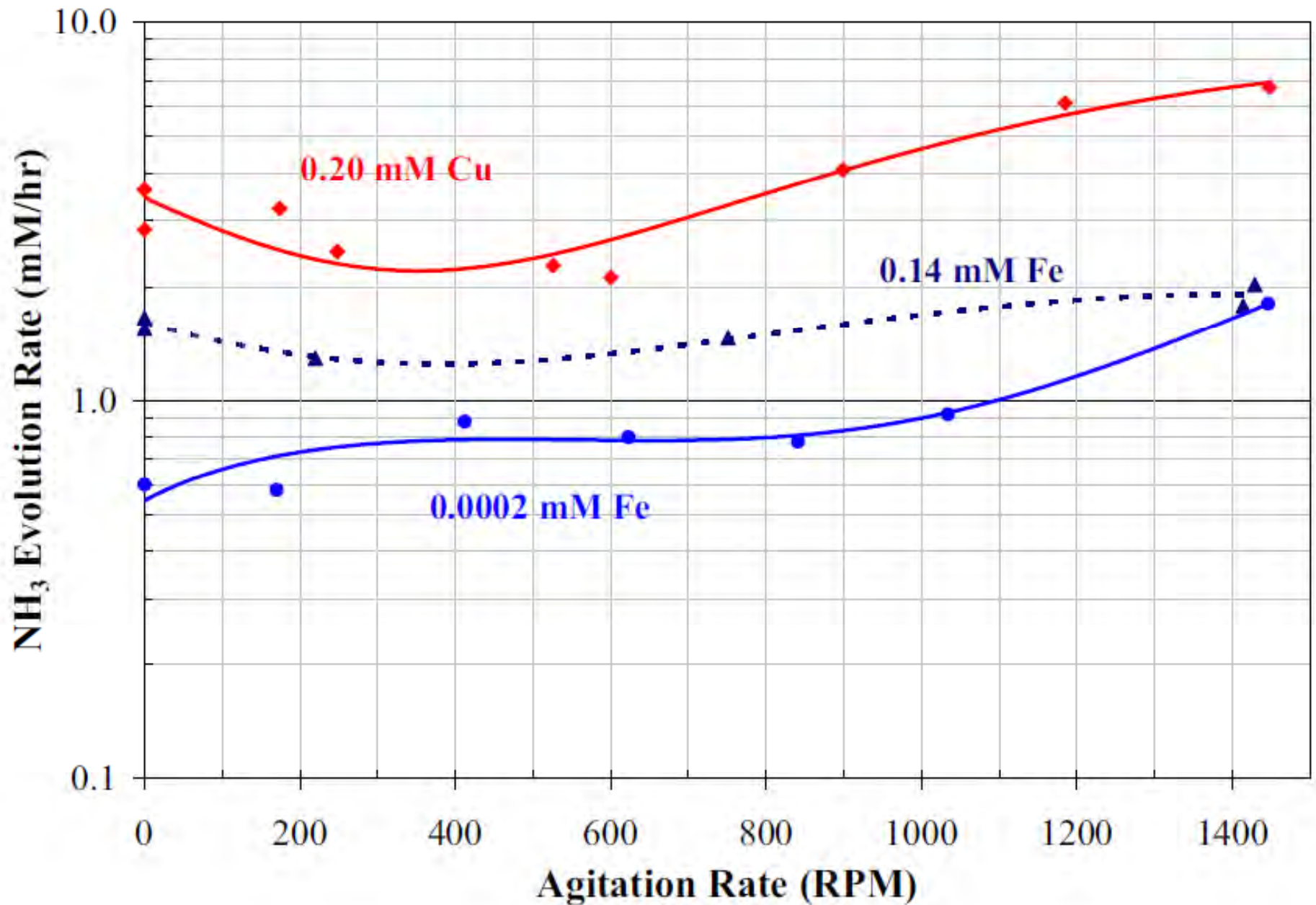
Previous Work

- Amine screening
 - Many primary and secondary amines oxidize (MEA, DEA, DGA)
 - Many tertiary amines (MDEA) and PZ are stable
 - Amino acids??
- Material balance
 - 50 – 70% of oxidized MEA was “found” in products
 - Major oxidation products for MEA include fragments and condensation products
 - Many unlikely products have been proposed

Types of Catalysts and Inhibitors

- Transition metal catalysts
 - Iron
 - Copper
- Inhibitors
 - Tertiary amines
 - Chelating agents
 - [organic] peroxide decomposers
 - Oxygen scavengers
 - Free radical scavengers

Dependence of NH_3 rate on Agitation

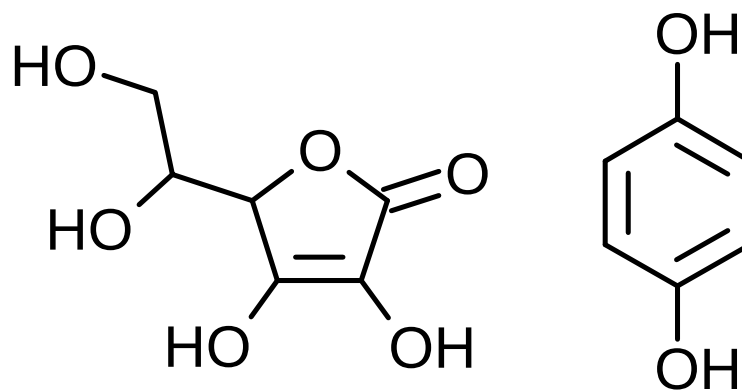


Products and Material Balance

- MEA oxidizes to ammonia and aldehydes
- Aldehydes react with MEA to form imines

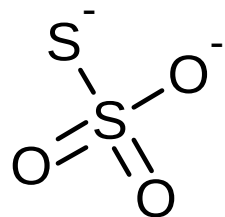
Catalysts of MEA oxidation

- Metals (corrosion, additives, fly ash)
 - Cu > Fe > Cr
 - ?Ni, Mn, V?
- Gas-phase contaminants (very little data)
 - NO₂•
 - NO•
 - SO₂
- Organics (additives)
 - Ascorbic acid
 - Hydroquinone

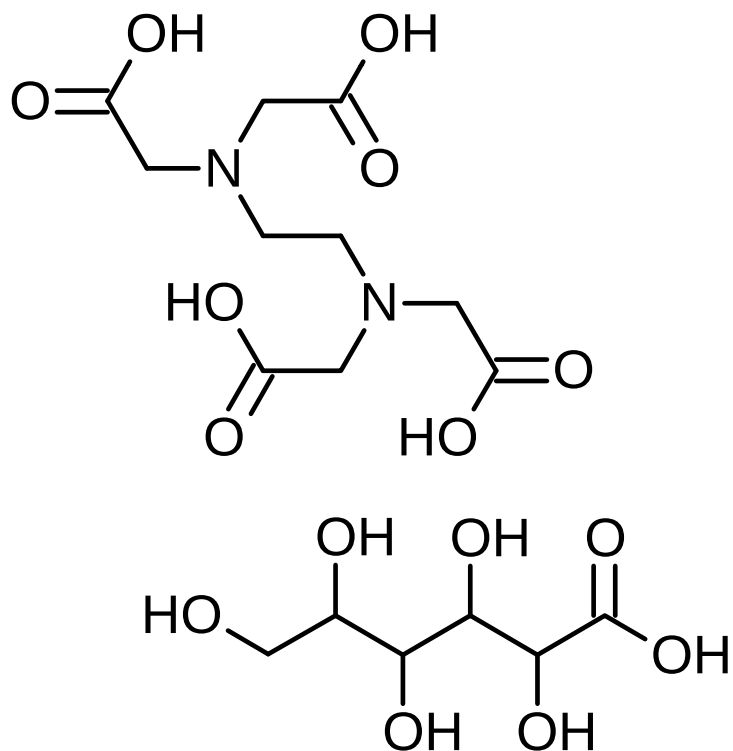
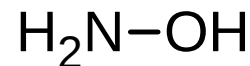
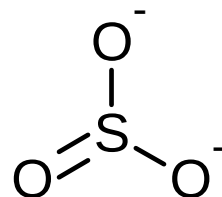


Inhibitors for MEA Oxidation

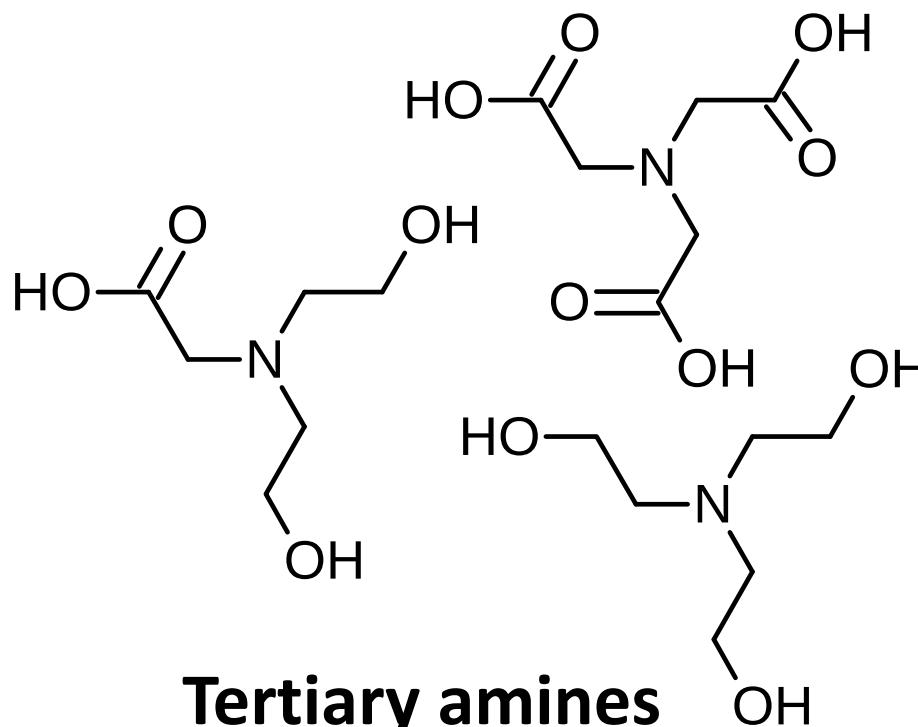
Free radical scavengers



Oxygen scavengers

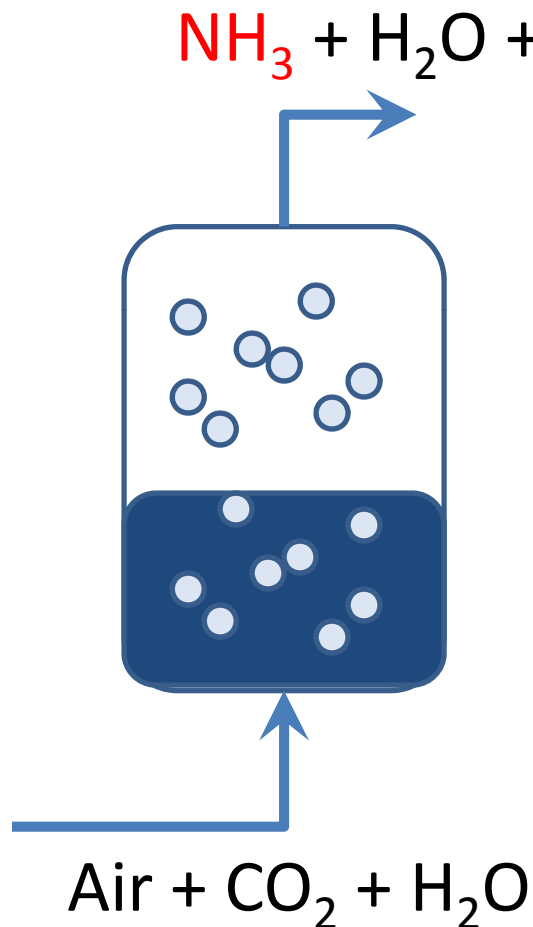


Chelating agents



Tertiary amines

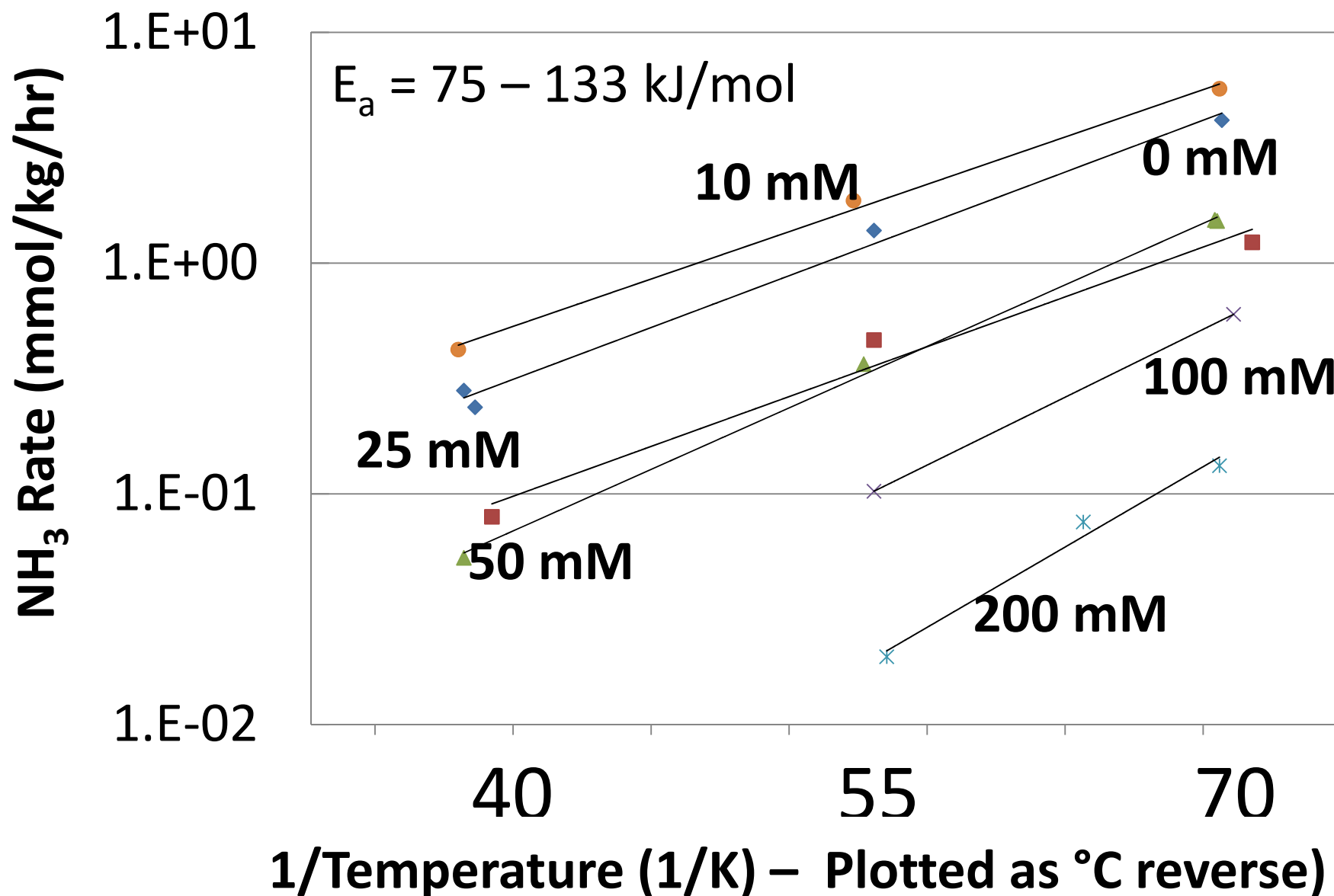
Oxygen mass transfer in the HGF Apparatus



NH₃ rate is a mild function of agitation rate

- Increase mass transfer of O₂
- Increase mass transfer of NH₃
- Metals contamination for stir shaft
- Increased liquid entrainment
- Shearing action on suspended Fe(OH)₂ particles
- Reaction of liquid phase NH₃

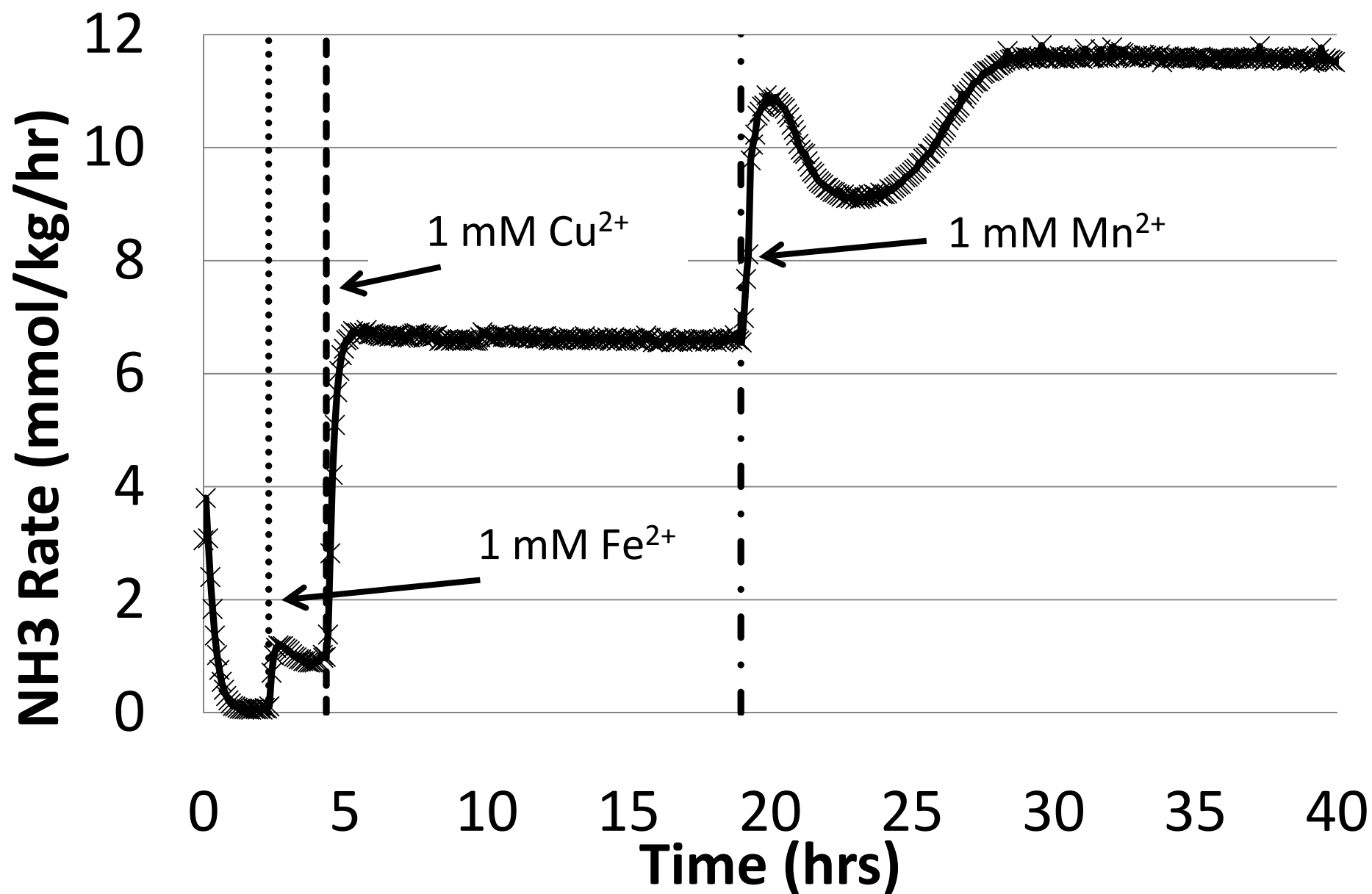
Temperature Dependence of NH_3 rates in MEA oxidation
Conditions: 40-70°C, 98kPa air, 2kPa CO_2 , SS metals



MEA Data

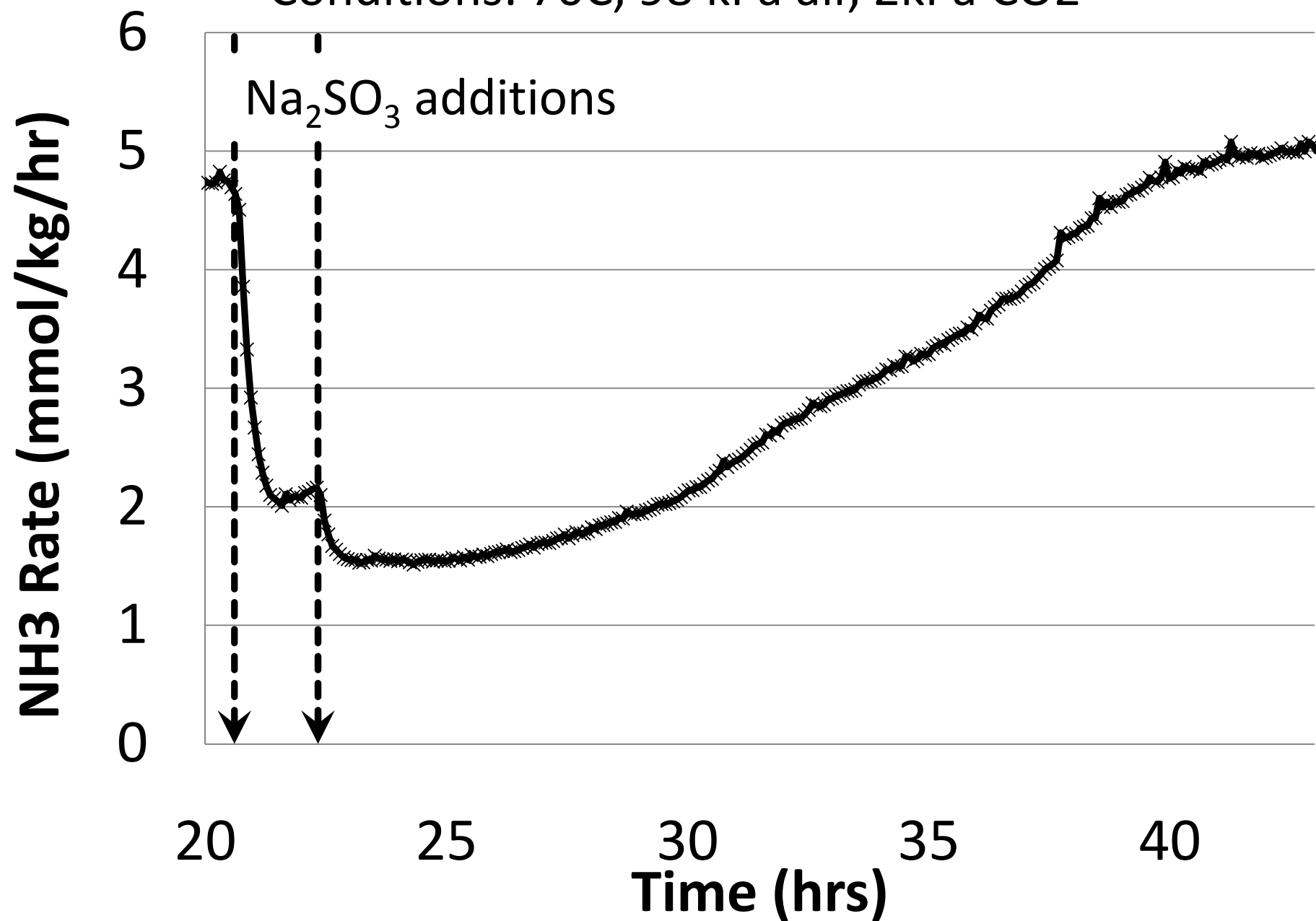
Catalysts and Inhibitors

Oxidation of 7 m MEA in the HGF. Conditions:
70C, 98kPa air, 2kPa CO₂

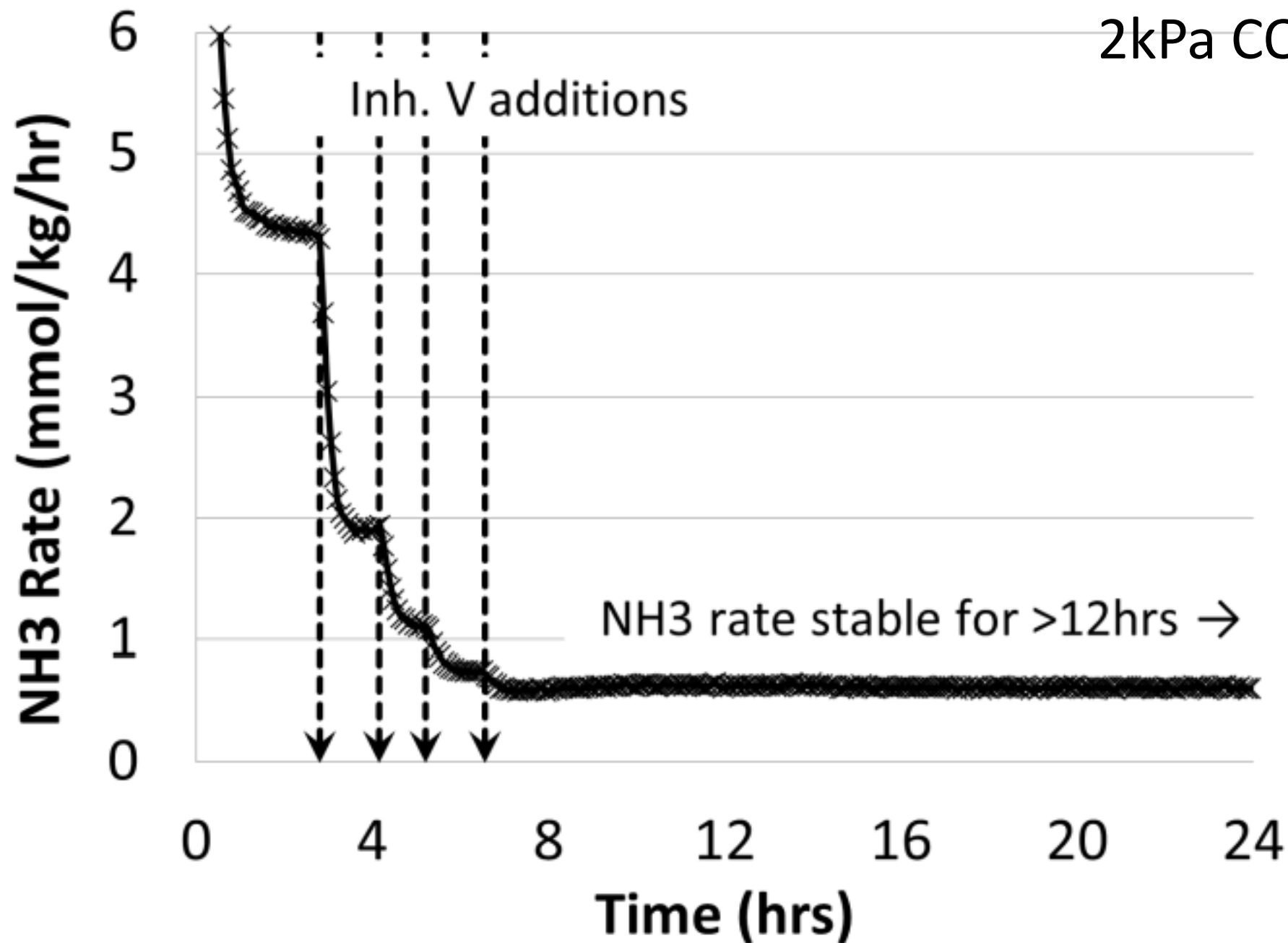


Oxidation of 9 m pilot plant MEA with Sulfite

Conditions: 70C, 98 kPa air, 2kPa CO₂



Oxidation of 9 m pilot plant MEA: 70°C, 98kPa air,
2kPa CO₂



Summary of MEA Catalysts and Inhibitors

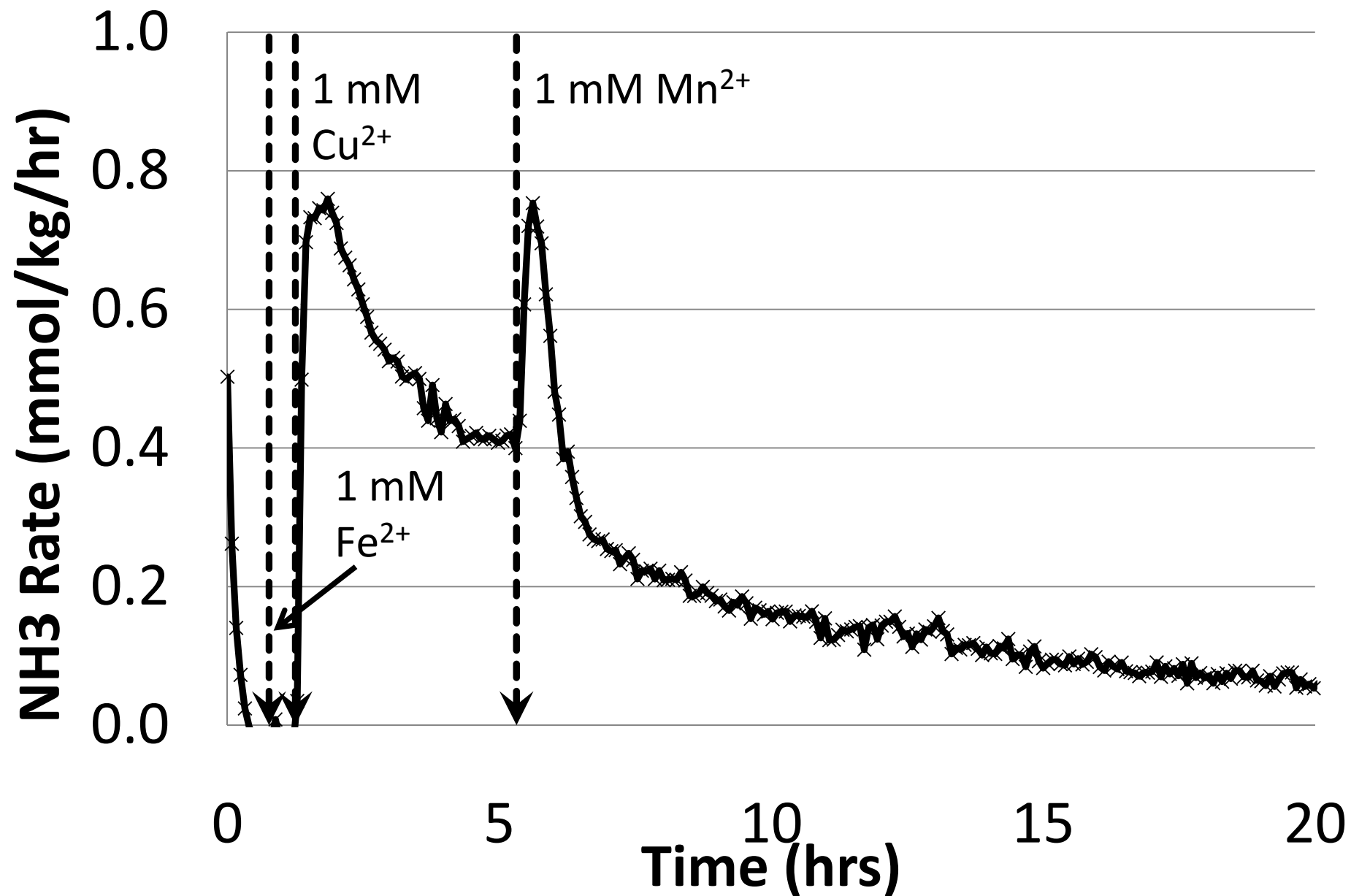
Catalyst	Effect on NH ₃ Rate (mmol/kg/hr)	Inhibitor	NH ₃ Inhibition (1.5%wt Inh.)	NH ₃ Rate (%) / Inh. (%wt)	Stability at 70°C
Cr ³⁺	↑ NH ₃ 0.06	V	86	56 / 0.06	Good
Fe ²⁺	↑ NH ₃ 1.17	Z	91	55 / 0.08	Good
Cu ²⁺	↑ NH ₃ 5.70	X	--	80 / 0.2	Fair
Mn	↑ NH ₃ 4.96	Y	77	45 / 0.04	Poor
VO ³⁻	↓ NH ₃ rate 40%	O	67	56 / 0.65	Poor
		Q	55		Fair
Mn ²⁺	↓ NH ₃ rate 80– 90%	A, W, U- P	<55	--	--

New inhibitors offer greater “bang” on a weight basis,
greater long-term stability

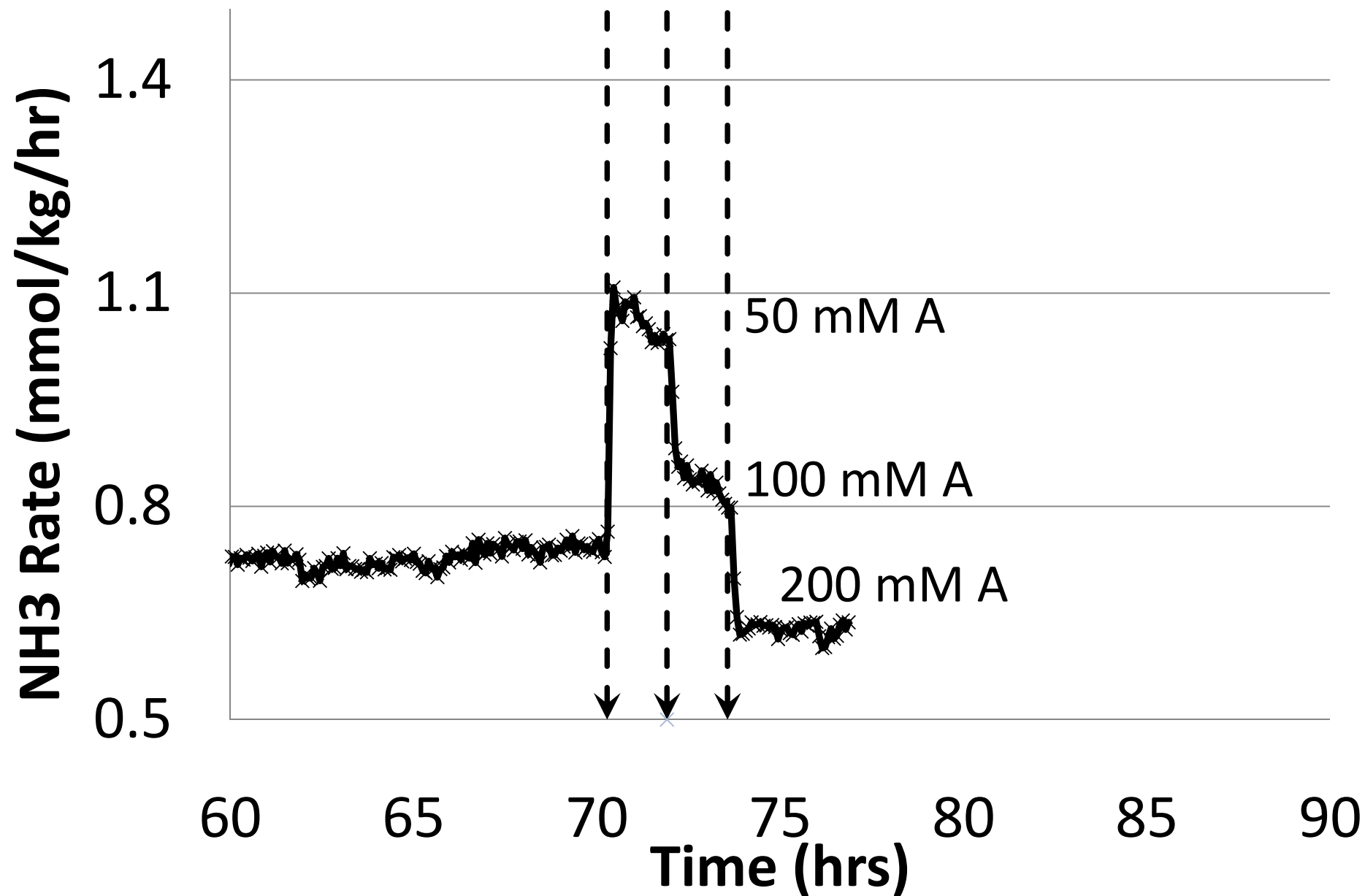
PZ Data

Oxidation of 8 m PZ with metals

Conditions: 70C, 98kPa air, 2kPa CO₂



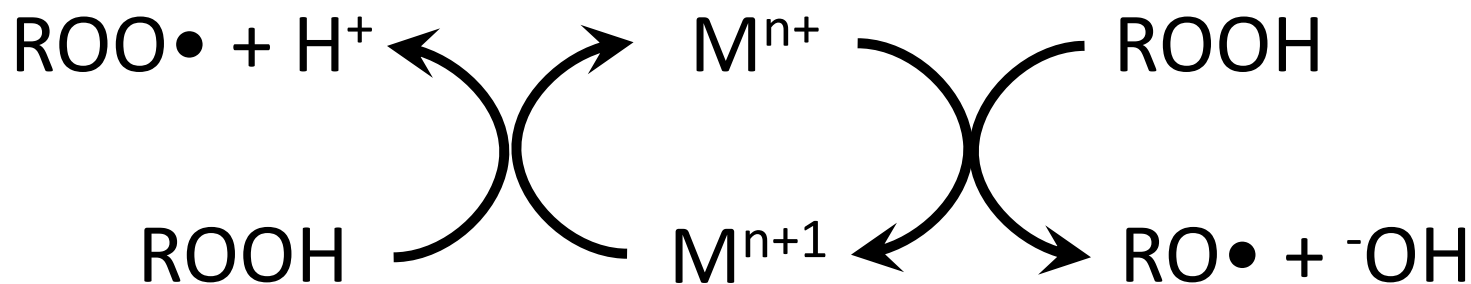
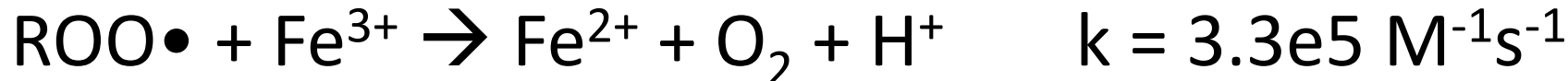
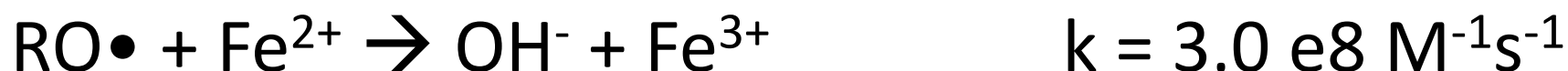
Oxidation of 8 m PZ with Fe, Cu, Mn
Conditions: 83°C, 98kPa air, 2kPa CO₂

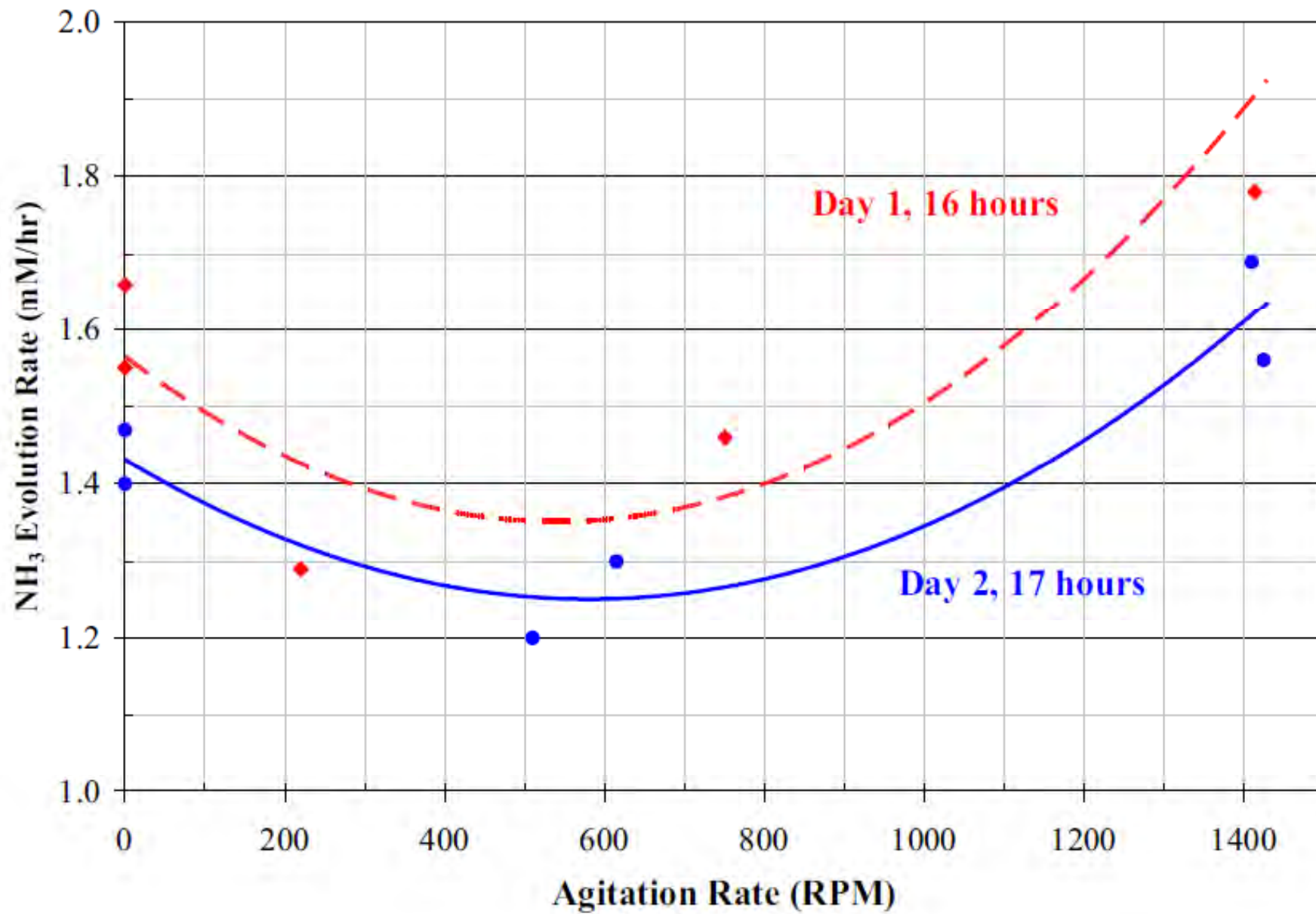


Ongoing and Future Work

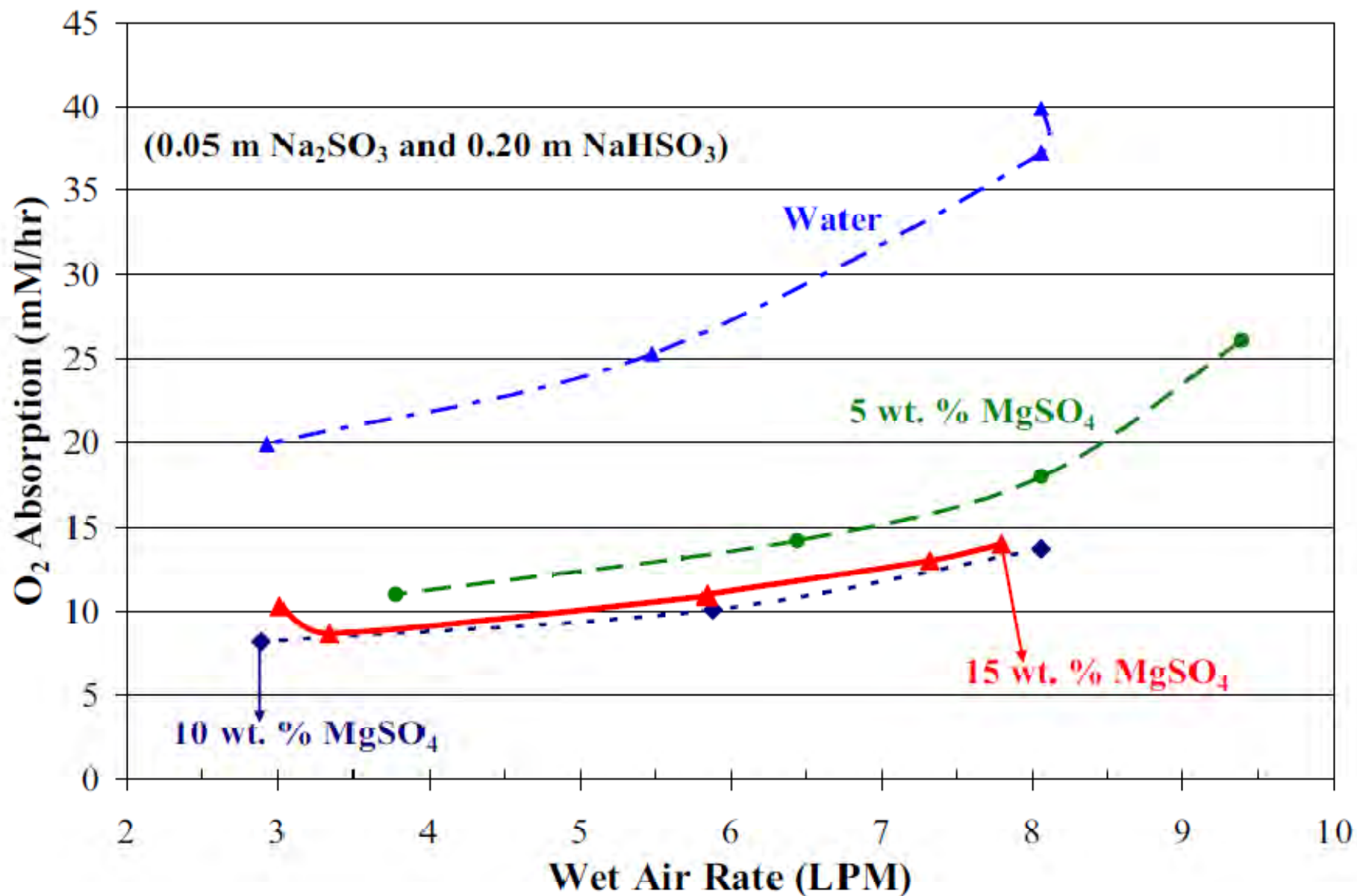
- Continue inhibitor screening
- Inhibitor “stress-testing”
 - LGF experiment for extended oxidation
 - Batch cycling for temperature stability
- NO₂ investigation
 - LGF experiment with PZ + 50ppm NO₂
 - HGF experiment with PZ + 50ppm NO₂

Homolytic Decomposition of Peroxide by Ferrous and Ferric





Oxygen Mass Transfer in the HGF



Reaction of Metal Ions with Radicals

Metal Ion	$\bullet\text{OH}$ k (298) ($\text{M}^{-1}\text{s}^{-1}$)	Conditions	$\bullet\text{OH}_2$ k (298) ($\text{M}^{-1}\text{s}^{-1}$)	
Fe(II)	3.2e8	Water, pH = 7	1.3e6	
Fe(III)	7.9e7	Water		
Mn(II)	1.4e8	Water		
Cu(I)	2.0e10	Water	4.3e9	Water
Cu(II)	3.5e8	Water, pH = 7		
Cr(II)	4.8e9	Water, pH = 1		
Cr(III)	3.1e8	Water, pH < 7		

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Stephanie Anne Freeman
2011

**The Dissertation Committee for Stephanie Anne Freeman Certifies that this is the
approved version of the following dissertation:**

**Thermal Degradation and Oxidation of Aqueous Piperazine
for Carbon Dioxide Capture**

Committee:

Gary T. Rochelle, Supervisor

Jennifer Maynard

Danny Reible

Lynn Katz

James Critchfield

**Thermal Degradation and Oxidation of Aqueous Piperazine
for Carbon Dioxide Capture**

by

Stephanie Anne Freeman, B.S.Ch.E; M.S.Ch.E.Prac.

Dissertation

Presented to the Faculty of the Graduate School of

The University of Texas at Austin

in Partial Fulfillment

of the Requirements

for the Degree of

Doctor of Philosophy

The University of Texas at Austin

May 2011

Dedication

To my parents

for always encouraging me to do more than I thought was possible

Acknowledgements

The dedication, support, and ingenuity of Prof. Gary Rochelle inspired me throughout the completion of this dissertation. Prof. Rochelle showed enormous compassion for me during my years in his group that I will be forever grateful for. His dedication to our research inspired in me the desire to strive for more and to not shy away from difficult problems that require collaboration and innovation to solve. His dedication to us, his graduate students, and his undergraduate students demonstrate his love of learning that is contagious and that we are all influenced by in his group.

I would like to thank the Luminant Carbon Management Program (LCMP) for kindly providing funding for our research group. None of my work could have been completed without the generosity of the 30+ companies that have been involved with the LCMP and the Industrial Associates Program.

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ChemE Machine Shop were always a tremendous help in fabricating items for the lab and were a riot to work with during recruitment weekends. Mike Ronalter of the UT Glass Shop is a genius of glass fabrication and designed and built my TOR reactors, a unique loader for $^{13}\text{CO}_2$ experiments, and fixed countless CO_2 loaders. Hector Garcia was enormously helpful in using the IC-MS/LC-MS system. Karin Keller of the UT Chemistry Department was also a priceless source of information when I was sorting through the science and art of MS. Steve Sorey and Jim Wallin of the UT Chemistry Department NMR Laboratory were always helpful in explaining NMR fundamentals to a chemical engineer trying to be a chemist. Finally, Kay Costales-Swift, Kevin Haynes, Eddie Ibarra, T Stockman, Karen Eikner, Randy Rife, Patrick Danielewski, and Tammy McDade of the UT Chemical Engineering Department were always supportive in a variety of capacities and a pleasure to work with day in and day out.

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Finally, the most important people have yet to be thanked. My family is the most supportive and generous family someone could ask for. We’ve all suffered trials and tribulations in the last four years that have made us stronger and brought us together. To my parents, it is difficult to express how thankful I am for your support and encouragement through the years. I knew I could always count on you to give me some supportive words after a rough day in the lab and remind me why I was here. I sincerely thank you for all your support and I know I am fortunate to have you as my parents. To my brothers and sisters, Greg, Kathryn, and Nathan, I’d like to thank for so many years of support. To Tracy, who has been especially supportive of my years of school, I’d like to thank you for all of your encouragement. Finally, I’d also like to posthumously thank my grandparents whose love of education instilled in me a desire to better myself from a very early age.

Thermal Degradation and Oxidation of Aqueous Piperazine for Carbon Dioxide Capture

Stephanie Anne Freeman, Ph.D.

The University of Texas at Austin, 2011

Supervisor: Gary T. Rochelle

Absorption-stripping with aqueous, concentrated piperazine (PZ) is a viable retrofit technology for post-combustion CO₂ capture from coal-fired power plants. The rate of thermal degradation and oxidation of PZ was investigated over a range of temperature, CO₂ loading, and PZ concentration. At 135 to 175 °C, degradation is first order in PZ with an activation energy of 183.5 kJ/mole. At 150 °C, the first order rate constant, k_1 , for thermal degradation of 8 m PZ with 0.3 mol CO₂/mol alkalinity is $6.12 \times 10^{-9} \text{ s}^{-1}$. After 20 weeks of degradation at 165 °C, 74% and 63%, respectively, of the nitrogen and carbon lost in the form of PZ and CO₂ was recovered in quantifiable degradation products. N-formylpiperazine, ammonium, and N-(2-aminoethyl) piperazine account for 57% and 45% of nitrogen and carbon lost, respectively. Thermal degradation of PZ likely proceeds through S_N2 substitution reactions. In the suspected first step of the mechanism, 1-[2-[(2-aminoethyl) amino]ethyl] PZ is formed from a ring opening S_N2 reaction of PZ with H⁺PZ. Formate was found to be generated during thermal degradation from CO₂ or CO₂-containing molecules.

An analysis of k_1 values was applied to a variety of amines screened for thermal stability in order to predict a maximum recommended stripper temperature. Morpholine, piperidine, PZ, and PZ derivatives were found to be the most stable with an allowable stripper temperature above 160 °C. Long-chain alkyl amines or alkanolamines such as N-(2-hydroxyethyl)ethylenediamine and diethanolamine were found to be the most unstable with an allowable stripper temperature below 120 °C.

Iron (Fe^{2+}) and stainless steel metals (Fe^{2+} , Ni^{2+} , and Cr^{3+}) were found to be only weak catalysts for oxidation of PZ, while oxidation was rapidly catalyzed by copper (Cu^{2+}). In a system with Fe^{2+} or SSM, 5 kPa O_2 in the inlet flue gas, a 55 °C absorber, and one-third residence time with O_2 , the maximum loss rate of PZ is expected to 0.23 mol PZ/kg solvent in one year of operation. Under the same conditions but with Cu^{2+} present, the loss rate of PZ is predicted to be 1.23 mole PZ/kg solvent in one year of operation. Inhibitor A was found to be effective at decreasing PZ loss catalyzed by Cu^{2+} . Ethylenediamine, carboxylate ions, and amides were the only identified oxidation products. Total organic carbon analysis and overall mass balances indicate a large concentration of unidentified oxidation products.

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Chapter 1 – Introduction

1.1 ANTHROPOGENIC CARBON DIOXIDE (CO₂) EMISSIONS

The levels of carbon dioxide (CO₂) in the atmosphere have been steadily rising since the industrial revolution. The Intergovernmental Panel on Climate Change (IPCC) recently estimated that CO₂ levels have increased 30% since pre-industrial times and are currently increasing 0.4% per year (IPCC, 2001). Primary causation for the change in atmospheric conditions and global climate change is anthropogenic CO₂ releases and deforestation (IPCC, 2001).

The CO₂ emissions from electricity generated from the combustion of coal constitute a large fraction of overall CO₂ emissions, up to 33% of across the board CO₂ emissions for 2006 (EIA, 2007a). As shown in Figure 1.1, the CO₂ emissions from electricity generation, differentiated by individual fuel sources, have increased

approximately ten times since 1949. Emissions from coal combustion are dominant as compared to petroleum or natural gas combustion. In addition, coal combustion has the largest CO₂ emissions per kilowatt of power generated at 2.10 compared to 1.97 and 1.32 for petroleum and natural gas, respectively (IPCC, 2001). In terms of GHG emissions, electricity derived from coal is the least efficient and most detrimental to our atmosphere.

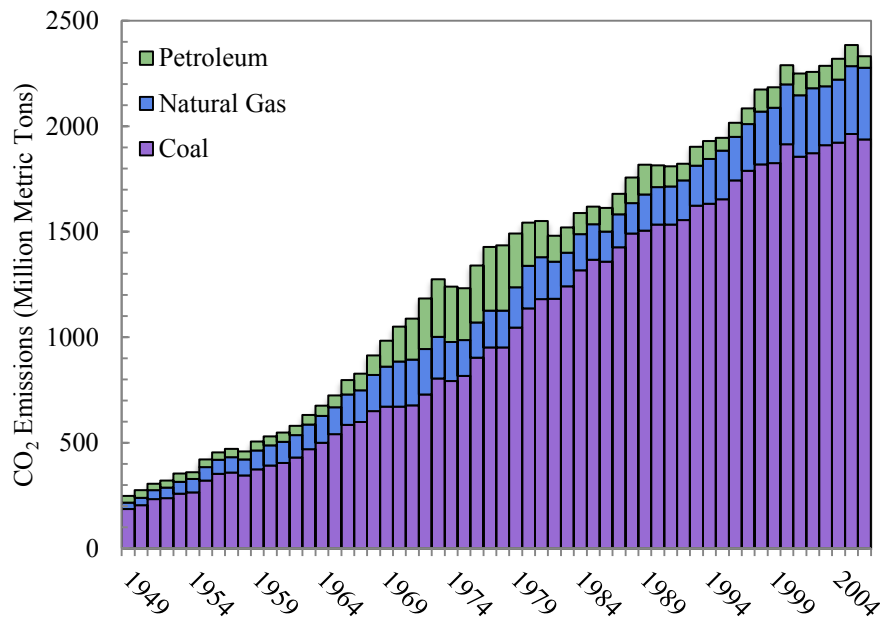


Figure 1.1: CO₂ Emissions in the US Since 1949 in the Electricity Generation Sector (EIA, 2007a)

Despite its obvious environmental disadvantages, coal continues to be a favorite method of electricity generation throughout the world, most notably in China and the US. It was estimated in 2006 that China was building a new coal-fired power plant at the rate of one every week to 10 days (Bradsher and Barboza, 2006). China is experiencing a burgeoning industrialization and newly built coal fired power plants are a large part of China's growing industrial emissions as they lead the world in annual coal production (Thieleman et al., 2007). The US has extensive coal reserves while only 49% of US

electricity is generated from coal in 2006, compared to 80% of Chinese electricity while in the same year (EIA, 2007b; Watts, 2005).

The fact that coal-fired power plants are large, stationary, point sources of CO₂ makes them the perfect candidate for a focused attempt at decreasing world-wide CO₂ emissions. With post-combustion CO₂ capture technology, for example, plants can be retrofitted with additional units that perform the needed capture of CO₂ without interfering with existing plant operations. Outside of a loss of electricity generating capacity, the power plant remains untouched and unaffected by the CO₂ control measures implemented on the waste flue gas.

1.2 CARBON DIOXIDE CAPTURE USING AMINE-BASED ABSORPTION-STRIPPING

The most promising technology for CO₂ capture is the post-combustion removal of CO₂ with an absorption-stripping system using an aqueous, amine solvent (Bottoms, 1930; Rochelle, 2009). Alkanolamines such as monoethanolamine (MEA) and diethanolamine (DEA) have been traditionally investigated for this application (Aaron and Tsouris, 2005; Bottoms, 1930; Hilliard, 2008). Other amines such as 2-amino-2-methyl-1-propanol (AMP) (Arcis et al., 2007; Mandal and Bandyopadhyay, 2006; Mandal et al., 2005; Paul and Mandal, 2006b; Reza and Trejo, 2006) and diglycolamine (DGA[®]) (Huntsman Corporation, 2005; Al-Juaied and Rochelle, 2006a; Al-Juaied and Rochelle, 2006b; Al-Juaied and Rochelle, 2006c; Al-Juaied, 2004) have been proposed as well. Piperazine (PZ) has been proposed as a kinetic promoter in a blend with methyldiethanolamine (MDEA) (Bishnoi, 2000; Bishnoi and Rochelle, 2000b; Bishnoi and Rochelle, 2002a; Bishnoi and Rochelle, 2002b; Derks et al., 2008; Liu et al., 1999; Paul and Mandal, 2006a; Paul and Mandal, 2006b; Zhang et al., 2001), AMP (Paul and Mandal, 2006a; Paul and Mandal, 2006b; Samanta and Bandyopadhyay, 2009; Sun et al.,

2005; Yang et al., 2010), or potassium carbonate (Cullinane and Rochelle, 2004; Cullinane and Rochelle, 2005; Cullinane and Rochelle, 2006; Oyekan and Rochelle, 2009; Plaza et al., 2009) to enhance the rate of CO₂ absorption.

Absorption-stripping systems for CO₂ capture are based on a recycled flow of aqueous amine solution that absorbs CO₂ in the absorber and then regenerates the solvent in the stripper (Figure 1.2). Lean amine enters the top of the absorber and absorbs CO₂ while descending through the column, counter-currently contacting the flue gas. The rich amine exiting the absorber is sent to the main cross exchanger to be heated using the hot lean stream leaving the stripper. The rich solvent enters the top of the stripper and the solution flashes to release any remaining oxygen (O₂) in solution and a portion of the CO₂. The rich solution flows down the stripper and steam heating is used to desorb the captured CO₂. The stripper reboiler is heated with steam taken off of the medium pressure turbines in the coal-fired steam cycle in the power plant. This steam draw off point can be optimized, but will likely be at the intermediate pressure/low pressure (IP/LP) crossover in existing plants that are being retrofitted.

1.3 SOLVENT LOSSES IN ABSORPTION-STRIPPING SYSTEMS

Solvent losses in an absorption-stripping system can occur at multiple points in the system through different processes. As shown in Figure 1.3 below, solvent losses occur through three primary avenues: volatility, oxidation, and thermal degradation.

Volatility is the loss of volatile amine off the top of the absorber in the exiting, treated flue gas. A well-designed water wash column can be used to treat the flue gas exiting the top of the absorber to recover a majority of the amine lost through volatility and this approach can typically mitigate or completely control volatile losses. The volatility of an amine can be precisely measured using an equilibrium cell, such as is used

in the Rochelle laboratory (Nguyen et al., 2010). This path of amine loss is generally well characterized.

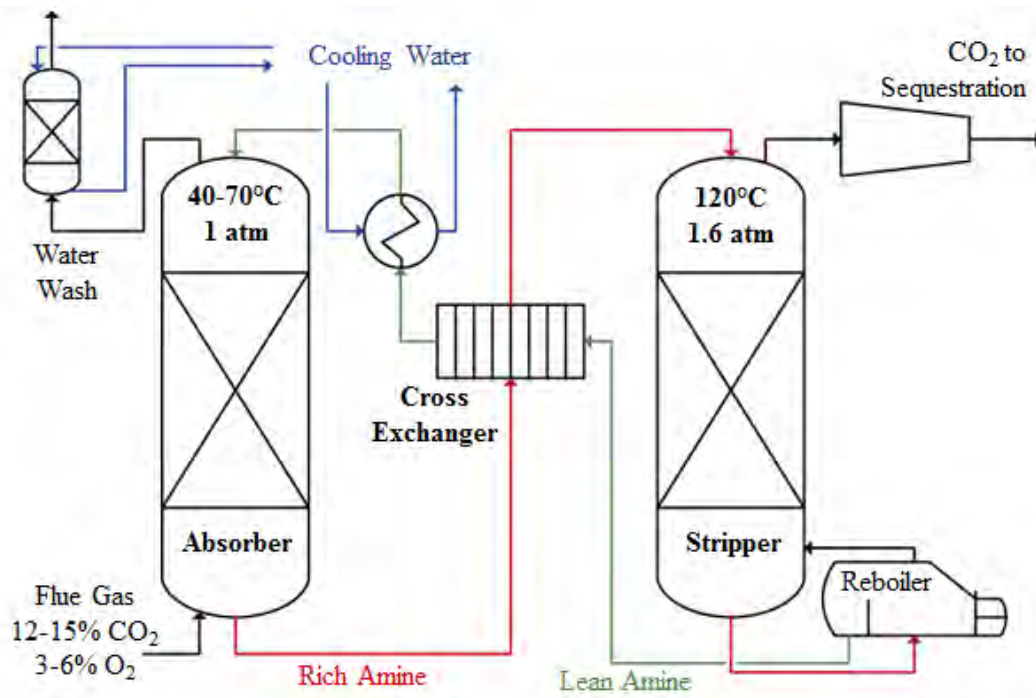


Figure 1.2: Schematic of typical amine-based absorption-stripping system for coal-fired flue gas

Oxidation is the chemical reaction of the amine with dissolved O₂ which enters the system with the flue gas. Oxidation occurs primarily in the absorber sump, absorber packing, and piping leading to the heat exchanger. Any O₂ remaining after the main cross exchanger will flash at the top of the stripper. In the absorber and absorber sump, the primary process to account for solvent loss is degradation of the amine through oxidation. Flue gas typically contains 3-5% O₂ that is carried into the absorber where it can react with the amine. The hold-up time in a sump is estimated to be 5 to 10 minutes, allowing oxidation reactions sufficient time to impact solvent loss. Research is needed into the oxidation characteristics of a specific amine in order to measure the expected loss

in this area of the system. Oxidation reactions, in general, involve fragmentation of the amine into a host of degradation products that can further react with each other, more O_2 , or the amine to produce more degradation products. Oxidation of amines is not well characterized for most amines as the primary degradation products are still being identified.

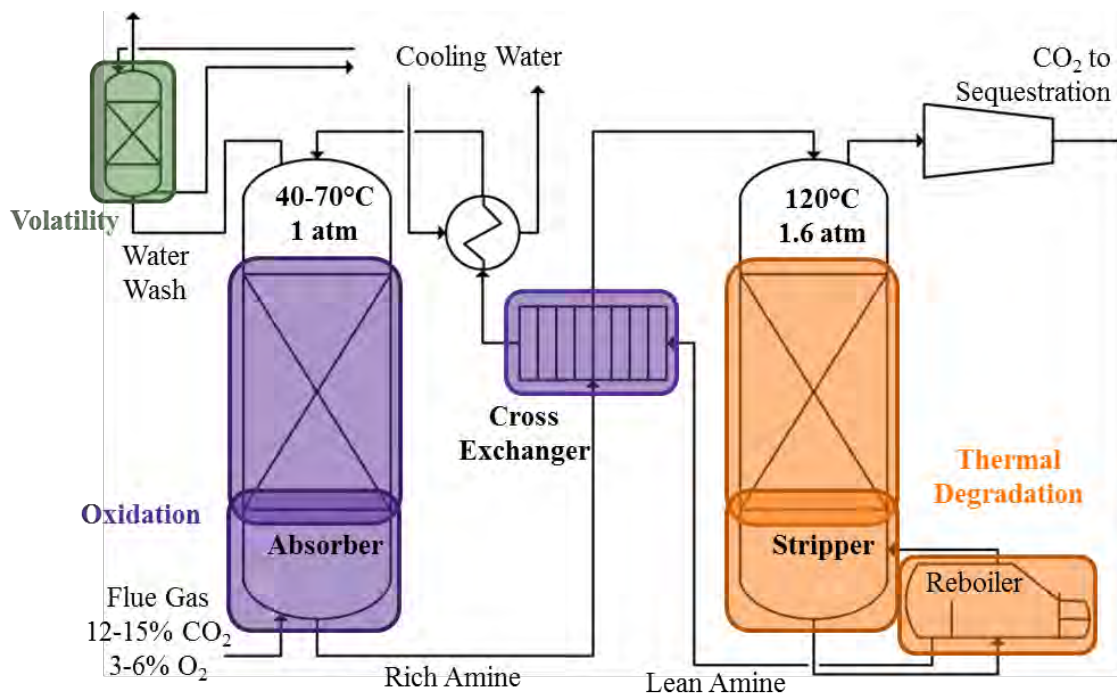


Figure 1.3: Schematic of absorption-stripping system with primary modes of amine loss highlighted

In the main cross-exchanger, the amine loss is primarily due to oxidation from any O_2 carried over from the absorber sump while there may be some thermal degradation of the rich amine as it exits the exchanger at high temperature and is fed to the stripper. This is also the primary area where the collaborative effect of oxidation and increased temperature are seen. Even with a temperature bulge in the absorber that may reach 70 °C, if any O_2 is present in the solution as it reaches the exit of the cross

exchanger, temperatures would be closer to 100 °C, and a significant effect of high temperature oxidation could be seen (Closmann and Rochelle, 2011; Plaza et al., 2009). The study of collaborative oxidation and thermal degradation, or high temperature oxidation, is an area of research that is decidedly lacking in that all research to date has focused on either oxidation or thermal degradation of amines separately. The collaborative effect is an important area where research is needed to fully understand the degradation characteristics of a solvent.

Thermal degradation is the reaction of an amine to degradation products based on exposure to high temperature. Stripper operating temperatures in current designs are between 100 and 120°C, significantly higher than the absorber. At these temperatures, the kinetic rates of degradation reactions that are suppressed in the absorber are elevated and cause solvent enhanced losses. Thermal degradation primarily occurs in the stripper packing (if present), stripper sump, reboiler, reclaiming system (if present) and may occur in the piping leading from the main cross exchanger to the stripper, if temperatures are high enough. If a thermal reclaiming system is used, the solvent would be subjected to high temperature degradation here as well. Novel stripper designs that do not include packing, such as flash-based designs, are still subject to thermal degradation (VanWagener and Rochelle, 2011). As with the absorber, the sump hold-up is between 5 and 10 minutes, allowing adequate time for significant amine loss.

The oxidation and thermal degradation of concentrated, aqueous PZ has not been explored previously outside of screening experiments. Preliminary tests showed enhanced resistance to both oxidation and thermal degradation, a significant advantage for this solvent (Davis, 2009; Sexton, 2008). PZ and PZ-based solvents also have advantageous kinetic rates and CO₂ capacity. The degradation characteristics of

concentrated PZ need to be fully understood before appropriate application of the solvent in pilot, demonstrate, and full scale CO₂ absorption-stripping systems.

This dissertation is focused on investigating the thermal degradation and oxidation of concentrated, aqueous PZ for use in CO₂ absorption-stripping systems. Experiments were designed to represent real systems as closely as possible

1.4 RESEARCH OBJECTIVES

The baseline solvent that has been used for CO₂ capture using aqueous amine solvents in an absorber-stripper system is MEA. This solvent has been studied extensively and has been proven at the pilot plant and demonstration level (Arnold et al., 1982; St.Clair and Simister, 1983). MEA has numerous advantageous properties such as high solubility in water, useful kinetic absorption rates, low viscosity, high heat of absorption of CO₂, ease of handling, and low cost. On the other hand, there are many disadvantages to this solvent that may prove to limit its use in industry. MEA degrades heavily at high temperatures, as found in the stripper, and in the presence of O₂, as found in the absorber (Davis, 2009; Davis and Rochelle, 2009; Sexton, 2008; Sexton and Rochelle, 2009b; Sexton and Rochelle, 2009c). MEA degrades to form heat-stable salts and polymerized products that permanently remove capacity from the solvent and increase corrosivity of the solution toward carbon steel equipment.

PZ offers a solution to some problems experienced by MEA. Preliminary investigations into PZ show a significant improvement in the areas of thermal and oxidative degradation over MEA (Davis, 2009; Sexton, 2008). Additionally, PZ has enhanced kinetic absorption rates, almost 1.5 times that of MEA (Dugas, 2008). Being a diamine, the capacity of PZ is also increased over MEA, a monoamine, which directly leads to the requirement of smaller equipment designs and less pump work. On the other

hand, PZ does have the disadvantage of high viscosity and low solubility in water, both of which create handling issues and may increase pump work.

The overall goal of this project is to explore the efficacy of concentrated, aqueous PZ as a solvent for industrial CO₂ capture applications. Since little work has been done on this subject previously, the first major hurdle is to understand the degradation characteristics of the system and discover ways to minimize solvent loss. The study of PZ degradation is a portion of a project that seeks to develop PZ as a viable solvent for CO₂ capture applications. Other parts of that project include rigorous analysis of PZ solid solubility, more extensive rate measurements, heat of absorption measurements, and eventual pilot and demonstration level projects with the help of industrial sponsors in order to evaluate the performance of the solvent.

Hilliard and Xu have measured the high and low temperature CO₂ solubility in PZ and Nguyen has measured PZ volatility over a range of conditions (Hilliard, 2008; Nguyen et al., 2010; Xu and Rochelle, 2011). With these thermodynamic properties, Frailie and Plaza have developed a thermodynamic model (Guy Fawkes model) for concentrated, aqueous PZ solutions which is useful for predicting speciation over a range of temperature and CO₂ loadings (Frailie et al., 2011; Plaza and Rochelle, 2010). Bishnoi, Cullinane, and Dugas have measured the rate of CO₂ absorption in aqueous PZ (Bishnoi and Rochelle, 2000a; Cullinane and Rochelle, 2006; Dugas, 2009). Van Wagener has utilized the Guy Fawkes model to predict the equivalent work of various stripper configurations for concentrated PZ systems (VanWagener and Rochelle, 2011).

Concentrated, aqueous PZ was identified as thermally stable in the presence of CO₂ based on a single screening experiment performed by Davis at during the course of a project focused on the thermal degradation of MEA (Davis, 2009). Davis determined PZ to be stable through a lack of degradation after 4 weeks at 135 °C, but did not identify

any degradation products. Early work on PZ oxidation as a promoter for potassium carbonate demonstrated resistance to oxidation of this blend compared to MEA (Alawode, 2005; Jones, 2003). Sexton also identified low concentration (2.5 and 5 m) aqueous PZ as stable to oxidation in the presence of up to 5 mM Fe^{2+} , but did not perform more concentrated experiments or identify any degradation products (Sexton, 2008). A few structural analogs of PZ such as 1,4-dimethylpiperazine, EDA, and substituted EDAs have been screened for thermal stability at low temperature (135 °C) with only a few degradation products identified (Eide-Haugmo et al., 2011; Lepaumier et al., 2009a).

The degradation of PZ is one important aspect to understand in the development of this solvent. The specific goals of this dissertation were split into three categories relating to thermal degradation, oxidation, or physical properties. The specific goals were as follows:

Objectives for studying PZ thermal degradation

1. Quantify the rate of PZ thermal degradation at conditions representative of the stripper, stripper sump and reboiler of a CO_2 capture system.
2. Identify and quantify degradation products from PZ thermal degradation.
3. Develop a fundamental understanding of the mechanisms that produce the primary thermal degradation products of PZ.
4. Estimate the rate of PZ loss due to thermal degradation at industrially relevant conditions.

Objectives for studying PZ oxidation

1. Quantify the rate of PZ oxidation at conditions representative of the absorber and absorber sump of a CO_2 capture system.

2. Identify and quantify degradation products of PZ oxidation.
3. Evaluate the effect of metal catalysts on the oxidative degradation of PZ.
4. Evaluate effectiveness of inhibitors in decreasing oxidation of PZ.
5. Estimate the rate of PZ loss due to oxidation at industrially relevant conditions

Objectives for studying the physical properties of PZ

1. Measure the viscosity and density of concentrated PZ solutions over a useful range of CO₂ loading, PZ concentrations, and temperature.
2. Study the PZ solid solubility in order to determine the CO₂ loading, PZ concentration, and temperature where aqueous solutions exist.

Chapter 2 - Concentrated, Aqueous Piperazine as a Solvent for CO₂ Capture

The primary purpose of this chapter is to establish concentrated, aqueous PZ as a viable solvent for post-combustion CO₂ capture from coal-fired flue gas using amine based absorption-stripping. This is achieved by describing the relevant speciation, history of the solvent, physical properties, and thermodynamic properties that would be important for designing a full scale PZ-based CO₂ capture system. From within these topics, the important advantages and disadvantages of PZ can be ascertained. Sections of this chapter are taken from a published paper where PZ was first discussed as a novel solvent (Freeman et al., 2010b).

The secondary purpose of this chapter is to serve as an overview of literature relevant to the degradation of concentrated PZ systems, but is not all inclusive. An

extensive review of literature relating to a variety of amine solvents, comparisons of kinetic rates, degradation mechanisms, and other important thermodynamic properties has been completed previously (Rochelle et al., 2001). All-encompassing reviews of literature relating to the oxidation and thermal degradation of amines have been done previously with a focus on MEA (Davis, 2009; Sexton, 2008). The degradation literature, as it particularly pertains to PZ, is expanded beyond what has been explored previously. Additional literature is included in subsequent chapters when appropriate to the subject being discussed.

2.1 PIPERAZINE (PZ) AND ITS SPECIATION

Piperazine (PZ) is a cyclic diamine with a molecular formula of $C_4H_{10}N_2$ that is crystalline in its pure anhydrous form at room temperature. When exposed to water, either in aqueous solution or absorbed from air, PZ can easily hydrate to form PZ hexahydrate ($PZ \cdot 6H_2O$). In aqueous solution with CO_2 , the two amino functions on PZ can react and create numerous PZ-based species. The PZ species present in solution, as shown in Figure 2.1, include PZ carbamate ($PZCOO^-$), PZ dicarbamate ($PZ(COO^-)_2$), protonated PZ (H^+PZ), deprotonated PZ ($H_2^{+2}PZ$), and protonated PZ carbamate (H^+PZCOO^-).

The speciation of PZ in solution is a function of the CO_2 concentration, or CO_2 loading. In the absence of CO_2 in solution, PZ exists primarily as free PZ with a small portion of H^+PZ . As the CO_2 concentration increases, $PZCOO^-$ begins to form with the H^+PZ concentration increasing and the free PZ concentration decreasing. Once a CO_2 loading of about 0.28 mole CO_2 per mole alkalinity is reached, $PZCOO^-$ reaches its maximum concentration and H^+PZ begins to level out. Leading up to this loading, the concentration of H^+PZCOO^- is steadily increasing, lagging the production of both H^+PZ

and PZCOO^- . After a loading of 0.28 mole CO_2 per mole alkalinity, the concentrations of H^+PZ , PZCOO^- , and free PZ are decreasing while H^+PZCOO^- is increasing. A loading of 0.5 mole CO_2 per mole alkalinity represents the amount of CO_2 needed in order to have half of the PZ basic groups react with CO_2 while the other half are protonated. This is essentially the maximum realistic loading. At this point, the solution is primarily made up of the zwitterion H^+PZCOO^- with a small concentration of H^+PZ present. Through the entire range of loading, the concentration of $\text{PZ}(\text{COO}^-)_2$ is very small, demonstrating that this species is not a preferred form of PZ. The concentrations of H^+PZH^+ and $\text{PZ}(\text{COO}^-)_2$ are not represented on the graph because their concentrations are nearly negligible.

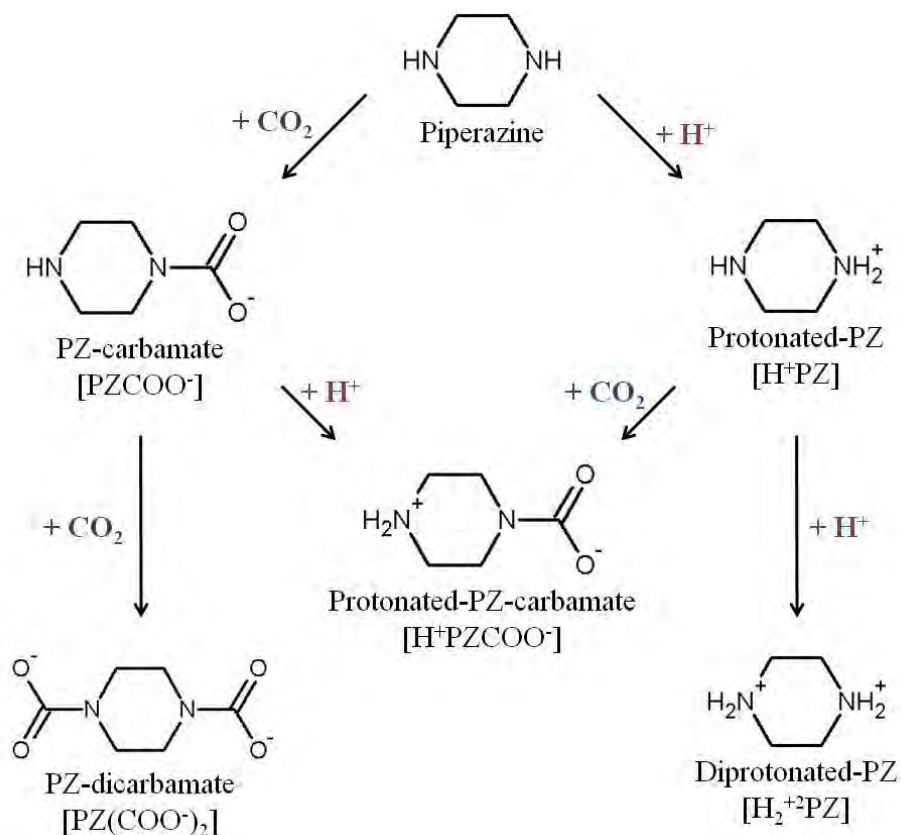


Figure 2.1: Speciation of PZ in aqueous solutions

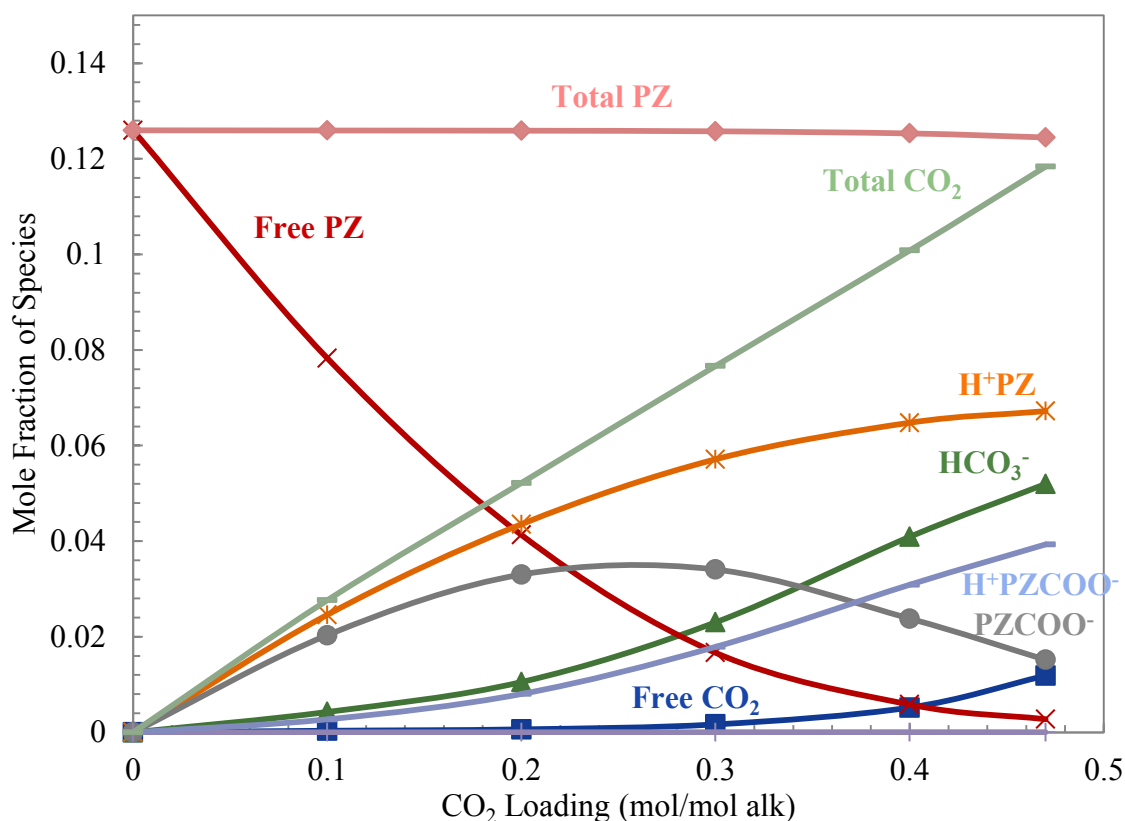


Figure 2.2: Speciation of 8 m PZ at 40°C (Frailie et al., 2011)

2.2 HISTORICAL USE OF PZ

2.2.1 PZ Used in gas treating

PZ was first identified as a possible promoter in alkanolamine solutions for use in gas treating in the 1980s (Appl et al., 1982). In gas treating, and the specific application of CO₂ capture, PZ has been identified as a kinetic promoter in amine systems with advantageous solution characteristics but diminished kinetic rates. In one of the first applications, a small concentration of PZ in combination with MDEA utilized the enhanced kinetic rate of the PZ molecule with the decreased heat of absorption of CO₂ of the tertiary amine, MDEA (Appl et al., 1982; Bishnoi and Rochelle, 2002a; Xu et al., 1992; Zhang et al., 2001). Another example is potassium carbonate (K⁺CO₃⁻)/PZ systems

where PZ enhances the overall kinetic rate of the system (Chen, 2007; Cullinane and Rochelle, 2004; Hilliard, 2008). Since its start as a kinetic promoter, the properties of PZ have been studied to determine its efficacy and usefulness in gas treating and CO₂ capture applications.

Although researchers quickly identified that PZ had enhanced reaction rates with CO₂, the limited solubility of PZ restricted its use to below 2.0 or 2.5 molal (m) in blended amine systems. Most literature available on PZ is either a blended system, where solubility issues are remediated by dilution in another solvent, or at very low PZ concentration, below the 1.9 m PZ solubility limit at room temperature.

2.2.2 Pharmaceutical use of PZ

Outside of the CO₂ capture field, PZ is a backbone molecule used in the pharmaceutical industry since 1953 in various types of stimulants (antidepressants), antihistamines, antipsychotics, and is contained in numerous recreational drugs (Mouriquand et al., 1951; White and Standen, 1953). PZ itself has anthelmintic properties and is used as a deworming agent for humans and animals with great efficacy in the form of PZ hydrate or PZ citrate (Brown and Chan, 1955; Brown and Serman, 1954). The use of PZ as a pharmaceutical agent has also motivated more recent interest in research on the treatment of drinking water contaminated with PZ or molecules containing the PZ moiety (Burhenne et al., 1997; Dewitte et al., 2008; Dodd et al., 2006; Pietsch et al., 2001; Thabaj et al., 2007).

2.3 PHYSICAL AND THERMODYNAMIC PROPERTIES OF PZ

The physical properties of PZ have been studied since the compound was first identified. The low solubility of PZ has limited the amount of data available in literature for aqueous solutions of PZ above room temperature solubility.

2.3.1 Solid solubility of PZ

Previous authors have investigated the solid-liquid equilibrium (SLE) or solid solubility of PZ solutions. The SLE has been reported in terms of the transition temperature at which a given $\text{H}_2\text{O} + \text{PZ}$ solution would experience a transition between the liquid or solid phase.

Bishnoi (2000) measured the SLE for unloaded PZ solutions by adding anhydrous PZ to a given amount of water and observing where crystallization occurred at a given temperature (Bishnoi, 2000). The solution was allowed to mix and reach equilibrium to allow any crystals to settle and separate from the aqueous phase. The resulting liquid was then titrated using 2 N HCl to determine the exact PZ concentration of the saturated, liquid phase. Bishnoi measured SLE for 0 to 70 °C which resulted in data for 0.5 to 40 m PZ solutions.

The Dow Chemical Company published physical property data for a group of ethylenediamines including PZ (The Dow Chemical Company, 2001). That brochure included a graph of SLE data for PZ in the form of temperatures (0 to 90 °C) and the corresponding wt % of PZ for SLE. The method of determination was not provided and data was read off of the graph manually with some inherent error. One solubility data point was also included in an MSDS published by Merck Corporation, a pharmaceutical company (Merck Corporation, 2009).

More recently, Hilliard (2008) determined solid-liquid equilibrium data for unloaded PZ solutions from heat capacity measurements on a differential scanning calorimeter (DSC) (Hilliard, 2008). The data was obtained for a wide range of PZ concentrations, from 0.5 to 40 m PZ (4.3 to 77 wt % PZ), and was calculated based on assigning the phase transition to the position of the maximum peak on the thermal profile when heating a sample from -10 to 100 °C. Finally, Muhammad and colleagues most

recently duplicated the data of Bishnoi using the same method and similar ranges of PZ concentration (Bishnoi, 2000; Muhammad et al., 2009).

All of the PZ solubility data described above is for unloaded solutions. No literature has been found that investigates SLE on the $\text{H}_2\text{O} + \text{PZ} + \text{CO}_2$ system. The data of the aforementioned authors can be summarized and compared on a figure showing the SLE for the $\text{H}_2\text{O} + \text{PZ}$ system. The data from -10 to 80 °C and 0 to 0.80 weight fraction PZ is compared in Figure 2.3.

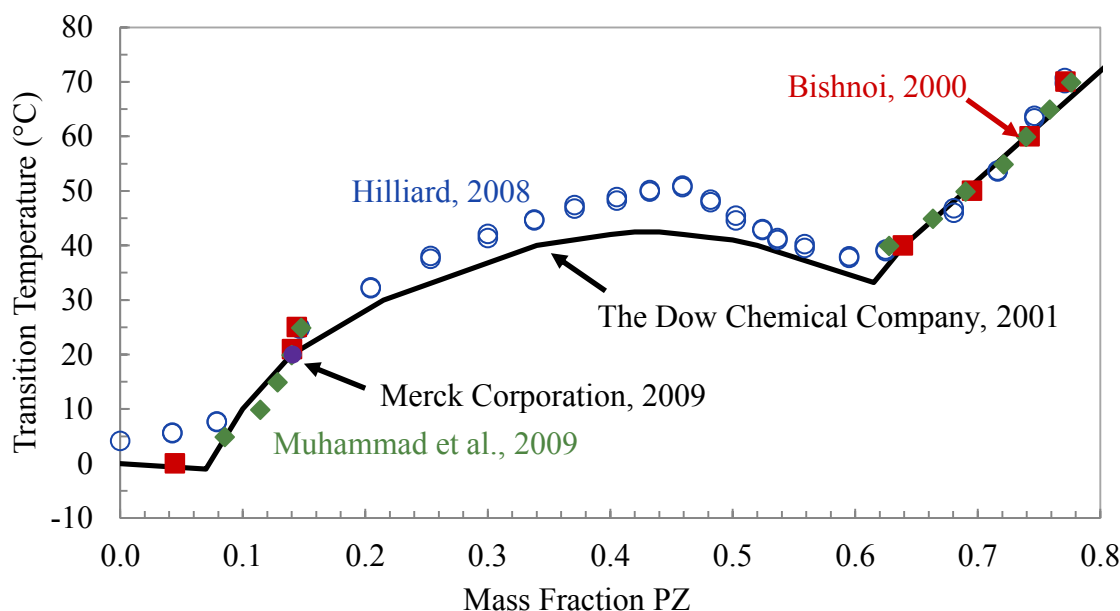


Figure 2.3: Comparison of Solid-Liquid Equilibrium Data for $\text{H}_2\text{O} + \text{PZ}$. Line: (The Dow Chemical Company, 2001). Data: ■, (Bishnoi, 2000); □, (Hilliard, 2008); ●, (Muhammad et al., 2009); ○, (Merck Corporation, 2009).

2.3.2 Density and viscosity of PZ solutions

There are numerous sources reporting the density and viscosity in aqueous, low concentration, unloaded PZ solutions (Cook and Lowe, 1976; Derks et al., 2005; Derks et al., 2008; Muhammad et al., 2009; Samanta and Bandyopadhyay, 2006). Physical

property data of aqueous PZ solutions loaded with CO₂ are of particular importance to this research but, unfortunately, this type of data are rare in the current literature. Chapter 4 of this thesis reports on the density and viscosity of loaded PZ solutions.

In comparison with other amine solvents of interest to CO₂ capture applications, PZ has high viscosity. The viscosity of 7, 8, 9, and 10 m PZ is compared with other amines in Figure 2.4 (Huntsman Corporation, 2005; Closmann et al., 2009). The amine concentration is plotted in units of moles alkalinity per kilogram of water in order to compare mono- and diamines on a similar basis. All of the viscosities shown in Figure 2.4 are at 40 °C and at the rich loading of the system (0.3 mole CO₂ per mole alkalinity for MDEA and MDEA/PZ blend; 0.4 mole CO₂ per mole alkalinity for PZ and DGA; 0.5 mole CO₂ per mole alkalinity for MEA).

Comparison of the viscosity on this basis demonstrates how the amine basic group affects overall viscosity. As the number of basic groups increases in a molecule, the viscosity increases in a linear direction. The viscosity of 8 m PZ is higher than that of 7 m MEA, but compared to 60 wt % DGA[®], the viscosity of PZ is lower for a higher alkalinity. PZ has the advantage over DGA[®] of having two amine functional groups without suffering an increase in viscosity. DGA[®] solutions at 60 wt % are successfully used in natural gas treating (Al-Juaied and Rochelle, 2006b; Al-Juaied, 2004).

2.3.3 CO₂ solubility in PZ solutions

The solubility of CO₂ in concentrated, aqueous PZ has been studied by numerous authors in the Rochelle group. Ermatchkov and colleagues were the first to study CO₂ solubility in 1 to 4 m PZ at 40, 80, and 120 °C (313.15 to 393.15 K) (Ermatchkov et al., 2006). Hilliard measured CO₂ solubility using a low temperature vapor-liquid equilibrium cell for solutions up to 5 m PZ (Hilliard, 2008). Dugas measured CO₂

solubility using a wetted wall apparatus used to measure kinetic rates of CO₂ absorption (Dugas, 2009). As with other amines, Hilliard and Dugas both found the solubility of CO₂ in PZ to not be a function of CO₂ concentration, even up to 12 m PZ, so low PZ concentration data from other authors are still helpful (Dugas, 2009; Hilliard, 2008). A summary of CO₂ solubility gathered to date is provided in Figure 2.5 and is shown as the equilibrium partial pressure of CO₂ ($P^*_{\text{CO}_2}$) plotted against the CO₂ loading in the liquid.

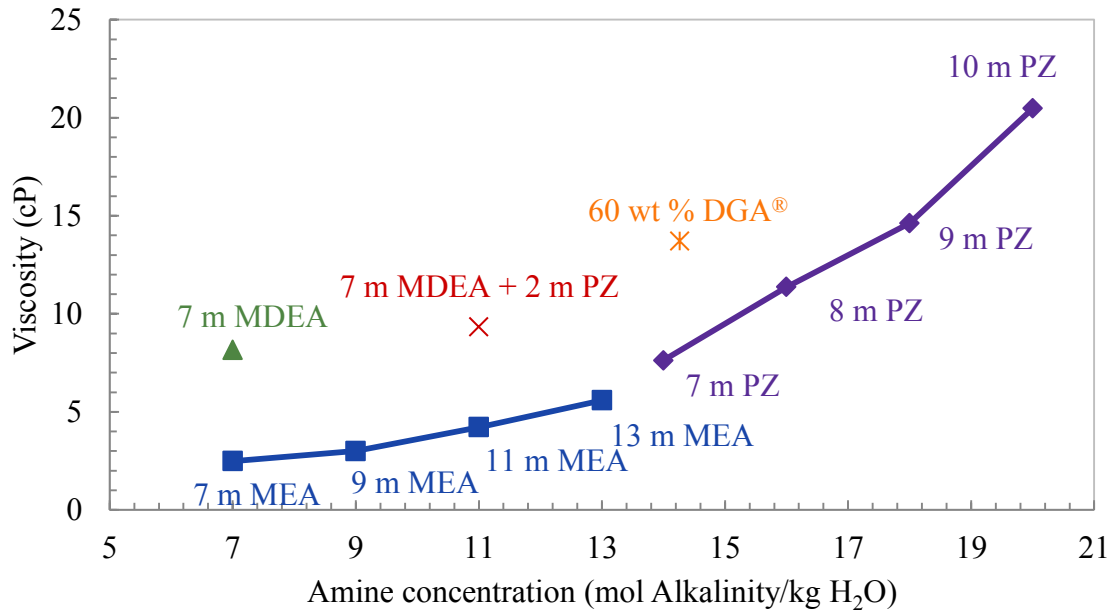


Figure 2.4: Viscosity of amine solutions at typical rich loading and 40 °C

The CO₂ solubility data for PZ were regressed by Xu cover 0.9 to 12 m PZ from 40 to 160 °C (Xu and Rochelle, 2011). The regression is the equilibrium partial pressure of CO₂ in Pa, $P^*_{\text{CO}_2}$, in terms of temperature, T , in Kelvin, CO₂ loading, α , in mole CO₂ per mole alkalinity, and the universal gas constant, R , in kJ per mole-K, as shown in equation 2.1.

$$\ln(P_{\text{CO}_2}) = 35.5 - \left(91.54 \frac{\text{kJ}}{\text{mol}} \right) \left(\frac{1}{RT} \right) - 18.0\alpha^2 + 4789 \left(\frac{\alpha}{T} \right) + 9765 \left(\frac{\alpha^2}{T} \right) \quad (2.1)$$

CO₂ solubility data has been used to determine the expected rich and lean CO₂ loadings in a full-scale PZ absorption-stripping system. Based on the required partial pressure driving forces in the absorber, it is expected that the rich amine stream will have an $P^*_{\text{CO}_2}$ of 5 kPa (5000 Pa). This is to provide a small driving force between the inlet flue gas entering the bottom of the absorber with 13 to 15% CO₂, or 13 or 15 kPa (13000 to 15000 Pa). At the top of the absorber, the lean amine stream will have an $P^*_{\text{CO}_2}$ of approximately 0.5 kPa (500 Pa) to provide a driving force with the gas stream exiting at 1.3 to 1.5% (130 to 150 Pa). Using the CO₂ solubility figure (Figure 2.5) with the expected $P^*_{\text{CO}_2}$ values, the expected CO₂ loadings can be determined directly. The dashed lines in Figure 2.5 indicate this procedure and show the expected lean and rich loadings of 0.31 and 0.41 mole CO₂ per mole alkalinity, respectively. These values will be used throughout this thesis as the standard CO₂ concentrations of interest.

The heat of absorption of CO₂ into an 8 m PZ solution was also estimated by Xu using the Gibbs-Helmholtz equation. The resulting expression for the heat of absorption in concentrated PZ is as follows (Equation 2.2).

$$\Delta H_{\text{abs}} = -R \frac{\partial \text{Ln} P_{\text{CO}_2}}{\partial \left(\frac{1}{T} \right)} = -R \left(-\frac{91542}{R} + 4789\alpha + 9765\alpha^2 \right) \quad (2.2)$$

2.3.4 CO₂ mass transfer rates in PZ

Mass transfer rates of CO₂ absorption into concentrated aqueous PZ were studied extensively in a wetted wall column (Dugas, 2009). The liquid-film mass transfer coefficient defined in gas-phase units, k_g' , is plotted against equilibrium partial pressure of CO₂, $P^*_{\text{CO}_2}$, for 8 m PZ and 7 m MEA at 40, 60, 80, and 100 °C in Figure 2.6 (Dugas and Rochelle, 2009). Rate data at 60, 80, and 100 °C are plotted as a function of the

equilibrium partial pressure of CO₂ at 40 °C. This x-axis provides a surrogate measurement of CO₂ loading and allows comparison of different solvents over their practical operating range.

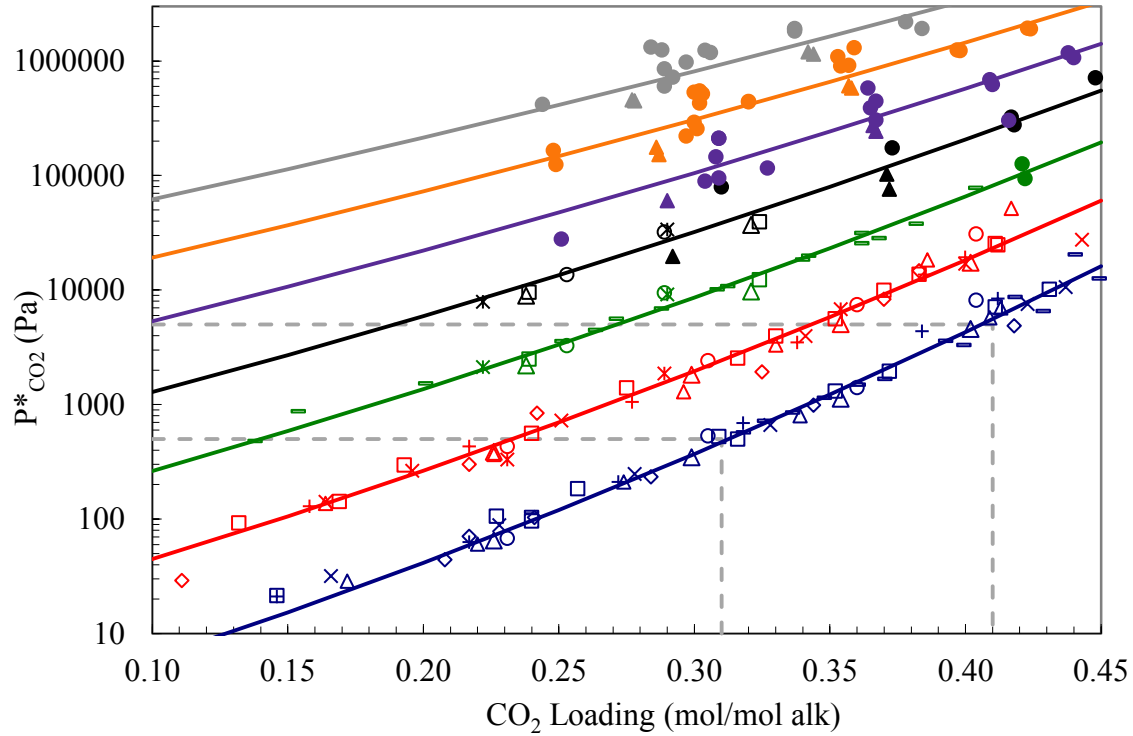


Figure 2.5: CO₂ solubility at 40 (blue), 60 (red), 80 (green), 100 (black), 120 (purple), 140 (orange), and 160 °C (gray). Data from (Dugas, 2009; Hilliard, 2008): 0.9 m, $\diamond$; 2 m, $\square$; 2.5 m, $\times$; 3.6 m, $+$; 5 m, Δ ; 8 m, $\circ$; 12 m $*$. Data from (Xu and Rochelle, 2011): 5 m, $\blacktriangle$; 8 m, $\bullet$. Data from (Ermatchkov et al., 2006): —, 2 to 4 m. Lines: solid, Equation 2.1; dashed, determination of CO₂ loading range.

As demonstrated in Figure 2.6, this normalized flux, k_g' , for 8 m PZ is 1.5 to 3 times greater than 7 m MEA. At 40 °C and a $P^*_{\text{CO}_2}$ of 500 Pa, the k_g' for 8 m PZ and 7 m MEA are 1.98×10^{-6} and 7.66×10^{-7} mol/s-Pa-m², respectively. This shows that the mass transfer rate of CO₂ into concentrated PZ is twice as fast as 7 m MEA at this condition. At the higher CO₂ loading, the improvement over MEA is less distinct with the mass

transfer rate only 1.5 to 2 times faster than MEA. The same trend is observed at 60 °C. Although PZ is faster than MEA at 80 and 100 °C as well, mass transfer rates are the most important from 40 to 60 °C, the expected temperature range of the absorber.

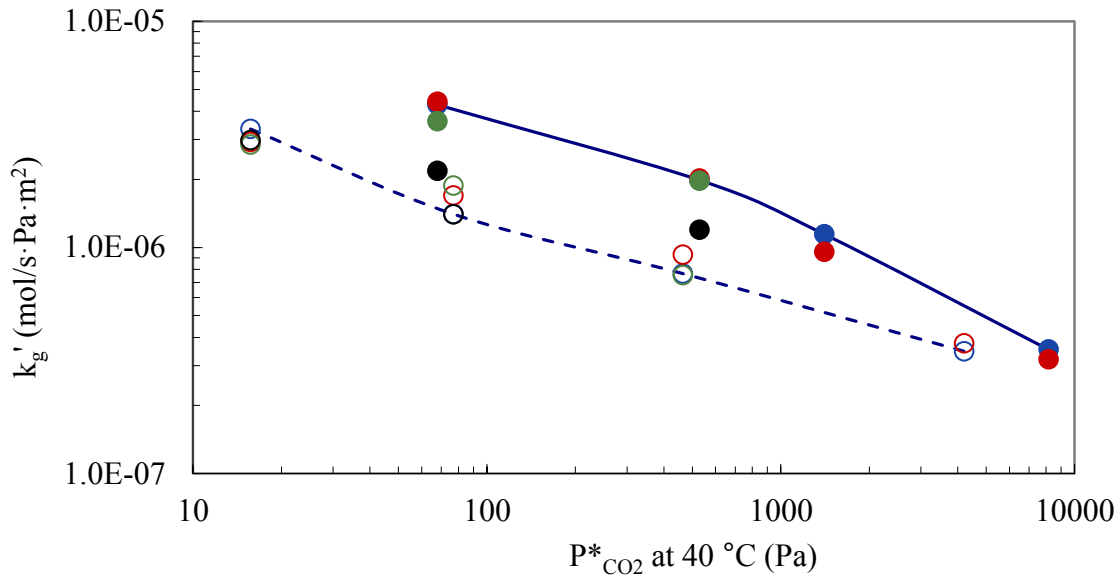


Figure 2.6: Mass transfer coefficients of 8 m PZ (filled circles) and 7 m MEA (open circles) at 40 °C (blue), 60 °C (red), 80 °C (green), and 100 °C (black) (Dugas, 2009)

2.3.5 Volatility of concentrated PZ

The volatility of PZ was measured in an equilibrium cell with hot gas FT-IR (Nguyen et al., 2010). The volatility of 8 m PZ solutions is compared to that of 5 m PZ and 7 m MEA at 40 °C in Figure 2.7. At 40 °C and atmospheric pressure, the volatility of 7 m MEA ranges from 19.0 to 64.9 ppm (MEA partial pressure of 1.93 to 6.6 Pa) over a loading range of 0.15 to 0.50 mole CO₂ per mole alkalinity. At 40 °C and atmospheric pressure, the volatility of 8 m PZ ranges from 1.07 to 7.74 ppm (PZ partial pressure of 0.11 to 0.78 Pa) over a loading range of 0.29 to 0.40 mole CO₂ per mole alkalinity. Finally, at 40 °C and atmospheric pressure, the volatility of 5 m PZ ranges from 5.53 to

50.5 ppm (PZ partial pressure of 0.56 to 5.1 Pa) over a loading range of 0 to 0.41 mole CO₂ per mole alkalinity.

At 40 °C, the volatility of PZ solutions is lower than the volatility of MEA solutions. It was anticipated that PZ would have a higher volatility than MEA because the boiling point of PZ, 146.5 °C, is lower than that of MEA, 170 °C. However, the volatility of both 5 and 8 m PZ is slightly lower at 40 °C. Modeling of PZ systems demonstrated this effect as a greatly decreased activity coefficient for PZ due to the solution non-ideality (Hilliard, 2008).

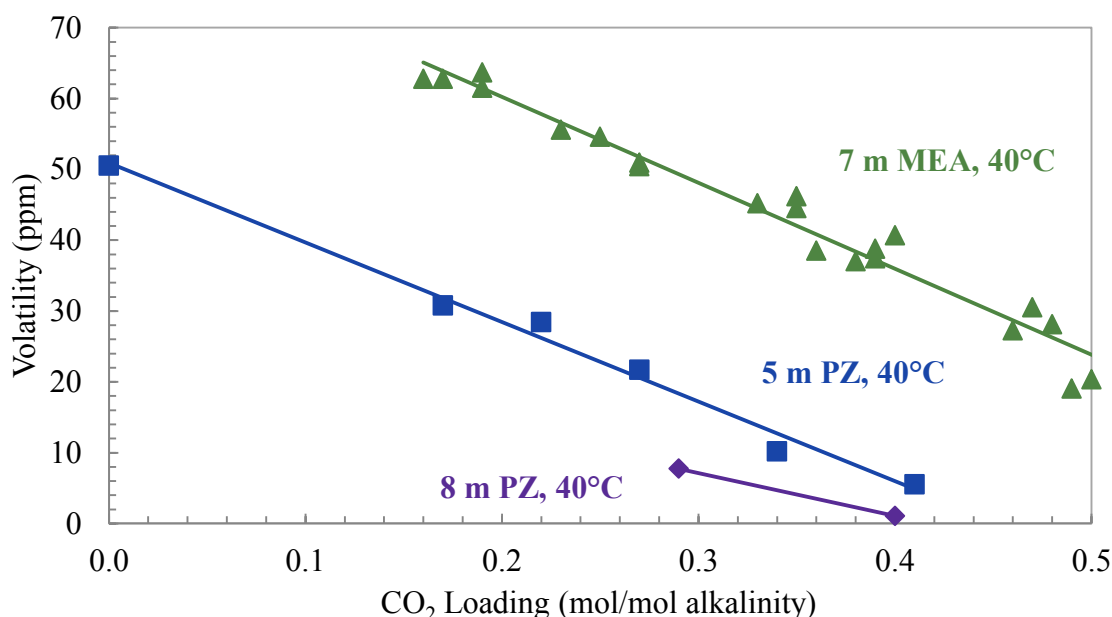


Figure 2.7: Comparison of Amine Volatility at 40 °C for 8 m PZ (♦), 5 m PZ (■), and 7 m MEA (▲) (Nguyen et al., 2010)

2.3.6 Diffusion coefficients of PZ solutions

The diffusion coefficients for N₂O and CO₂ in PZ solutions have been studied previously by various authors. Sun and colleagues measured the diffusivity of N₂O and CO₂ into water and N₂O in H₂O + PZ using a gas-liquid wetted wall contactor at

temperatures between 30 and 40 °C (303 to 313 K) and PZ concentrations between 0.23 and 0.92 kmole per m³ (0.24 to 1.0 m PZ) (Sun et al., 2005). The diffusivity of CO₂ in H₂O + PZ was estimated using the N₂O analogy. Samanta and colleagues used the same experimental procedure as Sun and estimated the diffusivity of CO₂ in H₂O + PZ for 1.7 to 12 wt% PZ (0.21 to 1.6 m PZ), and 25 to 40 °C (298 to 313 K) (Samanta et al., 2007). Hamborg and colleagues estimated the diffusivity of CO₂ in H₂O + PZ using the N₂O analogy, as with previous authors, for 0.3 to 1.4 mole per dm³ (0.31 to 1.6 m PZ) at 25 to 60 °C (293 to 333 K) but measured the N₂O diffusivity using a Taylor Dispersion technique which injects the solute into a laminar flow of solution rather than a wetted wall contactor (Hamborg et al., 2008). Derks (2008) also used the Taylor Dispersion technique to measure the diffusivity of the PZ molecule in a H₂O + PZ solution from 0.0008 to 1.46 mole per dm³ PZ (0.01 to 1.48 m PZ) and 20 to 95 °C (293 to 368 K) (Derks et al., 2008).

No literature measurements have been completed for concentrated PZ or PZ solutions containing CO₂. Since real PZ-based CO₂ capture systems will include concentrations of CO₂ up to 0.45 mole CO₂ per mole alkalinity and PZ concentrations higher than 5 m, there is currently a lack of useful diffusivity data. All of the measurements for diffusivities in aqueous PZ solutions are intended for use in thermodynamic modeling of systems for design of large scale application, but the lack of CO₂ in these measurements limits their ability to predict real values. Previous modeling efforts have approximated PZ diffusion characteristics by assuming the behavior is similar to that of MEA where more data is available in literature (Dugas, 2009).

2.3.7 Heat capacity of PZ solutions

The heat capacity of concentrated, aqueous PZ solutions has not been reported in literature. Recent work has measured the heat capacity of 8, 10, and 12 m PZ solutions over a range of temperatures but has not been formally published (Rochelle, 2009a). A portion of this data is shown in Figure 2.8 to demonstrate the trends observed. Overall, the heat capacity data for PZ follows similar trends observed with other amines including an increase of heat capacity with increased temperature and a decrease of heat capacity with increased CO₂ loading and PZ concentration.

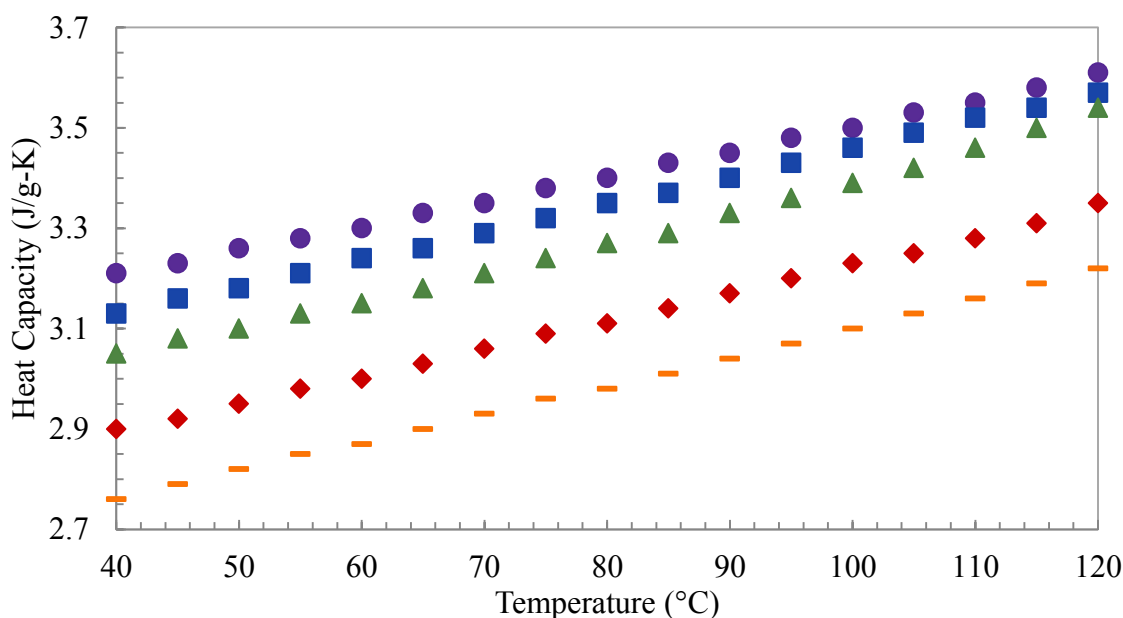


Figure 2.8: Comparison of heat capacity of concentrated PZ solutions. Data: ●, 8 m PZ with $\alpha=0.21$; ■, 8 m PZ with $\alpha=0.29$; ▲, 8 m PZ with $\alpha=0.40$; ◆, 10 m PZ with $\alpha=0.40$; —, 12 m PZ with $\alpha=0.29$ (Rochelle, 2009a)

2.3.8 Heat of absorption of PZ solutions

No studies on the heat of absorption of CO₂ into concentrated, aqueous PZ have been reported in literature prior to the publication of this work. Measurements for 8 m PZ from 0 to 0.5 mole CO₂ per mole alkalinity at 60, 80, 100, and 120 °C were made as a

part of this thesis and the results are included in Appendix F of this dissertation. The calorimeter used was not the appropriate set-up for solutions which precipitate in the absence of CO₂, so the data contains a significant portion of error.

2.4 OXIDATIVE DEGRADATION OF AMINES

The oxidative degradation, or oxidation, of amines has been investigated since the 1950s. Initial work on the topic was performed by the United States Navy during the 1950s and 1960s while investigating CO₂ scrubbers for submarine air purification (Girdler Corporation, 1950; Blachly and Ravner, 1964; Blachly and Ravner, 1965; Blachly and Ravner, 1966). Work performed by the Navy identified the first MEA oxidation products (Scheiman, 1962). Rooney and colleagues expanded the scope of oxidation research to include amines besides MEA and contributed to identifying unknown degradation products (Rooney et al., 1998).

The oxidation work in the Rochelle group began with Chi and Goff who looked at oxidation of MEA under various conditions (Chi, 2002; Goff, 2005). Goff looked extensively at oxygen mass transfer conditions in the laboratory experiments as well as inhibitors for metal catalyzed degradation. The dissertation of Sexton is the most comprehensive study of the oxidation of MEA to date (Sexton, 2008). He investigated numerous combinations of metal catalysts, inhibitors, and other additives on MEA degradation, as well as performing oxidation screening experiments on other amines, including PZ, and MEA analogs.

2.4.1 Catalyst effect of metal on amine oxidation

The connection between corrosion products and amine degradation was identified in the 1950s, indicating a link between metal-based corrosion products and degradation (Hofmeyer et al., 1956). A sub-set of oxidation research since then has been looking into

the catalytic effect of metals on the oxidation of various amines. United States Navy work performed by Blachly and Ravner included this sub-set of oxidation research after scrubber solvents were found to contain iron, nickel, chromium, and copper after use in submarines (Blachly and Ravner, 1964). Their results indicated that copper had a strong catalytic effect for enhancing MEA degradation while iron and nickel only enhanced degradation slightly. The pair also tested various oxidation inhibitors including EDTA and N,N-diethanolglycine (also known as VFS or bicine) with some success. The oxidation work of Sexton primarily looked at the effects of metals and inhibitors on the degradation characteristics of MEA (Sexton, 2008). Sexton's conclusions agree with that of Blachly and Ravner and also include the use of Inhibitors "A" and "B" to decrease MEA degradation.

2.4.2 Oxidation of PZ

One master's thesis in the Rochelle group has looked exclusively at PZ oxidation, but used gas chromatography (GC) to quantify PZ loss rather than the now preferred method of cation ion chromatography (IC) (Alawode, 2005). The high temperature used in the injection port and analytical column in the GC, up to 200 °C, was later found to over predict degradation of amines due to the thermal degradation at these temperatures (Davis, 2009). Another master's thesis focused on oxidation of PZ blended with potassium carbonate to control solubility of PZ (Jones, 2003). Although the work of Sexton was primarily focused on the degradation of MEA, one chapter of his thesis focused on low to mid-level concentration PZ experiments (Sexton, 2008). This work on PZ ranged from 2.5 to 5 m PZ and was primarily executed in the low-gas flow apparatus used by previous students (and described in detail in Chapter 3). The primary conclusion was that PZ does oxidize, but at rates significantly lower than that of MEA. The

conclusion of Sexton was that the metals tested ranked for catalyzing the most to least oxidation were: Cu > V > Fe.

2.4.3 Oxidation of PZ with other oxidants

The oxidation of amines has been studied with oxidizers other than O₂ itself in fields of environmental engineering in regards to water and wastewater treatment. Common oxidizers studied include ozone (O₃), chlorine dioxide (ClO₂) or chlorine (Cl₂).

Pietsch and colleagues found that PZ was quickly oxidized in the presence of ozone (Pietsch et al., 2001). Their ozonation studies found that PZ oxidized significantly faster than diethylamine, dimethylamine, MEA, cyclohexylamine, pyrrolidine, piperidine, or ethylenediamine (EDA) with a rate constant for PZ removal of $8.4 \times 10^{-2} \text{ s}^{-1}$. Morpholine behaved similarly and EDA demonstrated the third fastest ozonation rate. The rationale of Pietsch is that the low pKa values of PZ and morpholine compared to the other amines tested allow for more non-protonated amine groups at the experimental pH of 7.0. Ozone is known to only react with non-protonated amine groups, leaving PZ and morpholine with significantly higher ozonation rates (Hoigné and Bader, 1983). Their studied also concluded that at neutral pH, the ozonation of PZ is due to the direct oxidation from the ozone molecule, not a radical mechanism.

A series of studies performed by Rosenblatt and colleagues in the late 1960s and early 1970s explored the oxidation of various amines using ClO₂ as an oxidant (Davis et al., 1972; Dennis et al., 1967; Hull et al., 1969a; Hull et al., 1969b; Hull et al., 1969c; Hull et al., 1967; Hull et al., 1969d; Rosenblatt et al., 1963; Rosenblatt et al., 1968; Rosenblatt et al., 1972; Rosenblatt et al., 1967). One study examined the oxidation of PZ with ClO₂ and found that the PZ molecule fragmented to produce EDA and formaldehyde, but an exact mechanism was not suggested (Dennis et al., 1967). Dennis

(1967) found that amines with heteroatoms attached to the β -carbon to the amine underwent oxidative fragmentation in the presence of ClO_2 while the analog without a heteroatom did not fragment.

Pietsch and colleagues also investigated the oxidation of PZ with chlorine dioxide (ClO_2) and chlorine when studying applications of chlorine-based water treatment processes for pharmaceutical agents (Pietsch et al., 2001). When treated with ClO_2 , PZ showed the highest rate of oxidation of the primary and secondary amines tested. In this test, only 51% of the initial PZ remained after a typical drinking water treatment experiment. When treated with chlorine, however, minimal loss of PZ was observed, indicating that chlorine is a weaker oxidant.

2.4.4 Oxidation of compounds containing the PZ moiety

As mentioned in Section 2.2.2 above, a number of pharmaceutical agents contain the PZ moiety within a more complicated chemical structure. Fluoroquinolones are a class of synthetic antibacterial agents that are used for both humans and farm animals. A number of studies on municipal wastewater treatment have researched the oxidation of ciprofloxacin, a fluoroquinolone, as a representative antibiotic for waste water treatment aimed at removing pharmaceutical agents that propagate from hospital effluent, animal farms, and other sources (Burhenne et al., 1997; Dewitte et al., 2008; Dodd et al., 2006; Thabaj et al., 2007). These studies are notable because in most cases oxidation took place at the PZ moiety rather than any other position on the molecule and that similar products were produced in the presence of different oxidizers such as ozone (Dodd et al., 2006), potassium permanganate (Thabaj et al., 2007), or photo-induced oxidation (Burhenne et al., 1997). Multiple studies identify the oxidation products as the 3-piperazinone, EDA, 3-alcohol, N-oxide, or ammonia-derivatives of ciprofloxacin (where

the 1N connects to the rest of the ciprofloxacin molecule), shown in Figure 2.9. The oxidation of ciprofloxacin is selective for the PZ moiety and indicates the reactive nature of PZ compared to the pyridone or carboxylic acid functions contained within the same pharmaceutical molecule.

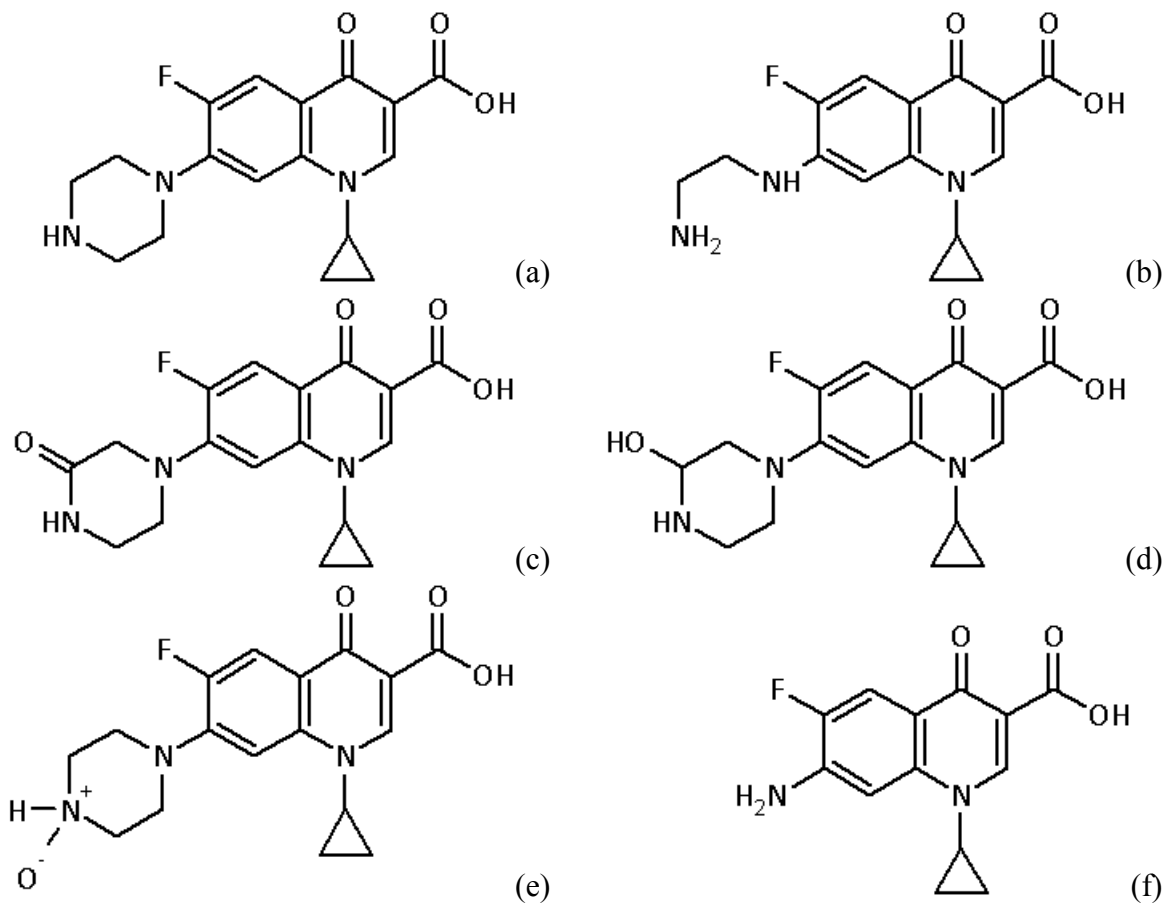


Figure 2.9: Chemical Structures of (a) Ciprofloxacin, (b) EDA derivative, (c) 3-piperazinone derivative, (d), 3-alcohol derivative, (e) N-oxide derivative, and (f) ammonia derivatives of ciprofloxacin.

2.5 THERMAL DEGRADATION OF AMINES

Thermal degradation of amines is a recent topic of interest as Reza and colleagues investigated the thermal degradation of MEA, diethanolamine (DEA), AMP, and blends

of the three amines (Reza and Trejo, 2006). The dissertation of Davis examined on thermal degradation of amines, focusing on MEA thermal degradation mechanisms and screening experiments on various amines and amine blends (Davis, 2008).

2.5.1 Thermal degradation of PZ

There is no thermal degradation data for concentrated PZ solutions available in literature outside of the Rochelle Group. The thesis work of Davis includes experiments performed on 5 m and 8 m PZ during screening experiments where the thermal degradation characteristics of a wide variety of solvents were examined (Davis, 2008). Davis found very little thermal degradation occurred at either PZ concentration at 100, 120 and 135°C. The amount of degradation detected was close to or within the system errors for the cation IC and were reported by him as essentially zero percent degradation. Along with morpholine, PZ was identified as the most thermally resistant amine screened. No degradation products were identified by Davis due to the overall lack of degradation. The thermal stability of PZ in varying conditions is still an area where much can be discovered.

Davis also screened a blend of 7 m MEA/2 m PZ for the rate of thermal degradation. PZ was found to be preferentially degraded with respect to the MEA (Davis, 2009). This has also been observed in other blends of PZ with another amine such as AMP or MDEA. In these cases, the stronger nucleophile, PZ, degrades faster even though at a lower concentration and interacts with the initial degradation products of the other, less stable amine (Closmann et al., 2009; Zhou et al., 2010)

In the degraded blend of 7 m MEA/2 m PZ, Davis identified N-(2-hydroxyethyl) ethylenediamine (HEEDA), N-(2-hydroxyethyl) imidazolidone (HEI), N-(2-aminoethyl) piperazine (AEP), and ethylenediamine (EDA) as the dominant degradation products

using cation IC-MS. HEEDA and HEI are present in MEA degradation while AEP and EDA are new products due to the presence of PZ in the blend. The suggested mechanism for producing AEP is the reaction of PZ with the oxazolidone produced during the first step of the carbamate polymerization mechanism of MEA. Given the relative concentrations of AEP and HEEDA, Davis estimated that PZ reacts up to five times faster to create AEP than MEA reacting with oxazolidone to create HEEDA, indicating the strength of PZ as a reacting nucleophile. Even in a blend with MEA, the degradation results of Davis (2009) indicate some of the characteristics of PZ thermal degradation.

2.6 CONCLUSIONS

The use of concentrated PZ as a CO₂ capture or gas treating solvent has not been previously investigated. The physical and thermodynamic properties of concentrated PZ have not been examined while a small amount of data is available for low concentration PZ without CO₂. Research into some thermodynamic characteristics of low concentration PZ and PZ in a blend has been performed. Although the low concentration work does not specifically apply to the work of this project, it provided a foundation to begin examining concentrated PZ. For properties where there is not a strong effect of amine concentration, like CO₂ solubility, the literature data can be drawn upon widely. One area where even low concentration data is not available is in the area of oxidation and thermal degradation. Widespread work on the degradation of concentrated PZ is needed to fully understand potential large scale application of this solvent. The higher price of PZ as a raw material over other amines such as MEA, DEA, or MDEA further enhances the need to understand its degradation characteristics. Understanding the degradation rates and the production of degradation products under oxidation and thermal degradation conditions is the focus of this dissertation.

Chapter 3 – Analytical Methods and Experimental Equipment

The analytical techniques methods and experimental equipment used throughout this dissertation are described in this chapter. Analytical methods are focused on liquid phase analysis for the concentration of amines, CO₂, degradation products and on the measurement of physical properties such as solid solubility, density, and viscosity. The two experimental methods used for thermal degradation and oxidation, thermal cylinders and the low gas flow reactor, are described in detail. Both the analytical techniques and the experimental equipment are described with the intention of providing enough detail to allow reproduction. Detailed description of the chemicals used including abbreviations, pseudonyms, purity, and the commercial source can be found in Appendix B of this dissertation.

3.1 ANALYTICAL METHODS

3.1.1 Amine solution preparation

3.1.1.1 Preparation of concentrated, aqueous PZ solutions

Loaded solutions of PZ were prepared gravimetrically as shown in Figure 3.1 and as described previously (Hilliard, 2008; Kim et al., 2008). The calculated amounts of DDI water and anhydrous piperazine (99% pure, Fluka) were first weighed and combined in 500 mL or 1 L glass storage jar. With the cap slightly ajar, the bottle was heated with magnetic stirring until the PZ crystals have completely melted into a solution, approximately 50 °C. Meanwhile, the gas sparging column and cap are placed in a 100°C oven to warm up.

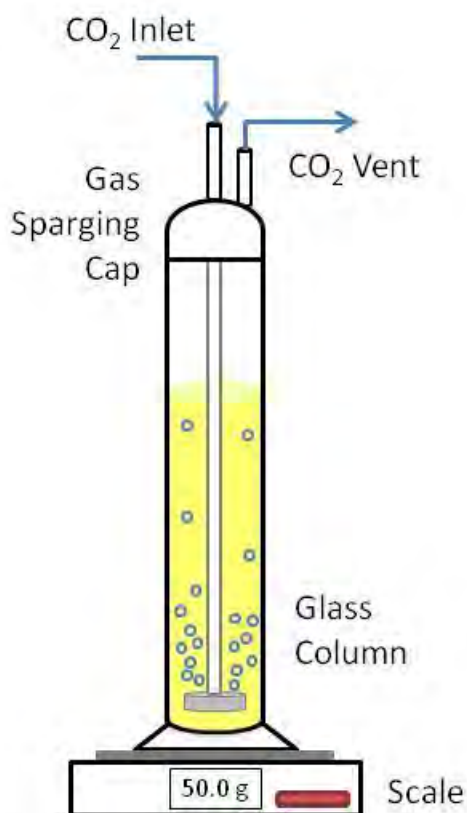


Figure 3.1: Schematic of gravimetric solution preparation

When the PZ was melted, the glass sparging column was removed from the oven and the base column was placed on the scale. The warm solution was then transferred to the column and the gas sparging cap was placed on top of the column, creating a tight seal at the top of the column. The CO₂ inlet line and CO₂ vent lines were then attached to the glass flanges on the sparging cap. Once the CO₂ lines were attached, the entire set-up was allowed to rest and settle for a few seconds. The scale was tared and once a stable zero was achieved, the CO₂ flow was started. CO₂ was sparged until the desired amount of CO₂ was absorbed by the solution, as determined gravimetrically.

Once loading was completed, the CO₂ flow was turned off. The set-up was again allowed to settle to achieve a stable final mass of CO₂ added to the solution. For disassembly, the two gas lines were removed from the cap and the cap was removed, allowing any solution to drain into the column as it was being removed. The cap was set aside and the solution was poured from the column back into the original storage bottle in which the solution was originally melted. Any PZ crystallized on the inside of the storage bottle or cap melted with the introduction of the warm, loaded PZ solution.

3.1.1.2 Preparation of non-PZ solutions

Special considerations were needed when some non-PZ solutions were made. The physical state of the amine dictated the procedure needed to prepare the solutions. Amines that were solid flakes or chunks in their pure state were created as described above for PZ. Slight heat was usually needed along with stirring to melt the starting amine. The liquid solutions were then loaded with CO₂ while warm. Amines that were liquid in their pure state were mixed with water and mixed either with a stir plate or by inverting a sealed bottle numerous times. Then, the solutions were loaded directly, without the need for heating. A few amines were not accessible in their pure form. For

example, homopiperazine (HomoPZ) and hexamethylenediamine (HMDA) are both completely solid in the bottle in their pure form. For these amines, the bottle was warmed in a water bath until the entire bottle of amine was melted into a liquid. Then, the amine was combined with water, mixed, and loaded directly. A summary of the special handling required for the amines used in this project is given in Table 3.1.

Table 3.1: Special handling required for various amines

Amine	State (at 25 °C)	Special Handling
1-Methylpiperazine (1-MPZ)	Liquid	None
2-Methylpiperazine (2-MPZ)	Solid chunks	Crush chunks with mortar and pestle, add to water, melt, and load
1,4-Dimethylpiperazine (1,4-DMPZ)	Liquid	None
<i>trans</i> -2,5-Dimethylpiperazine (t2,5-DMPZ)	Solid flakes	Add to water, melt, and load
Hexamethylenediamine (HMDA)	Solid	Melt, combine with water, and load
Homopiperazine (HomoPZ)	Solid	Melt, combine with water, and load
Morpholine (Morph)	Liquid	None
Piperazine (PZ)	Solid flakes	Add to water, melt, and load
Piperidine (PD)	Liquid	None
Pyrrolidine (Pyr)	Liquid	None

3.1.2 Amine titration

The concentration of total alkalinity of an amine solution was determined using acid titration at room temperature (Hilliard, 2008; Kim et al., 2008). An automatic Titrand series titrator with automatic equivalence point detection was used (Metrohm USA, Riverview, FL, USA). The software used to operate the titrator, measure, and record data was PC Control (Metrohm USA). The Titrand series titrators are potentiometric meters that measure the change in pH in a solution by measuring the

change in electric potential using a pH probe. The overall Titrand unit consists of a base unit, interchangeable dosing units, stir plate, and probe holder.

To perform a measurement, the sample of interest was diluted 300X by combining 60 mL of DDI water with 0.2 g of sample in a 100 or 250 mL beaker. A magnetic stir bar was added to the beaker. To prepare the titrator, the dosing probe was placed in the probe holder and lowered into an empty waste beaker. In the PC Control software and under the section on manual controls, the dosing unit was manually dosed twice with 5 mL of acid. This cleared the dosing line of air bubbles and readied the doser to correctly dispense the acid. Once the lines are clear of air, the pH probe was placed in the probe holder. The pH probe was rinsed with distilled water and dried delicately, avoiding pressure on the bottom membrane of the probe. The sample beaker was then placed on the stir plate and the waste beaker was removed. The probe holder was then lowered into the beaker until the bulb of the pH probe is fully submerged in the sample liquid. The dosing line was adjusted so that it stays well above the liquid line to ensure that the acid was correctly dosed in drops that fell into the liquid.

In PC Control, the acid titration method was started and the sample was titrated with 0.1 N H_2SO_4 to a pH of 2.4. The titrator automatically began stirring when the method begins. Throughout the titration, the volume of acid added and the current pH were recorded each time an increment of acid was added to the sample beaker and were displayed in the PC Control window. A typical titration curve is shown below in Figure 3.2. The Titrand has automatic equivalence point detection which judged the change in slope of the titration curve to determine if an equivalence point had been reached. The software sometimes misidentifies points along the curve other than the two known equivalence points and those points were ignored. At the end of a titration, the equivalence points detected were displayed with the amount of acid needed to reach that

point. For PZ titration, the equivalence point of interest is around a pH of 3.9. The amine concentration by titration was consistently about 2.0 % less than that from the gravimetric preparation in undegraded PZ samples.

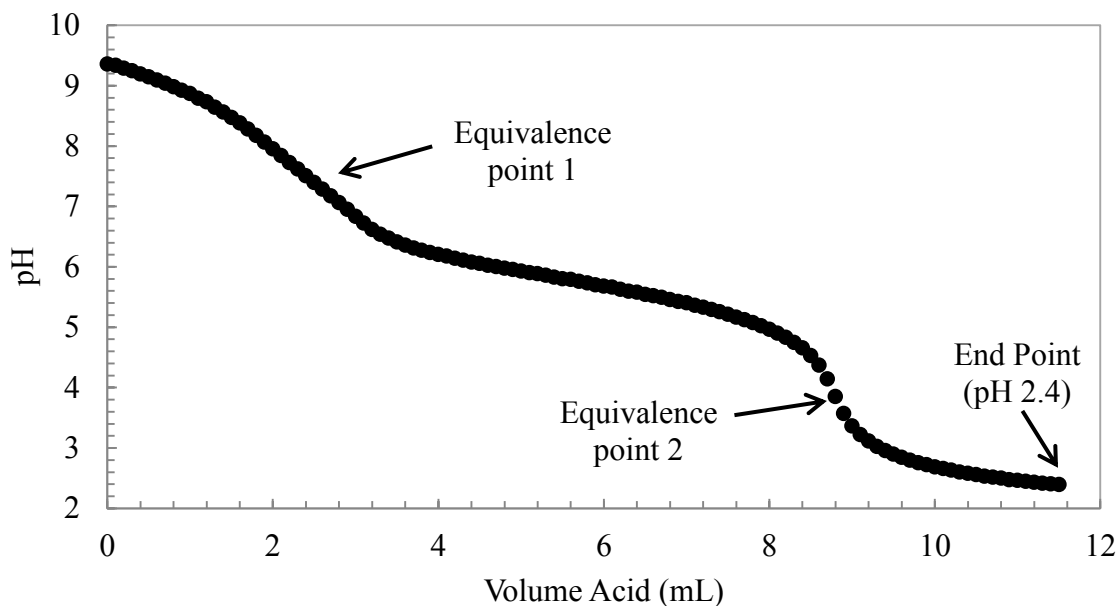
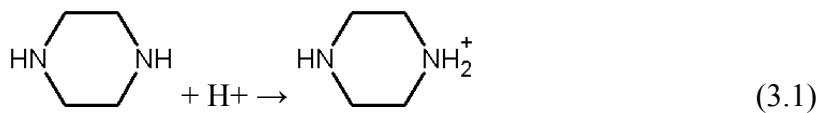
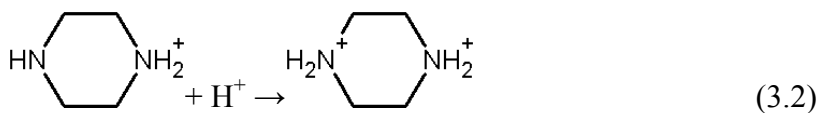


Figure 3.2: Typical acid titration curve (8 m PZ, $\alpha=0.3$)

In PZ titrations, there were usually two prominent equivalence points identified. The first equivalence point represented the conversion of anhydrous PZ species into monoprotonated PZ (protonated PZ or PZH^+) (Equation 3.1).



The second equivalence point represented the further conversion to diprotonated PZ (Equation 3.2).



The equilibrium constant for an equilibrium reaction, K_a , can be defined for each of the two dominant reactions. The two protonation reactions written in reverse as deprotonations are shown in equations 3.3 and 3.4.



The K_a value for the first ($K_{a,1}$) and second deprotonation ($K_{a,2}$) can then be defined for each based upon equations 3.3 and 3.4, as shown in equations 3.5 and 3.6.

$$K_{a,1} = \frac{[PZ][H^+]}{[H^+PZ]} \quad (3.5)$$

$$K_{a,2} = \frac{[H^+PZ][H^+]}{[H^+PZH^+]} \quad (3.6)$$

Rearranging each K_a equation yields the Henderson-Hasselbalch equation relating the pH of a solution to the pKa of the species and the concentration of the species and its conjugate acid (equations 3.7 and 3.8).

$$pH = pK_{a,1} + \log\left(\frac{[PZ]}{[H^+PZ]}\right) \quad (3.7)$$

$$pH = pK_{a,2} + \log\left(\frac{[H^+PZ]}{[H^+PZH^+]}\right) \quad (3.8)$$

The measured pK_a of the first protonation, $pK_{a,1}$, ranges from 9.71 to 9.73 at 25 °C (Enea et al., 1972; Hamborg and Versteeg, 2009; Hetzer et al., 1968; Khalili et al., 2009). The measured pK_a value of the second protonation, $pK_{a,2}$, ranges from 5.33 to

5.41 at 25 °C, with Enea and colleagues reporting a value as low as 4.63 at 25 °C (Enea et al., 1972; Hamborg and Versteeg, 2009; Hetzer et al., 1968; Khalili et al., 2009). Using Equations 3.7 and 3.8, the ratio of the two pairs of species can be calculated over the range of pH experienced during the titration, as shown in Table 3.2.

Table 3.2: Change in protonated PZ species during titration

Solution pH	$\frac{[PZ]}{[H^+PZ]}$	$\frac{[H^+PZ]}{[H^+PZH^+]}$
11	15.1	251189
10	1.51	25119
9	0.151	2512
8	0.0151	251
7.5	0.00479	79.4
7	0.00151	25.1
6	0.000151	2.51
5	1.514E-05	0.251
4	1.514E-06	0.0251
3.9	1.202E-06	0.0200
3	1.514E-07	0.00251
2.4	3.802E-08	0.000631

When the first equivalence point at pH of 7.5 is reached, the concentration of PZ is only a fraction (0.000479) of the concentration of PZH^+ , indicating that nearly all the PZ has been protonated once. At the second equivalence point of 3.9 pH, the concentration of PZH^+ is only a small fraction (0.02) the concentration of H^+PZH^+ , indicating that most of the singly protonated PZ is now diprotonated. This second equivalence point, therefore, represented the amount of acid needed to fully protonate all of the amino groups on the PZ species.

Using the volume of acid needed to reach the equivalence point at a pH of 3.9, the concentration of total alkalinity can be calculated. It is important to make a distinction between the concentration of PZ and the total alkalinity of solution. The titration

procedure measures the total alkalinity of solution. This is true for both neat and degraded solutions. In neat solutions, however, all the alkalinity should be in the form of PZ so the calculation can proceed with this assumption. For degraded samples, the results represent the concentration of total alkalinity which carries a different, although still useful, meaning. Titrations of oxidized or thermally degraded samples result in a measure of the total alkalinity where degradation has likely decreased the PZ concentration and generated degradation products that also contain alkalinity.

The calculation of total alkalinity from the titration data is very direct and can be demonstrated assuming a case where 0.2 gram of a test sample required 8.4 mL of 0.2 N H_2SO_4 to reach a pH of 3.9. First, the amount of alkalinity in the sample can be calculated from the amount of acid added. Then, the concentration can be calculated in terms of moles of alkalinity per kilogram of solution using the original sample mass.

$$8.4 \text{ mL } \text{H}_2\text{SO}_4 \times \frac{0.2 \text{ mole } \text{H}_2\text{SO}_4}{1000 \text{ mL}} \times \frac{1 \text{ mole Alk}}{1 \text{ mole } \text{H}_2\text{SO}_4} = 0.00168 \text{ mole Alk}$$

$$\frac{0.00168 \text{ mole Alk}}{0.2 \text{ g soln}} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 8.4 \frac{\text{mole Alk}}{\text{kg soln}}$$

In the instance of an undegraded PZ sample, for instance those used for physical property measurements, the PZ concentration can be calculated as well if the CO_2 loading of the sample is known. Starting with the calculation demonstrated above for total alkalinity, the PZ concentration can be calculated in units of either mole PZ per kg of solution or molal. The first calculation is direct using the two amino functions in the PZ molecule.

$$\frac{0.00168 \text{ mole Alk}}{0.2 \text{ g soln}} \times \frac{1 \text{ mole PZ}}{1 \text{ mole Alk}} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 4.2 \frac{\text{mole PZ}}{\text{kg soln}}$$

To calculate the concentration in molal, the CO₂ loading must be known or estimated. When the CO₂ concentration is measured (see Section 3.1.3), the units first calculated are moles of CO₂ per kg of solution. Therefore, the CO₂ loading can be calculated directly using this value and the value calculated above for the PZ concentration.

$$\text{CO}_2 \text{ Loading} = \frac{\frac{\text{mole CO}_2}{\text{kg soln}}}{\frac{\text{mole PZ}}{\text{kg soln}} \times \frac{2 \text{ mole Alk}}{\text{mole PZ}}} = \frac{\text{mole CO}_2}{\text{mole Alk}}$$

This calculation procedure avoids the need to assume either a PZ concentration or CO₂ concentration when analyzing either set of data. Once the CO₂ concentration is calculated as a loading (units of mole CO₂ per mole alkalinity), this value can be used in the calculation of PZ concentration in molality. Continuing the example given above with an additional assumption of a CO₂ loading of 0.3 mole CO₂ per mole alkalinity, the concentration of CO₂ in the sample is then calculated in terms of the amount of water in the sample.

$$\frac{0.3 \text{ mole CO}_2}{\text{mole Alk}} \times \frac{2 \text{ mole Alk}}{\text{mole PZ}} \times \frac{8 \text{ mole PZ}}{\text{kg H}_2\text{O}} \times \frac{44.01 \text{ g CO}_2}{\text{mole CO}_2} = 211.2 \frac{\text{g CO}_2}{\text{kg H}_2\text{O}}$$

Next, the mass of CO₂ in the sample is calculated by using the sample mass and the mass fraction of CO₂ in the sample. The mass fraction is calculated by assuming a basis of 1 kg of water and a nominal PZ concentration.

$$0.2 \text{ g sample} \times \left[\frac{\left(\frac{211.2 \text{ g CO}_2}{\text{kg H}_2\text{O}} \right)}{\frac{211.2 \text{ g CO}_2}{\text{kg H}_2\text{O}} + \left(\frac{8 \text{ mole PZ}}{\text{kg H}_2\text{O}} \times \frac{86.14 \text{ g PZ}}{\text{mole PZ}} \right) + \frac{1000 \text{ g H}_2\text{O}}{\text{kg H}_2\text{O}}} \right] = 0.0222 \text{ g CO}_2$$

The mass of water in the original sample can be determined by subtracting the amount of PZ and CO₂ in the original sample. First, the mass of PZ is calculated by assuming all the alkalinity is PZ.

$$8.4 \text{ mL H}_2\text{SO}_4 \times \frac{0.2 \text{ mole H}_2\text{SO}_4}{1000 \text{ mL}} \times \frac{1 \text{ mole Alk}}{1 \text{ mole H}_2\text{SO}_4} \times \frac{1 \text{ mole PZ}}{2 \text{ mole Alk}} \times \frac{86.14 \text{ g PZ}}{1 \text{ mole PZ}} = 0.0724 \text{ g PZ}$$

$$(0.2 \text{ g sample}) - (0.0222 \text{ g CO}_2) - (0.0724 \text{ g PZ}) = 0.1052 \text{ g H}_2\text{O}$$

Finally, the CO₂-free molality of PZ can be calculated:

$$\frac{0.00084 \text{ mole PZ}}{0.1054 \text{ g H}_2\text{O}} \times \frac{1000 \text{ g H}_2\text{O}}{\text{kg H}_2\text{O}} = 7.969 \text{ m PZ}$$

Using this calculation procedure, the concentration of a single amine can be determined in terms of molality directly from a simple and quick titration procedure.

3.1.3 Total Inorganic Carbon (TIC) measurement

The concentration of CO₂ in amine solutions was determined by the measurement of the total inorganic carbon present in the sample as developed previously (Critchfield, 1988; Hilliard, 2008; Lee, 1986). A schematic of the TIC apparatus is shown in Figure 3.3. The apparatus consists of a rotameter type gas flow meter, glass injection tube with injection port and frit, two glass cylinders used as desiccant tubes, CO₂ detector, and a computer. CO₂ loading throughout this thesis is reported in units of moles CO₂ per mole alkalinity. This unit is defined for amine alkalinity, or equivalence of amine, based on the number of amino functions on the parent amine and is used for convenience in the field of CO₂ capture. This definition is not based on an alkalinity result from a titration procedure

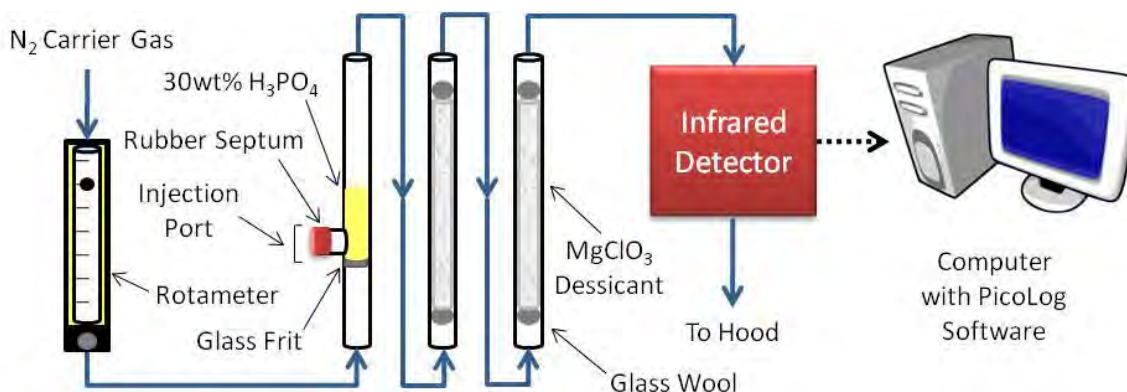


Figure 3.3: Schematic of Total Inorganic Carbon (TIC) apparatus

To set up the apparatus for use, two $\frac{3}{8}$ inch diameter glass tubes were first filled with magnesium perchlorate ($MgClO_4$) desiccant. To fill the tubes, a small ball of glass wool was placed approximately one-half inch from one end of the tube. Large pieces of desiccant were added to the tube to fill the tube until one-half inch from the other end of the tube. Another piece of glass wool was placed at the top of the tube to securely hold the desiccant in place. A new septum was placed on the injector port for each new analysis. Using a 3 mL syringe, 1 to 1.5 mL of phosphoric acid (H_3PO_4) was injected through the septum to fill the injection chamber. The nitrogen (N_2) gas was then turned on at the source and the rotameter was adjusted to achieve the desired flow rate. Usually the rotameter was maintained at a reading of 12 or 13. The rotameter was periodically checked throughout the measurements to ensure that the N_2 flow was maintained.

To begin the analysis, the samples were first gravimetrically diluted 10, 50, or 100X, depending on the expected concentration of CO_2 . The dilute sample was injected into the injection port on the side of the first glass tube using a syringe pressed through the septum. This injection tube had a glass frit below the injection port that allows the carrier N_2 to pass through the frit, through the acid, and up the tube but did not allow the

acid to fall through. The injected sample entered the system in the pool of acid and was quickly acidified. This acidification released all of the CO₂ present in solution.

The released CO₂ entered the N₂ carrier gas stream that traveled through the two desiccant tubes before finally reaching the Horiba PIR 200 infrared detector (Horiba, Irvine, CA, USA). The resulting change in voltage detected by the infrared detector produces peaks that were recorded with PicoLog software (Pico Technology, Cambridgeshire, United Kingdom). The infrared detector is very sensitive to any water vapor that reaches it, so two tubes of desiccant were always used. The first tube was replaced for every run while the second tube was replaced less often, approximately every 5 to 7 runs or as needed. Not shown in Figure 3.3 is a stand that supports the three tubes on a metal plate with tube holders where the tubes can snap into place. An airtight seal is maintained with Swagelok® ultra-torr vacuum fittings (Arthur Fluids System Technologies, a Swagelok® Distributor, Austin, TX).

A calibration curve was prepared at the end of each analysis using a 1000 ppm standard inorganic carbon solution, which was a mixture of K₂CO₃ and KHCO₃ (Ricca Chemical Company, Arlington, TX). The TIC method quantified the CO₂, carbonate (CO₃²⁻), bicarbonate (HCO₃⁻), and carbamate (PZCOO⁻, PZ(COO⁻)₂, etc.) species present in solution. These species are in equilibrium in the series of reactions shown in equation 3.9 below.



Acidification shifted the equilibrium toward CO₂ which bubbles out of solution and was detected in the analyzer. CO₂ loading is reported throughout this thesis as moles of CO₂ per mole of alkalinity or moles of CO₂ per equivalence of PZ, where there are two moles of alkalinity per mole PZ.

At the end of a run, the N₂ flow was turned off at the rotameter and the source. The data recorded by PicoLog, a set of time versus voltage data, were exported to excel and saved. The first desiccant tube was removed from the apparatus and emptied. If the second desiccant tube was not wet, it remained in the apparatus for the next user. The acid in the injection port was removed using the 3 mL syringe and placed in the appropriate acid waste container. The injection port and first desiccant tube were then washed with distilled water.

In order to calculate CO₂ concentration, the areas of each peak were first calculated for the samples and the calibration peaks using trapezoidal rule integration. The area of the peaks, rather than the height or another characteristic, was used to compare samples to the calibration curve. A calibration curve was produced plotting the peak area (independent variable) versus the moles of CO₂ (dependent variable) in each calibration injection. The mass of each injection was used to calculate the moles of CO₂ from the 1000 ppm standard. The peak areas of the standards were then compared to the calibration curve to produce a value for the moles of CO₂ in each sample peak. Using the injection mass of the sample and the dilution factor, a CO₂ concentration was calculated as follows.

$$\frac{\text{mole CO}_2}{\text{g injection}} \times \underbrace{\frac{\text{g sample} + \text{g H}_2\text{O}}{\text{g sample}}}_{\text{DilutionFactor}} \times \frac{1000 \text{ g H}_2\text{O}}{\text{kg H}_2\text{O}} = \frac{\text{mole CO}_2}{\text{kg sample}}$$

If the same sample was titrated for total alkalinity, the CO₂ loading can be calculated directly with this CO₂ concentration value without the assumption of PZ concentration. From the PZ titration, the PZ concentration represented by alkalinity in units of moles of PZ (alkalinity) per kg sample can be easily calculated for a neat, non-degraded solution. This procedure would not be appropriate for degraded samples where

the titrated alkalinity represents changes to the solution and is not related to the PZ concentration after the first sample. Then, this value can be combined with the TIC result above to directly and accurately calculate the CO₂ loading.

$$\alpha = \frac{\overbrace{\left(\frac{\text{mole CO}_2}{\text{kg sample}} \right)}^{\text{Directly from TIC}}}{\underbrace{\left(\frac{\text{mole PZ}}{\text{kg sample}} \right)}_{\text{Directly from titration}} \times \left(\frac{2 \text{ mole Alk}}{1 \text{ mole PZ}} \right)} = \frac{\text{mole CO}_2}{\text{mole Alk}}$$

If the total alkalinity is known for a degraded sample, that result can also be used directly to calculate CO₂ loading. In this case, the number is direct from the amount of acid added to the titration without a conversion to PZ units. Loading can be calculated in the following case in that instance.

$$\alpha = \frac{\overbrace{\left(\frac{\text{mole CO}_2}{\text{kg sample}} \right)}^{\text{Directly from TIC}}}{\underbrace{\left(\frac{\text{mole Alk}}{\text{kg sample}} \right)}_{\text{Directly from titration}}} = \frac{\text{mole CO}_2}{\text{mole Alk}}$$

This direct calculation is the most accurate way to calculate the CO₂ loading. With this value, the titration results can then be interpreted with an accurate value for CO₂ loading to calculate amine concentration (See section 3.1.2).

Alternatively, the CO₂ loading can be calculated another way that involves assuming a PZ concentration if it is not known. The calculation uses the moles of CO₂ per kg of sample calculated above as the starting point. The overall calculation has this form below using the mass of total solution (TS) and mass of CO₂-free solution (CFS):

$$\alpha [=] \frac{\text{mole CO}_2}{\text{mole Alk}} = \frac{\text{mole CO}_2}{\text{kg TS}} \times \frac{\text{g TS}}{\text{g CFS}} \times \frac{\text{g CFS}}{\text{g H}_2\text{O}} \times \frac{\text{kg H}_2\text{O}}{\text{mole Alk}}$$

The two conversion factors are then based on a basis of 1000 g of TS or 1000 g of water:

$$\frac{\text{g TS}}{\text{g CFS}} = \frac{\text{g TS}}{(\text{g TS} - \text{g CO}_2)} = \frac{\text{g TS}}{\left(\text{g TS} - 2.5 \text{ mole CO}_2 \times \frac{44.01 \text{ g CO}_2}{1 \text{ mole CO}_2} \right)}$$

$$\frac{\text{g CFS}}{\text{g H}_2\text{O}} = \frac{\text{g H}_2\text{O} + \text{g PZ}}{\text{g H}_2\text{O}} = \frac{\left(1000 \text{ g H}_2\text{O} + 8 \text{ mole PZ} \times \frac{86.14 \text{ g PZ}}{1 \text{ mole PZ}} \right)}{\text{g H}_2\text{O}}$$

The last piece is the use of the PZ concentration to convert kg of H₂O to mole of alkalinity. The whole equation then looks like the following:

$$\alpha = \frac{2.5 \text{ mole CO}_2}{\text{kg TS}} \times \frac{\text{g TS}}{\left(\text{g TS} - 2.5 \text{ mole CO}_2 \times \frac{44.01 \text{ g CO}_2}{1 \text{ mole CO}_2} \right)}$$

$$\times \frac{\left(1000 \text{ g H}_2\text{O} + 8 \text{ mole PZ} \times \frac{86.14 \text{ g PZ}}{1 \text{ mole PZ}} \right)}{\text{g H}_2\text{O}} \times \frac{\text{kg H}_2\text{O}}{8 \text{ mole PZ}} \times \frac{1 \text{ mole PZ}}{2 \text{ mole Alk}}$$

The result is loading in terms of moles CO₂ per mole alkalinity.

$$\alpha = \frac{\text{mole CO}_2}{\text{mole alkalinity}}$$

If you have a blend of two amines, the following changes can be made to incorporate that second amine, A2. The concentration, molecular weight, and number of alkaline groups of A2 are represented by C, MW, and N, respectively.

$$\alpha = \frac{2.5 \text{ mole CO}_2}{\text{kg TS}} \times \frac{\text{g TS}}{\left(\text{g TS} - 2.5 \text{ mole CO}_2 \times \frac{44.01 \text{ g CO}_2}{1 \text{ mole CO}_2} \right)} \\ \times \frac{\left(1000 \text{ g H}_2\text{O} + 8 \text{ mole PZ} \times \frac{86.14 \text{ g PZ}}{1 \text{ mole PZ}} + C \text{ mole A2} \times \frac{\text{MW g}}{1 \text{ mole A2}} \right)}{\text{g H}_2\text{O}} \\ \times \left(\frac{\text{kg H}_2\text{O}}{8 \text{ mole PZ}} \times \frac{1 \text{ mole PZ}}{2 \text{ mole Alk}} + \frac{\text{kg H}_2\text{O}}{C \text{ mole A2}} \times \frac{1 \text{ mole A2}}{N \text{ mole Alk}} \right)$$

3.1.4 Anion Ion Chromatography (IC)

Anion IC was used to quantify negatively charged ions (anions) in solution as previously (Sexton, 2008). The types of molecules quantified include carboxylate ions (formate, acetate, glycolate, and oxalate), nitrogen containing anions (nitrite and nitrate), and tracers (sulfate and chloride). The chemical structures of molecules quantified using anion IC are shown in Figure 3.4.

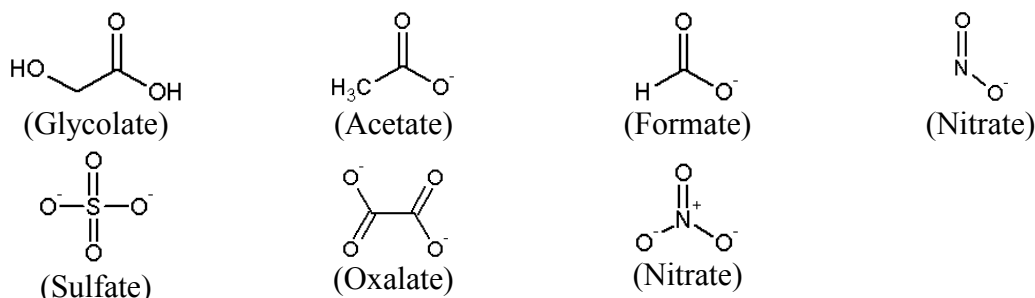


Figure 3.4: Chemical structures of molecules quantified with anion IC

3.1.4.1 Apparatus description

A Dionex ICS-3000 modular Dual RFIC Ion Chromatography System with AS autosampler is used (Dionex Corporation, Sunnyvale, CA). The eluent contains varying concentrations of KOH in analytical grade water. The separation occurred using an IonPac AG15 guard column (4 x 50 mm) and an IonPac AS15 analytical column (4 x 250

mm). Both columns contained ethylvinylbenzene cross-linked with 55% divinylbenzene resin affixed with quaternary ammonium groups as the primary separation medium. The system contained a 4-mm Anionic Self-Regenerating Suppressor (ASRS) to remove cationic species before anionic species were detected with the conductivity cell. Two carbonate removal devices were in place to remove excess carbonate species from the samples (Continuously Regenerated Anion Trap Column – CR-ATC) and the analytical water (Carbonate Removal Device – CRD). Chromeleon[®] software analyzed the conductivity output and controlled the entire system. The overall flow schematic of the anion IC is shown below in Figure 3.5.

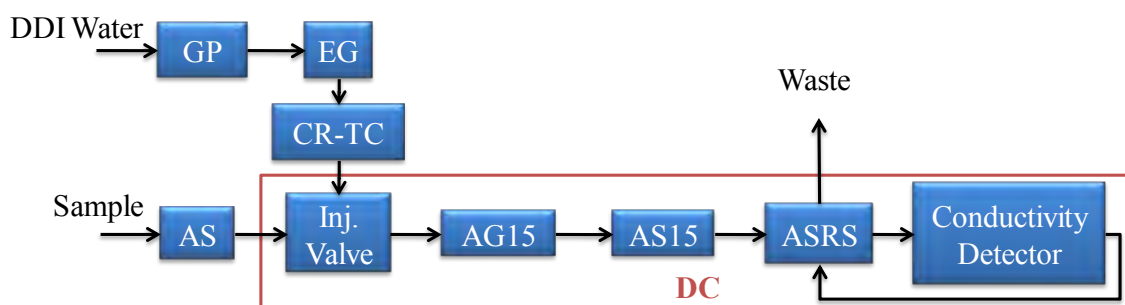


Figure 3.5: Flow schematic for the anion IC showing the AS autosampler, injection valve, AG15 guard column, AS15 analytical column, ASRS, EG eluent generator, CR-TC, DC detector compartment, and conductivity detector.

3.1.4.2 Analysis procedure

The Dionex ICS-3000 system was a dual system with two separate pumps, columns, eluents, and detectors using a common AS autosampler that holds 100 samples. The ICS-3000 system fully controlled the AS autosampler and samples in any position can be accessed by either chromatography system. The standard set-up for the ICS-3000 was to have anion IC operating in parallel with an amino acid detection method.

In Chromeleon[®], a sequence was made to direct the anion IC to analyze the samples of interest. A sequence contained all the information needed for the anion IC to

determine which method to use and how much to inject of each sample. The sequence also contained an identifying name of each sample and the quantification method to be used afterward to analyze the resulting chromatogram. Sequences were generally set up with standards first and then the unknown samples with DDI placed between varying groups of samples to eliminate any cross-contamination of samples.

The flow path through the anion IC began with the samples in the autosampler. The arm of the autosampler flushed the injection needle with DDI water and then moved to the sample. The needle withdrew a small amount of sample and moved to the injection port. The sample was injected and sent through a 25 μL injection loop and then on to the ASRS suppressor. In the suppressor, the sample was passed through a channel with two membranes on opposites of the chamber, as shown in Figure 3.6 (Dionex Corporation, 2007). One membrane separated the flow path from the cathode chamber and the other from the anode chamber. In this type of suppressor, the anode membrane allowed hydronium ion (H_3O^+) from the anode chamber to enter the flow stream in order to neutralize the hydroxide present in the flow stream from the eluent KOH. At the same time, cations in the flow stream, including the potassium portion of the eluent KOH, were attracted to the cathode chamber by the electric potential applied and travel through the cathode membrane in the chamber in order to maintain electroneutrality with the H_3O^+ entering the flow stream from the anode. The result was a flow stream exiting the suppressor with only anions, which were the molecules of interest, and water formed from H_3O^+ and OH^- from KOH.

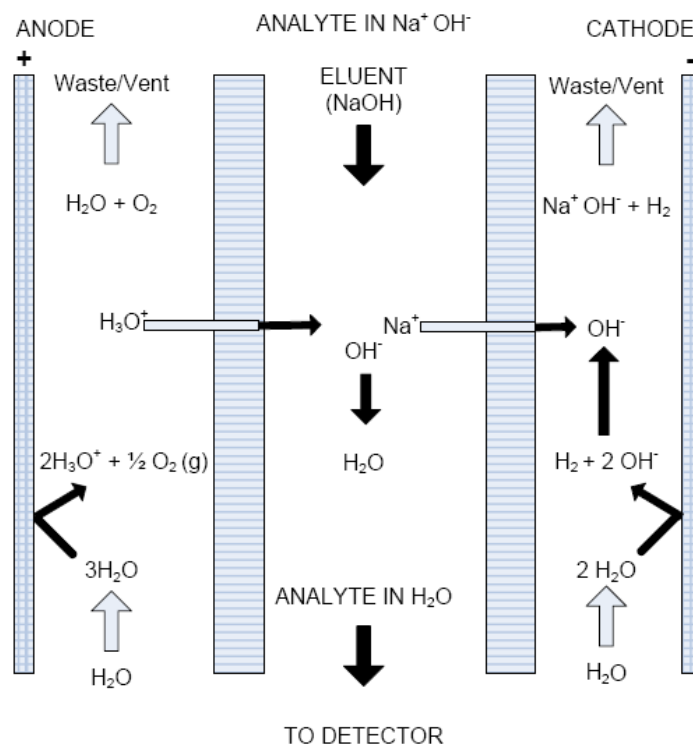


Figure 3.6: Schematic of ASRS 300 in auto-suppression mode (Source: (Dionex Corporation, 2007))

The stream exiting the suppressor was then sent through the IonPac AG15 guard column and the IonPac AS15 analytical column. The guard column was used to prevent sample contaminants from eluting onto the analytical column which would affect separation of the compounds of interest. The analytical column was where the primary separation of compounds occurs. Molecules attached to the cross-linked column internals and detached based on their adhesion properties. As the concentration of acid increased through the program, more difficult molecules to elute detached from the column internals and flowed to the detector. This difference in adhesion to the column internals was the reason for the concentration gradient in KOH. After exiting the analytical column, the flow entered the ECD. Changes in solution conductivity were detected in the

ECD and are recorded in time to create a chromatogram. As a group of anions in solution reached the detector, peaks were formed representing that specific species.

A method was used to control the various components of the system as well as adjusting the eluent gradient and setting the overall time for analysis. The primary method used for anion IC analysis was entitled “Anions.pgm”. In this program, various constraints and settings were used, as shown in Table 3.3.

Table 3.3: Settings and constraints for the anion IC

Setting	Value	Units
Pressure.LowerLimit	200	Psi
Pressure.UpperLimit	3000	Psi
CellHeater	35	°C
Column_TC	30	°C
Compartment_TC	30	°C
Suppressor_Type	CSRS_4mm	-
Suppressor_Current	179	mA
Flow	1.6	mL/min

In this method, there were six minutes before each sample, indicated as negative time, which allowed the system to equilibrate to a lower KOH concentration after completion of the previous sample in preparation of the current sample. At negative six minutes, the flow rate was set at 1.6 mL/min with a 0.1 min window to decrease the concentration from 45 mM to 2 mM of KOH in preparation for the new sample. At time zero, the sample was injected and data acquisition from the electrochemical detector (ECD) was turned on. The eluent concentration remains 2 mM KOH until minute seventeen where a gradient began and increased the concentration to 45 mM by 25 minutes. The concentration then remained at 45 mM KOH until the end of the run at 35 minutes. The KOH concentration over the course of “Anions.pgm” is shown in Figure 3.7. Every analytical sample in this dissertation was analyzed using this “Anions.pgm” unless otherwise indicated. At the end of each run of samples, there was a final sample

with the “Shutdown.pgm” method. In this method, the suppressor and detector were turned off at time zero. Also, the pump flow rate was decreased to 0.2 mL/min at time zero to allow the machine to remain idle until the next time it was used.

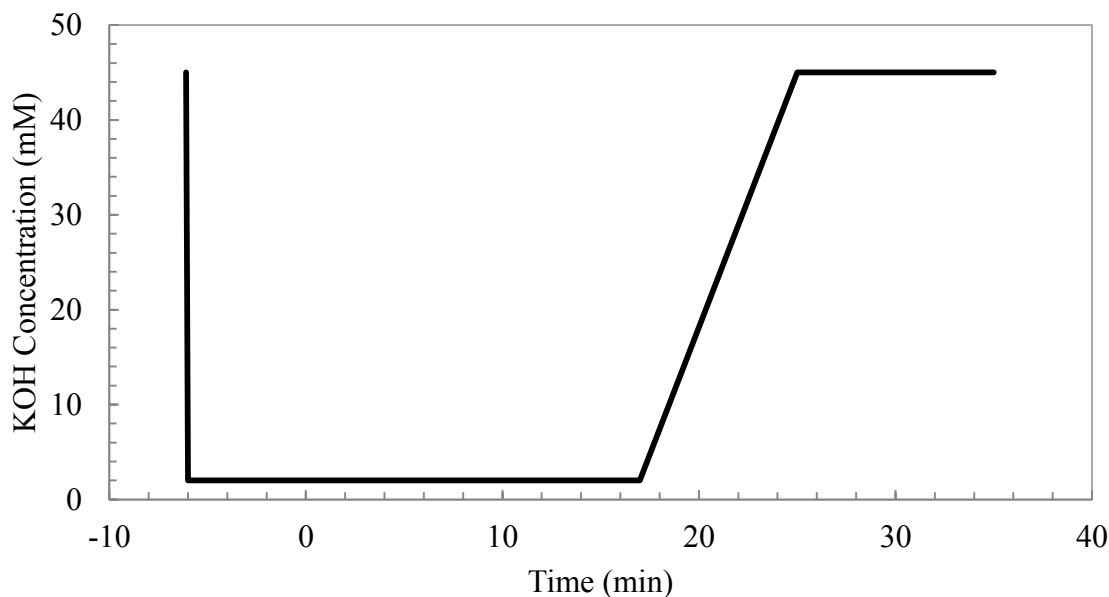


Figure 3.7: KOH gradient in anion IC method

A typical chromatogram for anion IC analysis of a thermally degraded PZ sample is shown in Figure 3.8 (TE44, $t=5$). A dominant formate peak can be seen at a retention time of 20.2 minutes while smaller carbonate and sulfate peaks can be seen at 25.6 and 26.9, respectively. Other peaks such as glycolate, acetate, chloride, and oxalate are not visible with this zoomed out view. Calibration curves were created in order to quantify the concentrations of species in the original sample. At least four or five calibration standards were analyzed for each anion of interest. Usually, standards were created in the range of 1 to 50 ppm for anions that are expected in low concentration such as formate, acetate, and others. The calibration curves used were always at least three different concentration standards and a quadratic regression was used to create the curve. The

calibration and quantification was performed using the quantification wizard in the Chromeleon[®] software. The output at the end of analysis was a ppm concentration of each analyte in the dilute sample. This ppm concentration was adjusted using the dilution factor and then converted to mmole per kg for reporting.

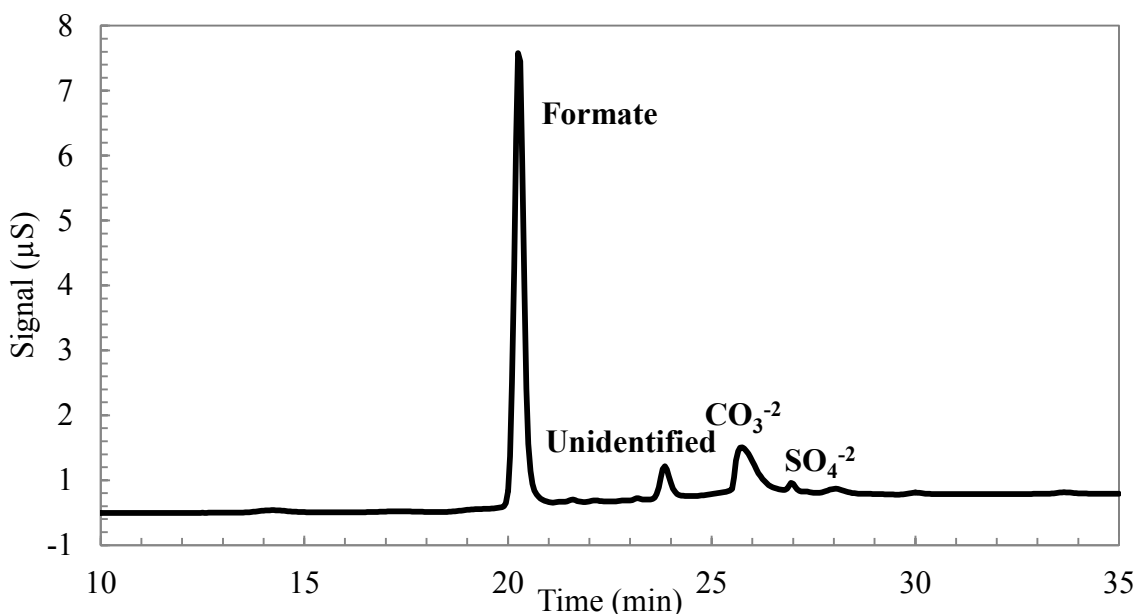


Figure 3.8: Typical anion IC chromatogram for thermally degraded PZ sample

3.1.4.3 Limitations and expected error

There was opportunity for error throughout the ICS-3000 system. The primary avenue for error being introduced into the results was through a high or unsteady baseline. When the baseline was high or had a large bulge in it, all the peak areas calculated were suspect because their areas were decreased from what they would normally be with good separation and a low baseline. This happened occasionally with the anion IC and the source of a bulge in the baseline was usually not clear. In theory, the detector should produce an additive signal where the effect of an anion on top of the

bulge was not decreased, but the size of the bulge in comparison with most anion signals makes this assumption likely not very accurate.

Error was likely introduced in the generation of the calibration curves. Standards of the anions of interest were created through serial dilution and there was always the possibility of error in this gravimetric procedure. As an estimate of this, a comparison of six calibration curves for formate performed over the course of 3.5 years are compared in Figure 3.9. Using the calibration curves shown in Figure 3.9, the concentration of formate predicted for a peak area of 3.0 $\mu\text{S-min}$ ranges from 25.84 to 35.41 mmole per kg with a standard deviation of 3.35 mmole per kg, or 11% of the average of 29.96 mmole per kg. Though the system itself has undergone many changes during this time including replacing the analytical and guard columns, suppressor, and eluent generator, the relative error in the position of the calibration curves is less than 15%.

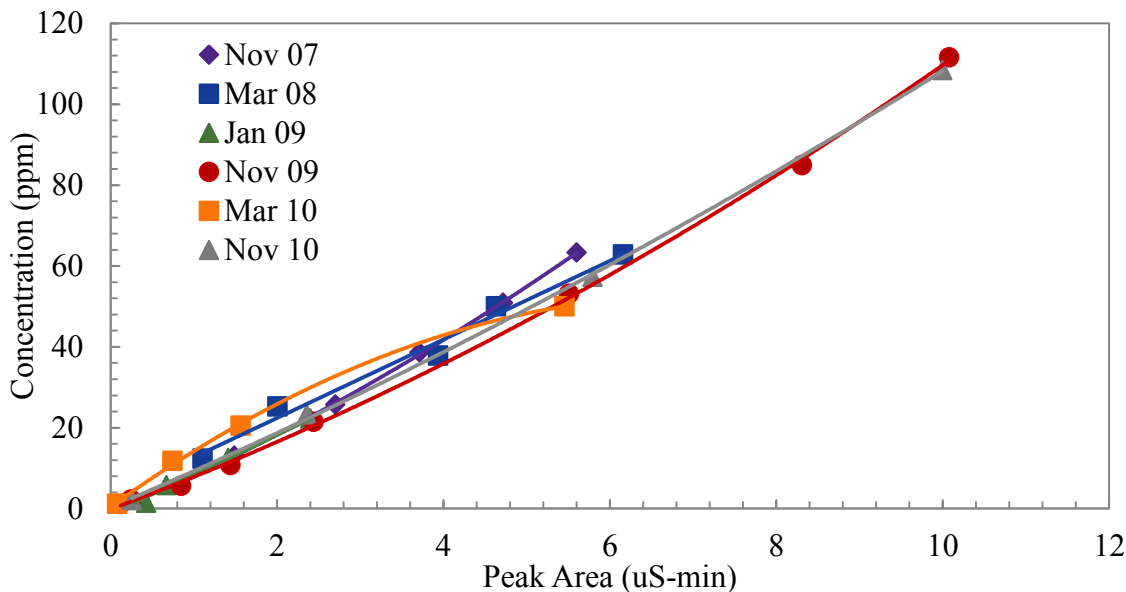


Figure 3.9: Comparison of calibration curves for formate over 3 years of operation

In order to assess the overall error of the anion IC when it is in proper working order, a random sample, the fourth time point of experiment TE51, was analyzed 18 times in a row. The measured concentration and standard deviation are shown for the three dominant peaks, formate, sulfate, and chloride, in Table 3.4 below. All three average deviations are less than 5.0%, indicating acceptable repeatability in the anion IC analysis.

Table 3.4: Assessment of error on anion IC for repeated analysis of one sample

Anion	Average Concentration mmol/kg	Standard Deviation mmol/kg	Average Deviation %
Formate	96.874	1.652	1.71
Chloride	0.103	0.00487	4.74
Sulfate	0.290	0.00368	1.27

3.1.5 Cation Ion Chromatography (IC)

Cation IC was used to identify and quantify positively charged ions (cations) in solution. The types of molecules quantified include simple cations (K^+ or Na^+), amines (PZ, EDA, 1-MPZ, HEP, and others), amides (N-formyl PZ), and polymeric amines (DETA and others). The cation IC procedure developed by Davis served as a basis of the analysis used in this work (Davis, 2009)

3.1.5.1 Apparatus description

Two separate cation IC units were used for this project. An older Dionex ICS-2500 modular Ion Chromatography System with AS-40 autosampler was initially used and then replaced with a new Dionex ICS-2100 modular IC system with AS-DV autosampler (Dionex). The method was maintained between the two instruments and the only real change was the autosampler used. For the remaining discussion, the newer ICS-2100 unit is discussed.

The flow of eluent was generated using a gradient pump that could deliver flow up to a pressure of 3000 psi. The eluent contained varying concentrations of methanesulfonic acid (MSA) in analytical grade water generated by an Eluent Generator (EG). The separation occurred in an IonPac CG17 guard column (4 x 50 mm) and an IonPac CS17 analytical column (4 x 250 mm). Both columns contained ethylvinylbenzene cross-linked with 55% divinylbenzene resin as the primary separation medium. The system also contained a 4-mm Cationic Self-Regenerating Suppressor (CSRS) to remove anionic species before cationic species finally reached the conductivity detector (CD). Chromeleon[®] software analyzed the conductivity output and controlled the entire system. The overall flow schematic of the cation IC is shown below in Figure 3.10.

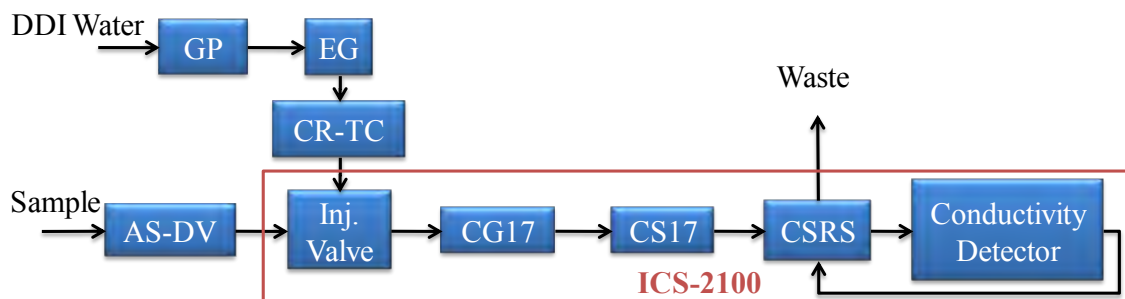


Figure 3.10: Flow schematic for the cation IC showing the AS-DV autosampler, injection valve, CG17 guard column, CS17 analytical column, CSRS, ICS-2100 housing, and conductivity detector.

The cation IC was used to quantify Na⁺, K⁺, NH₄⁺, PZ, EDA, FPZ, 1-MPZ, 1,4-DMPZ, 2-MPZ, 2,5-DMPZ, EPZ, HEP, AEP, Mor, HomoPZ, Pyr, PD, HMI, HMDA, and other amine based degradation products. The molecular structures of the major cations quantified in this dissertation are shown below in Figure 3.11.

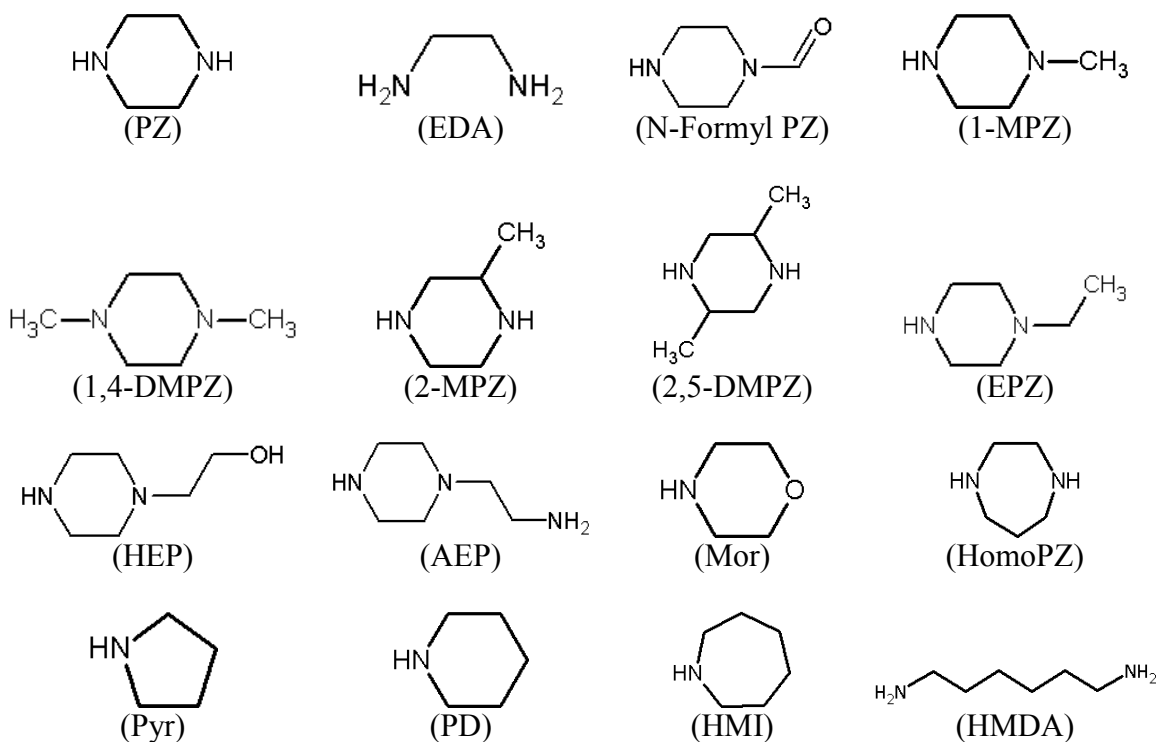


Figure 3.11: Chemical structures of molecules quantified with cation IC

3.1.5.2 Analysis procedure

The Dionex AS-DV autosampler can hold up to 50 samples, allowing high throughput of samples when needed. Samples were loaded into 5 mL sample vials with filter caps and placed into the autosampler. The autosampler was fully integrated with the Chromeleon[®] software and the program was written to inject only 1666 μL , or one-third of the sample volume. In this way, the sample can be injected up to three times, depending on the sequence.

In Chromeleon[®], a sequence was made to direct the cation IC to analyze the samples of interest. A sequence contained all the information needed for the cation IC to know which method to use, the position of the sample in the autosampler, and how much to inject of each sample. The sequence also contained the identifying name of each

sample and the quantification file to be used afterward to analyze the resulting chromatogram. Sequences were set up with standards first and then the unknown samples with DDI placed between varying groups of samples to prevent samples from being contaminated by the previous sample.

The flow path through the cation IC begins with the samples in the autosampler. When the sample was injected, a plunger was lowered onto the top of the sample to press the filter cap downward. This allows the sample to be pushed through the filter cap and into the cation IC system. All 1667 μL of sample are injected into the system from the autosampler even though only 25 μL was injected onto the column. The first portion of the injected sample was sent to waste since it was used to flush out the line between the autosampler and the injection valve. Then, the injection valve used an injection loop to send just 25 μL of the sample to the eluent stream and onto the column. The sample was then sent to the CSRS suppressor. In the suppressor, the sample was passed through a channel with two membranes on opposite sides of the chamber, as shown in Figure 3.12 (Dionex Corporation, 2007). One membrane separated the flow path from the cathode chamber and the other from the anode chamber. In this type of suppressor, the cathode membrane allowed hydroxide from the cathode chamber to enter the flow stream in order to neutralize the proton present in the flow stream from the eluent MSA. At the same time, anions in the flow stream, including the methane sulfonate portion of MSA, were attracted to the anode chamber by the electric potential applied and travel through the anode membrane in the chamber in order to maintain electroneutrality with the hydroxide entering the flow stream. The result was a flow stream with only cations, which are the molecules of interest, and water formed from hydroxide and the proton from MSA.

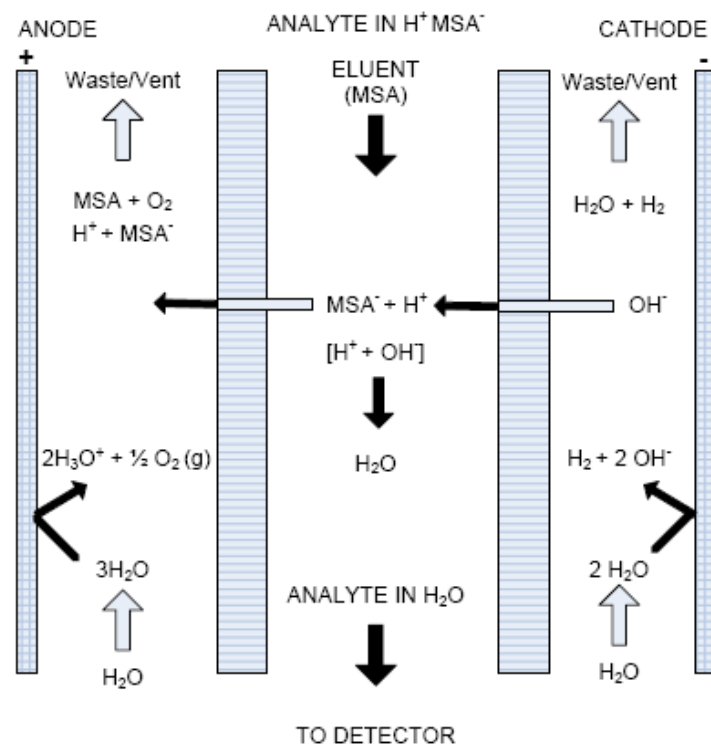


Figure 3.12: Schematic of CSRS 300 in auto-suppression mode (Source: (Dionex Corporation, 2007))

The stream that exited the suppressor was now sent through the IonPac CG17 guard column and an IonPac CS17 analytical column. The guard column was used to prevent sample contaminants from eluting onto the analytical column which would affect separation of the compounds of interest. The analytical column was where the primary separation of compounds occurs. Molecules attach to the cross-linked column internals and detach based on their adhesion properties. As the concentration of acid was increased, more difficult molecules to elute detached from the column internals and flow to the detector. This difference in adhesion to the column internals was the reason for the concentration gradient in MSA. After exiting the analytical column, the flow entered the CD. Changes in solution conductivity were detected in the CD and were recorded in time

to create a chromatogram. As a group of cations in solution reached the detector, peaks were formed representing that specific species.

A method was used to control the various components of the system as well as adjusting the eluent gradient and setting the overall time for analysis. The primary method used for cation IC analysis was entitled “Jason3 Auto”. In this program, various constraints and settings were used, as shown in Table 3.5.

Table 3.5: Settings and constraints for the cation IC

Setting	Value	Units
Pressure.LowerLimit	200	Psi
Pressure.UpperLimit	4000	Psi
Oven_Temperature	40	°C
Suppressor_Type	CSRS_4mm	-
Suppressor_Current	136	mA

In this method, there was three minutes before each sample, indicated as negative time, which allows the system to equilibrate after completion of the previous sample in preparation of the current sample. At negative three minutes, the flow rate was set at 1.2 mL/min with an initial concentration of 5.5 mM MSA in analytical grade water. At time zero, the sample was injected and data acquisition from the CD was turned on. At seven minutes, the gradient increased as a step change to 11 mM MSA. This eluent concentration remains until 12 minutes. Between 12 and 17 minutes, there was a gradient in the eluent concentration raising it from 11 to 38.5 mM MSA where the concentration remains for the rest of the method. The run ended at 20 minutes and the data acquisition was turned off. Each sample was analyzed using this “Jason3Auto.pgm” method unless otherwise indicated. At the end of each run of samples, the final sample was the “Shutdown.pgm” method. In this method, the suppressor and detector were turned off at

time zero. Also, the pump flow rate was decreased to 0.2 mL/min at time zero to allow the machine to remain idle until the next time it is used.

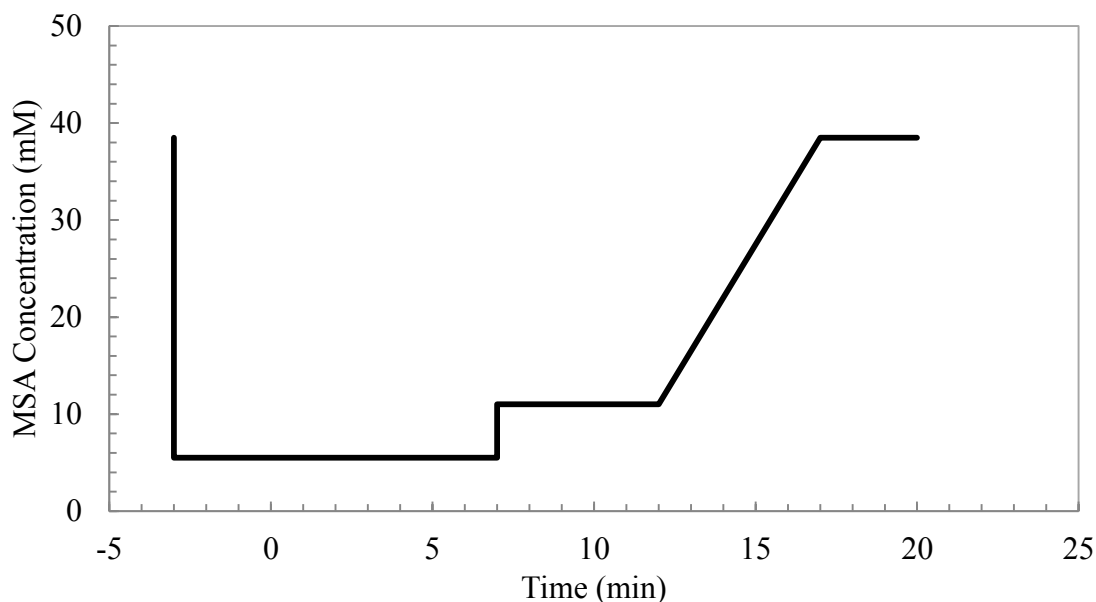


Figure 3.13: MSA gradient in cation IC method

A typical chromatogram for cation IC analysis of a thermally degraded PZ sample is shown in Figure 3.14. A dominant PZ peak can be seen at a retention time of 34.0 minutes while smaller N-formyl PZ, EDA, and AEP peaks can be seen at 15.5, 30.0, and 38.5 minutes, respectively. Calibration curves were created in order to quantify the concentrations of species in the original sample. At least four or five calibration concentrations were made for each cation of interest. Standards were created in the range of 10 to 50 ppm for amines that are expected in high concentration such as the parent amine of the given experiment. For amines that are expected in lower concentration, such as cation degradation products, calibration curves were created in the lower range of 1 to 30 ppm. The calibration curves used were always at least three different concentrations and a quadratic trendline was used. The calibration and quantification

was performed using the quantification wizard in the Chromeleon[®] software. The output at the end of analysis was a ppm concentration of each analyte in the dilute sample. This ppm concentration was adjusted using the dilution factor and then converted to mmole per kg for reporting.

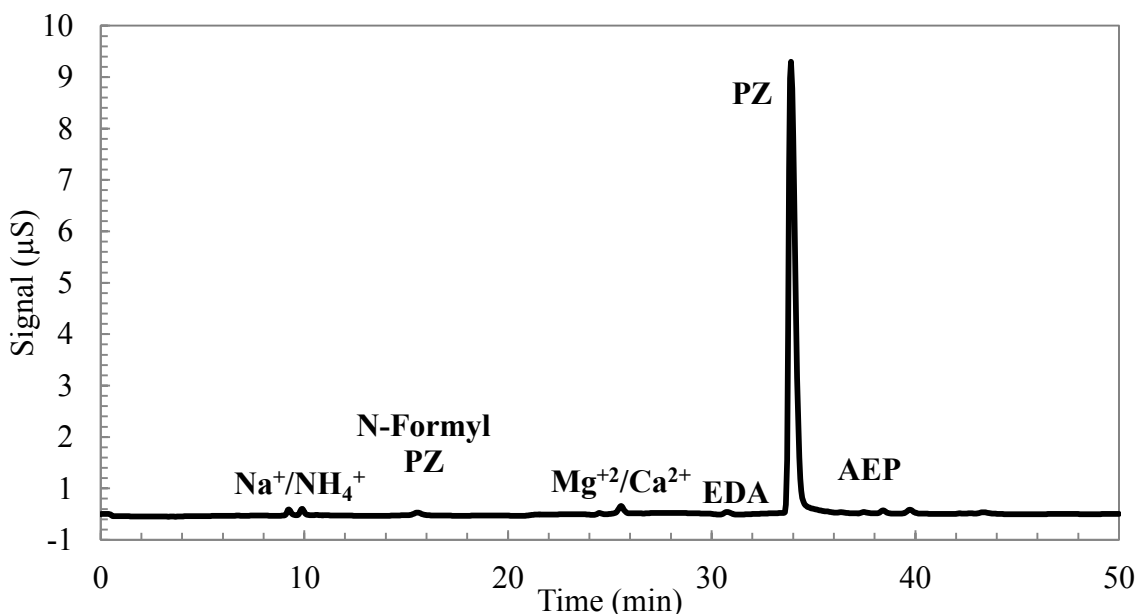


Figure 3.14: Typical cation IC chromatogram for thermally degraded PZ sample

3.1.5.3 Limitations and expected error

The primary limitation of the cation IC was the difficulty of accurately quantifying molecules that are very disparate in concentration. For example, most samples analyzed were 40 wt% in PZ (~4500 mmole per kg PZ) while amine degradation products were generated in the range of 1 to 300 mmole per kg. The large dilution needed to quantify PZ lead to the area of the degradation products being minimized. The separation of compounds was also limited by the applicability of the column, as with all types of chromatography. A CS-17 analytical and CG-17 guard column was used and particular compounds always co-elute. For example, PZ and 2-MPZ were retained

almost identically so samples containing both compounds produced a peak that could not fully resolve both compounds.

Overall, the uncertainty of the cation IC to quantify a compound of interest was less than 5%. There was error associated with every step of the analysis including the dilutions to prepare the sample, the dilutions to prepare the calibration standards, and the operation of the entire cation system that day. Overall, the system was quite accurate, but needs vigilance to ensure that the optimal operation is maintained.

In order to assess the overall error of the cation IC when it is in proper working order, a random sample, the third time point of experiment TE44, was analyzed 10 times in a row. The measured concentration and standard deviation are shown for the three dominant peaks, PZ, EDA, and NH_4^+ , in Table 3.6 below. All of the average deviations are less than 5% with that of EDA and PZ being less than 0.5%, indicating superior repeatability in the cation IC.

Table 3.6: Assessment of error on cation for repeated analysis of one sample

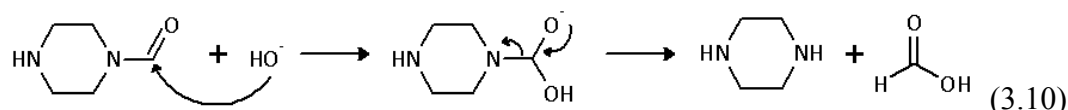
Anion	Average Concentration mmol/kg	Standard Deviation mmol/kg	Average Deviation %
PZ	3799.5	7.9	0.21
EDA	12.06	0.04	0.35
NH4+	3.10	0.14	4.64

3.1.6 Sodium hydroxide treatment for amide quantification

Amides are molecules with a $\text{R}_2\text{N-RC=O}$ functionality. The most basic amide is formamide ($\text{NH}_3\text{-CH=O}$). Amides themselves are not readily detectable with the analytical techniques employed for amines and carboxylic acids. A base hydrolysis was used to hydrolyze the amide to its corresponding carboxylic acid and amine which can be

detected as described below. This procedure was first described by Sexton who based it on the work of Koike and colleagues (Koike et al., 1987; Sexton, 2008).

Brown described how amides can be readily hydrolyzed by either acid or alkali (Brown, 1994). Water in an acidic solution or the hydroxide ion in an alkaline solution acts as a nucleophile to hydrolyze the amine to yield the corresponding carboxylic acid. An example of this hydrolysis is shown below in equation 3.10 for F PZ, a degradation product found in both oxidation and thermal degradation of PZ.



The concentration of total amides was determined by analyzing the hydrolyzed sample for the concentration of carboxylate anions. The increased detected in the carboxylate ions was the approximate concentration of total amides of that form (i.e. formyl amides, acetyl amides, etc.). The corresponding amine liberated from the hydrolysis was not generally used for the calculation of amide concentration because of the difficulty in detecting small changes on the cation IC. For example, an increase of 30 mmole per kg of formate was much easier to detect in a background of 20 mmole per kg of free formate compared to an increase of 30 mmole per kg of PZ in a background of 4000 mmole per kg of PZ. As mentioned in the previous section, the error in the cation IC methods can be assumed to be up to 5%, eliminating the opportunity to accurately detect small amounts of amines liberated from amides through this type of hydrolysis. In some cases where the amide concentration is sufficiently large, the increase in a particular amine was useful for determining the form of the amide originally present.

This hydrolysis was not quantitative in terms of which specific amides are present, but only quantifies the total amides of a particular carboxylic acid. Other

analytical methods are able to detect specific amides but require larger concentrations to be observed above the background in a diluted sample. Cation IC, for example, detected FPZ and gave a well separated peak around a retention time of 15 minutes on the standard “Jason3Auto.pgm” method. However, the dilution used for this technique needs to be at least 5000X, preferably 10000X, to decrease the PZ concentration to quantifiable levels. This requires at least 1-5 mmole per kg or more of FPZ to be present to produce a peak that is significant above the background at this dilution. Only highly degraded samples contain this much amide and so the hydrolysis procedure was used for all samples. Also, this hydrolysis does not take into account the possibility of multiple amide functionalities on one amine molecule. For example, two formate molecules would be liberated from the hydrolysis of N,N'-diformyl PZ. A few possible structures are listed below for PZ and EDA-based amides in Figure 3.15. These are combinations of formate, acetate, oxalate, and glycolate with both PZ and EDA, a common amine degradation product. Many more amides are possible once additional amine degradation products are generated.

The procedure for amide reversal was to treat a sample with an equal amount of 5 N NaOH and to allow the reaction to proceed overnight, at least 12 hours, before further dilution and analysis. Generally, 0.5 g or 1.0 g of each is used and the sample reacts for at least 24 hours. Tests performed on neat mixtures of loaded PZ and N-Formyl PZ showed conversion of amides within 24 hours. Thirty grams of 8 molal (m) PZ with a loading of 0.3 mole CO₂ per mole alkalinity was combined with 100 mM of N-Formyl PZ. Then, 1.0 g of this solution was treated with 1.0 g 5 N NaOH. At various time points, a sample of the treated solution was diluted 50X (to a total dilution of 100X), effectively stopping the amide reversal. The formate released during the amide reversal was then quantified using anion IC. The results are shown below in Figure 3.16. All of

the formate was released within 4 hours during this experiment. The amount of formate recovered was actually over 100% which is attributed to error in the anion IC and sample preparation. It was assumed that the FPZ standard used was not actually pure due to instability and calculations performed assumed only FPZ was present.

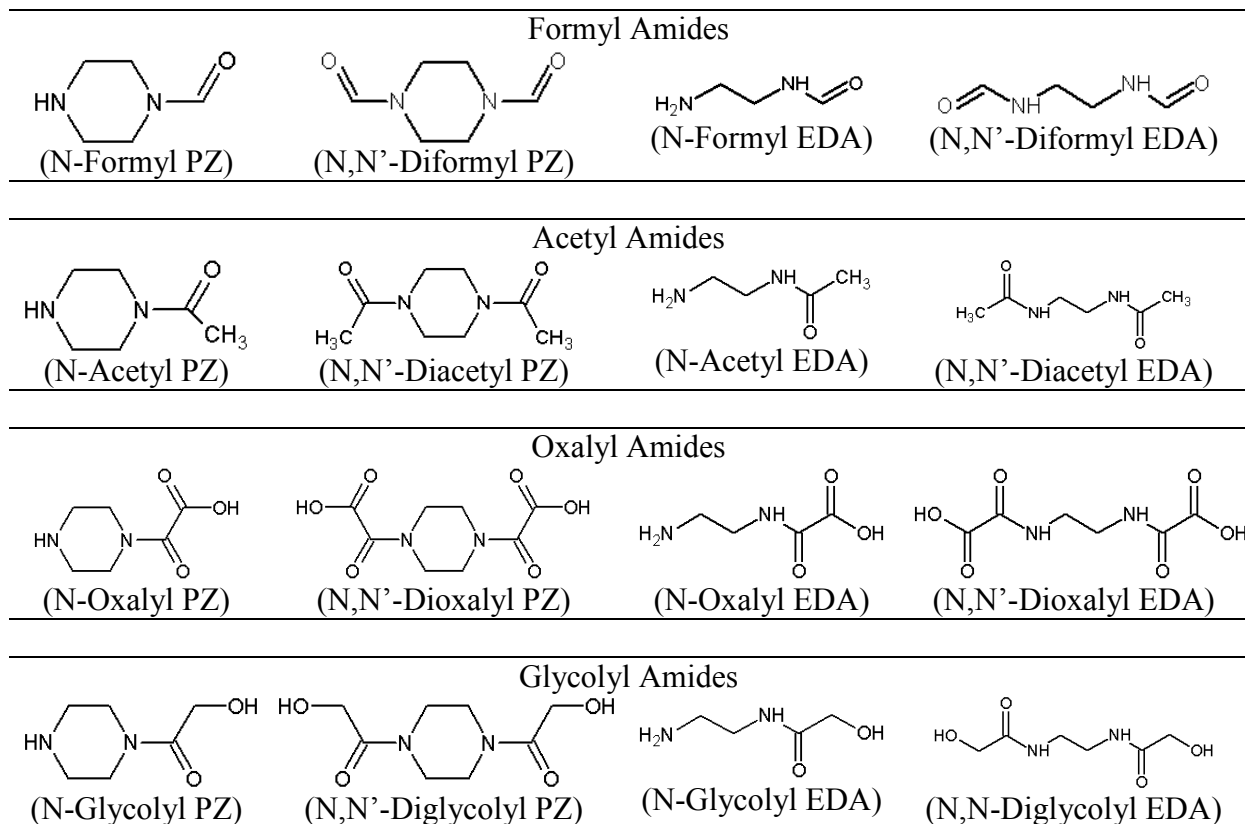


Figure 3.15: Chemical structures of possible amides in degraded solutions

The same procedure was performed on an 8 m PZ solution that was degraded for 360 hours in the Integrated Solvent Degradation Apparatus (ISDA) in order to assess the conversion of acetyl and oxalyl to their corresponding carboxylate ions (Closmann, 2011). This experimental solution was more complex than the previous test and contained a combination of both carboxylate ions (formate, acetate, and oxalate) and

amides (formyl, acetyl, and oxalyl amides) to begin with. Thirty grams of degraded PZ solution was spiked with 200 mmole per kg of FPZ and the release of carboxylate ions was observed through anion IC over the course of 48 hours. The percent of carboxylate ion released during hydrolysis is shown in Figure 3.17. The percent formate released was calculated as the increase of formate after hydrolysis compared to the 200 mmole per kg of FPZ spiked in the tested solution. The percent of acetate and oxalate released was calculated as the increase of each ion compared to the total amount released in hydrolyzed degraded PZ (without the 200 mmole per kg FPZ spike).

The anion IC results showed that the rate of reversal of acetyl and oxalyl amides was significantly slower than formyl amides. After 48 hours of hydrolysis, neither the acetate nor oxalate was fully recovered. Unfortunately, the original protocol for amide reversal only called for a 24-hour hydrolysis. This short treatment time will likely underestimate the total acetate and total oxalate, or acetyl and oxalyl amide concentrations.

3.1.7 Densitometer

3.1.7.1 Apparatus description

Density was measured using a Mettler Toledo DE40 densiometer (Mettler-Toledo, Inc., Columbus, OH). The DE40 had precise temperature control from 4 to 90 °C using a Peltier thermostat. The DE40 measured density from 0 to 3 g/cm³ with an accuracy of 0.0001 g/cm³. Approximately 3 mL of sample was required for each measurement and, in general, it was a destructive assay. The density was measured on neat (non-degraded) solutions due to this volume requirement.

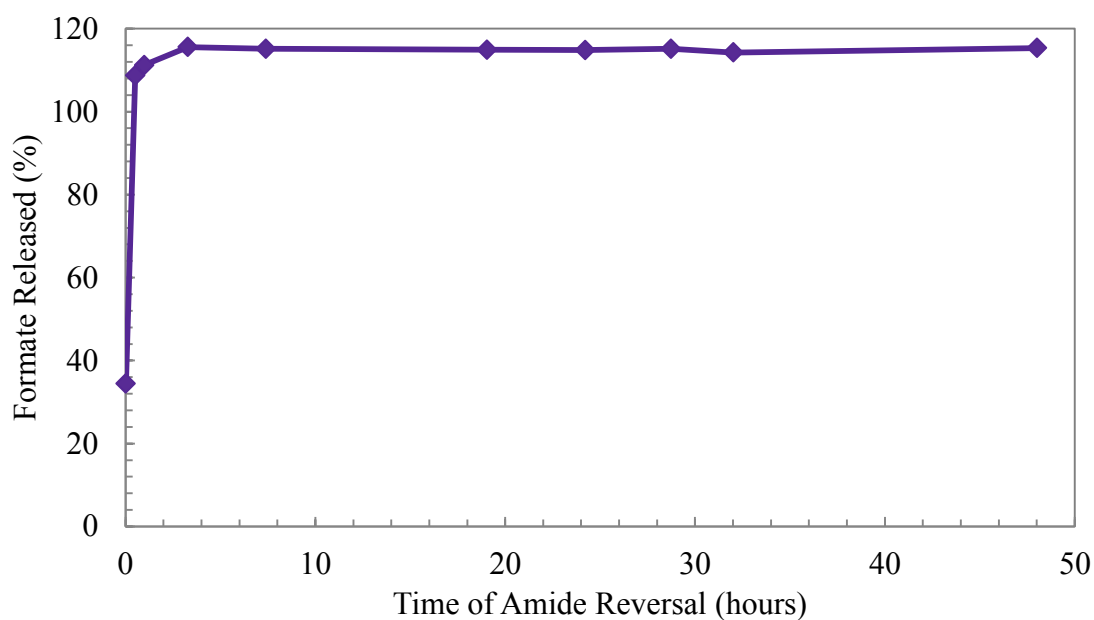


Figure 3.16: Recovery of formate during alkaline hydrolysis

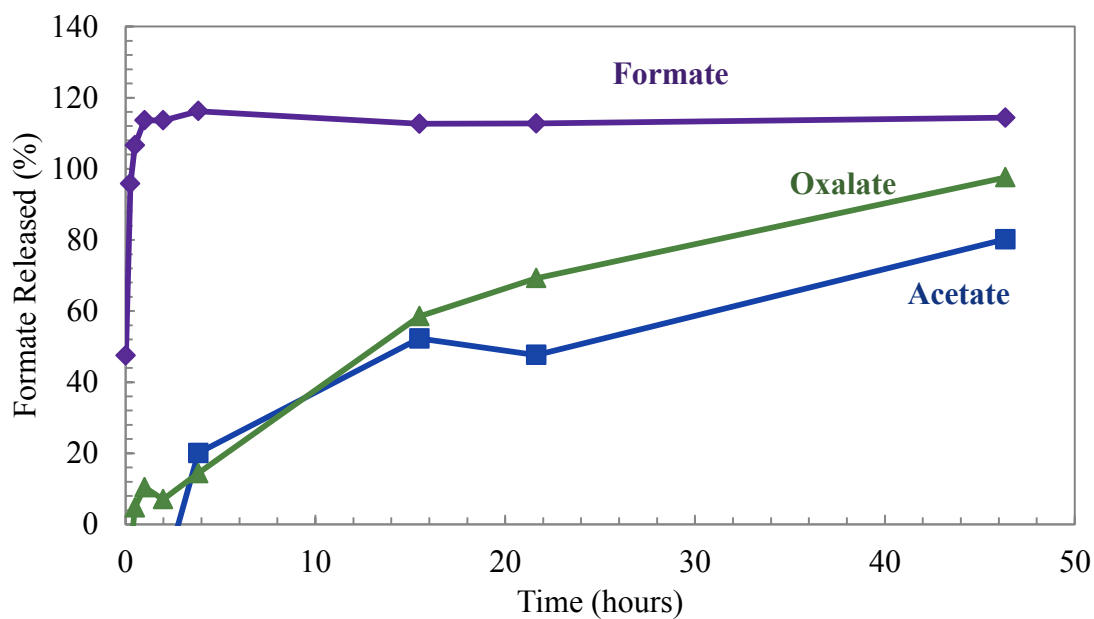


Figure 3.17: Recovery of carboxylate ions during alkaline hydrolysis of a PZ degraded for 360 hours

The DE40 measured the electromagnetically induced oscillation of a glass U-shaped tube to determine the density of a gas or liquid. The gas or liquid sample was pumped into the U-shaped tube that was contained within a thermo-conductive block, thermal insulation, and a Peltier element that maintained the U-tube temperature. A magnet was attached to the middle of the U-tube right next to a combination oscillator and vibration meter. The oscillator induced vibration in the U-tube and the period of oscillation was measured by the sensor. The frequency of oscillations was related to the calibration of air and water at each temperature to understand the characteristic frequency of oscillation of the glass tube itself. The frequency of vibration for samples was related to the mass inside the tube. A larger mass of sample inside of the U-tube would have produced a lower frequency of oscillation and, therefore, a larger the period of oscillation. The density, ρ , is related to the volume of the sample in the U-tube, V_C , the mass of the U-tube, m_C , a cell constant, K , and the period of oscillation, T , through Equation 3.11. Equation 3.11 can be rearranged in terms of ρ (Equation 3.12).

$$T = 2\pi\sqrt{\frac{\rho V_C + m_C}{K}} \quad (3.11)$$

$$\rho = \frac{K}{4\pi^2 V_C} T^2 - \frac{m_C}{V_C} \quad (3.12)$$

The value for K was determined by a two point calibration for dry air and degassed water. This constant was dependent on the type of U-tube used, the U-tube mass, and temperature. The DE40 was calibrated with air and water for each temperature of interest to determine this value of K at each experimental condition.

3.1.7.2 Analysis procedure

To measure density of a solution, the temperature of analysis was first selected by choosing the method. All the methods on the DE40 were the same except for the measurement temperature. The DE40 then needed time to reach the desired temperature and displayed “Ready” when the system was stable. To begin the analysis, the inlet tube was placed below the liquid level of the sample to be analyzed. Then, the green “Measure” button on the front of the DE40 was pressed. This activated the pump which then pulled approximately 5 mL of sample into the sample u-tube. There was excess liquid on each end of the u-tube to ensure a stable sample chamber. The DE40 then measured the density and when a stable density reading was reached, that value was displayed on the screen and the sample was pumped out of the sample tube to waste.

After the analysis of each sample, the u-tube was cleaned using three steps. After a sample was successfully analyzed, the screen on the DE40 displayed the message “Set Rinse 1 and Press Start”. To begin cleaning, the inlet tube was placed below the surface of DDI water and the “Start” button was pressed. Then, the pump speed toggle was immediately pressed upward to increase the pump speed to the “Rinse” setting. This first rinse flushed the sample tube with DDI water at a fast pace to wash away any remaining amine sample. The DE40 automatically stopped at the end of this rinse cycle and the screen displayed the message “Set Rinse 2 and Press Start”. Next, the inlet tube was placed below the surface of a beaker of acetone and the “Start” button was pressed. Then, the pump speed toggle was quickly set to “Rinse” and the inlet tube was lifted in and out of the acetone. This created an intermittent stream of air and acetone for this rinse cycle. When this was complete, the screen displayed the message “Set Air Purge and Press Start”. For the final step, the inlet tube was placed in an empty waste beaker and the “Start” button was pressed. After 10 to 15 seconds, the pump speed toggle was

pressed downward to the “Purge” setting. The “Purge” setting reversed the direction of the pump and drew air through the desiccant on the top of the unit and pumped it through the sample u-tube to remove all moisture. The purge lasted 2 minutes and the DE40 was then ready for another sample.

3.1.7.3 Limitations and expected error

The DE40 densitometer was a very accurate apparatus yielding four decimal places on each density reading. The calibration with air and water at each temperature ensured the measurement accuracy of the system at all times. This calibration, however, must be performed at least once every few months or after long breaks in the use of the DE40 to maintain its performance. The accuracy was only guaranteed if the unit was still correctly reading the density of its standards.

A major limitation of the DE40 for the specific application to CO₂ capture solvents was that the system was at atmospheric pressure. For most amine systems, the partial pressure of CO₂ in loaded solution was significant and atmospheric heating of a solution could release CO₂ from solution. The DE40 required a very stable reading to four decimal places before registering a density measurement. For loaded solutions, this meant that readings could only be taken at temperatures below where CO₂ would bubble out of solution or in regions of lower loading. This was an additional issue with loaded, high concentration PZ solutions where the weight fraction of CO₂ can be upwards of 20% in the rich loading region.

The expected precision of this measurement was 0.0001 gram per cm³, according to the manufacturer. A solution of 8 m PZ with 0.3 mole CO₂ per mole alkalinity has a density of approximately 1.12 gram per cm³, which would make the expected precision

less than 0.01% of the measured value. The error could be maintained at this low level if the density of air and water was verified before each round of measurements.

3.1.8 Rheometer

3.1.8.1 Apparatus description

Viscosity was measured using a Physica MCR 301 cone and plate rheometer (Anton Paar GmbH, Graz, Austria). The apparatus had precise temperature control for measuring viscosity at temperatures ranging from -30 to 150°C through heating or cooling of the cone and plate. The apparatus was also attached to a chiller that cooled the viscometer to maintain a stable performance. The plate at the bottom of the apparatus was at a set height while the cone was attached to an arm which moved vertically up to 150 mm above the plate. A computer with the US200 software package controlled the whole system.

For well-behaved Newtonian fluids in straight, fully developed flow, the shear stress (τ) is proportional to the velocity gradient in the direction perpendicular to the direction of motion ($\partial v / \partial x$). The coefficient of proportionality is defined as the viscosity (μ). This relationship is shown in Equation 3.13.

$$\tau = \mu \frac{\partial v}{\partial x} \quad (3.13)$$

The cone and plate rheometer was used to determine viscosity by measuring the torque applied to the fluid during the rotation of the cone. The liquid sample was placed on the plate and the cone was lowered to within a defined x-distance (0.05 mm) above the plate. The cone was then rotated at specified angular speeds creating variable shear stress in the liquid. The rheometer essentially acted as a precise torque meter that determined the resistance of the fluid to rotation by being situated between the plate and cone. The

measured torque was proportional to the shear stress in the fluid and equation 3.13 was used to determine viscosity using the applied rotation speed. The viscosity was measured 10 times over a range of rotational speeds to get an accurate reading.

3.1.8.2 Analysis procedure

To determine viscosity, the CP-50 cone was first placed into the holder on the upper portion of the viscometer. In the U200 software program, a new data file was created using the “Flow Curve/CSR” option. The viscometer was set-up by choosing the experimental conditions including temperature, angular speed settings, and analysis settings. The settings used were an increase of angular speed from 100 to 1000 s⁻¹ over a period of 100 seconds. The analysis involved measuring the shear stress exerted by the solution 10 times, every 10 seconds.

Once the experimental conditions were chosen, the gear box was used to initialize the instrument. In this box, the temperature was also set to match the temperature set in the “Analysis” window. Once this was done, the plate began to heat or cool to reach the experimental temperature. When the plate reached a stable experimental temperature, the zero gap was established by selecting the “Zero Gap” position for the top cone. The cone then moved down to find the zero gap that calibrates the cone at the temperature. This procedure accounted for any expansion of the bottom plate based on temperature change from the previous zero gap calibration. Then, the cone was lifted by selecting “Lift Position”.

To take a measurement, 700 µL of sample was transferred onto the center of plate. The cone was then set to “Measurement Position” in the gearbox. With this command, the cone was lowered first to a “Trim Position” above the plate where any solution that was pushed outside of the edges cone was removed. When trimming was done, the cone

was finally lowered to the measurement position 0.05 mm above the plate and the measurement began by selecting the “Start Analysis” icon. After the 10 measurements were complete, the data was copied into an Excel spreadsheet. The cone was then raised to “Lift Position” and DDI water was used to clean both the cone and plate surfaces. The next sample was then transferred to the plate and the measurements continued in the same fashion.

3.1.8.3 Limitations and expected error

The Physica MCR 300 rheometer was a very accurate instrument for measuring viscosity. Anton Paar reported that it can control temperature to within 0.01 °C. The overall uncertainty of viscosity measurements was expected to be less than 1.0 %. More error was introduced when measuring the CO₂ and PZ concentrations of the experimental solutions than with the viscosity measurement.

The primary limitation of the rheometer was its inaccuracy at low viscosities. Based on experimental observation, the cone-and-plate arrangement was most accurate for liquids that were at least two to three times more viscous than water (above 2 to 3 cP). At the beginning of most analyses, the viscosity of water was measured and the rheometer consistently underestimated its value when compared to the known value for water (DIPPR, 2010). Fortunately, most amine solutions were quite viscous compared to water having about ten times the viscosity of water at room temperature. This error is apparent though for high temperature measurements when the viscosity of amine solutions was decreased.

3.1.9 Mass spectrometry coupled with Cation IC (IC-MS)

Mass spectrometry (MS) was used to determine the elemental composition of a molecule or sample of interest. In MS, a sample was ionized to create charged particles

in a gas stream. This ionized stream of particles was then subjected to electromagnetic fields that sorted the particles by their mass. A detector then measured the amount of particles of each mass and the result was a spectrum comparing the various charge-to-mass ratios (m/z) compared to the abundance of which each was found in the liquid stream. The m/z was essentially the molecular mass of a molecule plus a proton, divided by its charge of plus one. The m/z was generally just one integer higher than the molecular weight of the molecule of interest, so this technique was useful in the identification of unknown molecules in a liquid mixture. The ionization setting of the apparatus could be changed to identify neutral and positive species by using positive ionization or to detect neutral and negative species by using negative ionization depending on the desired application. When positive ionization was used, a proton was added to each molecule so neutral molecules have a positive charge and positively charged molecules receive an additional charge. Any negative charged species in solution then become neutral and were not detected.

The technique was primarily qualitative in nature and was used in this project to help identify unknown degradation products. The MS could be run using direct injection of samples or coupled with a cation IC, anion IC, or HPLC system where a sample was first separated by an analytical separation column before being analyzed by the MS. In this way, unknown peaks on cation IC, anion IC, or HPLC chromatograms could be identified specifically. This technique was also useful in the case of PZ where the high concentration of PZ can overshadow the lower concentration degradation products in direct injection techniques. In this dissertation, all MS work was cation IC-MS analysis unless otherwise noted. Direct injection analyses were performed as described previously (Davis, 2009).

3.1.9.1 Apparatus description

The IC-MS system consisted of a Dionex ICS-2100 system coupled with a Thermo Finnegan TSQ MS with a triple-stage quadrupole and electro-spray ionization (ESI) (Thermo Fisher Scientific, Waltham, MA). The chromatographic separation followed the procedure described above for cation IC. The eluent exiting the conductivity detector of the ICS-2100 was fed directly to the inlet of the ESI system of the MS. Because of this, the CSRS suppressor was not operated in recycle, or auto-suppression, mode. A N₂ tank delivered 5 psi of pressure on an auxiliary DDI water bottle to feed a slow stream of water to the back of the suppressor membrane to flush waste from the suppressor. The main method used on the cation IC had a flow rate of 0.5 mL/min and a gradient from 5.5 to 38.5 that was 50 minutes long (See appendix C for method details).

3.1.9.2 Analysis procedure

The Xcalibur[®] software was used to control the operation of the MS. Through the DC-MS link, Xcalibur[®] also controlled the Chromeleon[®] timebase of the cation IC. The IC-MS was operated as described previously, with a few modifications (Davis, 2009). A flow splitter was installed between the exit of the conductivity detector of the cation IC and the inlet of the ESI in order to decrease the flow rate of liquid to the MS. Better results were observed when the flow was decreased by approximately half. The valve used to split the flow was a manually controlled valve, so the exact flow rate reaching the MS was not known with precision. Also, the line bringing water from the auxiliary water bottle to the regeneration side, or back side, of the suppressor was run through the valve on the front of the ICS-2000 unit. This valve followed the behavior of the DP pump and was closed when the pump was off and opens when the pump is in use. In this way, the flow to the back of the suppressor was stopped when the system was not in use to prevent

the auxiliary water bottle from emptying and delivering air to the suppressor. The method used was very similar to the original “Jason3Auto.pgm” described above for the cation IC, except the timing was stretched out to accommodate the lower flow rate of 0.5 mL per minute. Details of the method are included in Appendix C. The shutdown method was also modified to turn off the pump at the end of a run, rather than just decreasing the flow rate to 0.2 mL per minute as done previously.

3.1.9.3 Limitations and expected error

A main limitation of the IC-MS system was the inability to distinguish between molecules with the same m/z value. This was a function of the low resolution of this particular MS where it was only possible to measure m/z ratios to the first decimal place. When trying to identify unknown degradation products, the molecular weight was a very important key, but not the entire story. As degradation products increase in size, the possibilities for what the molecules could be grow in number. For example, a peak towards the end of the chromatograms for thermally degraded PZ was identified with a molecular weight of 198 g/mole or an m/z ratio of 199. This molecular weight corresponds to three possible products that were suspected in thermal degradation of PZ, as shown in panel A of Figure 3.18. Although the molecular weights are different at the first decimal place, the MS used in this study did not have low enough resolution to differentiate between the molecules. In another case, panel B of Figure 3.18, the molecules are isomers with exactly the same molecular weight and cannot be differentiated with only MS. Usually, isomers such as these have varying retention times in chromatographic techniques and could be differentiated with retention time matching with known standards. Unfortunately, standards for complicated molecules are not always commercially available, so retention time matching was not easily done.

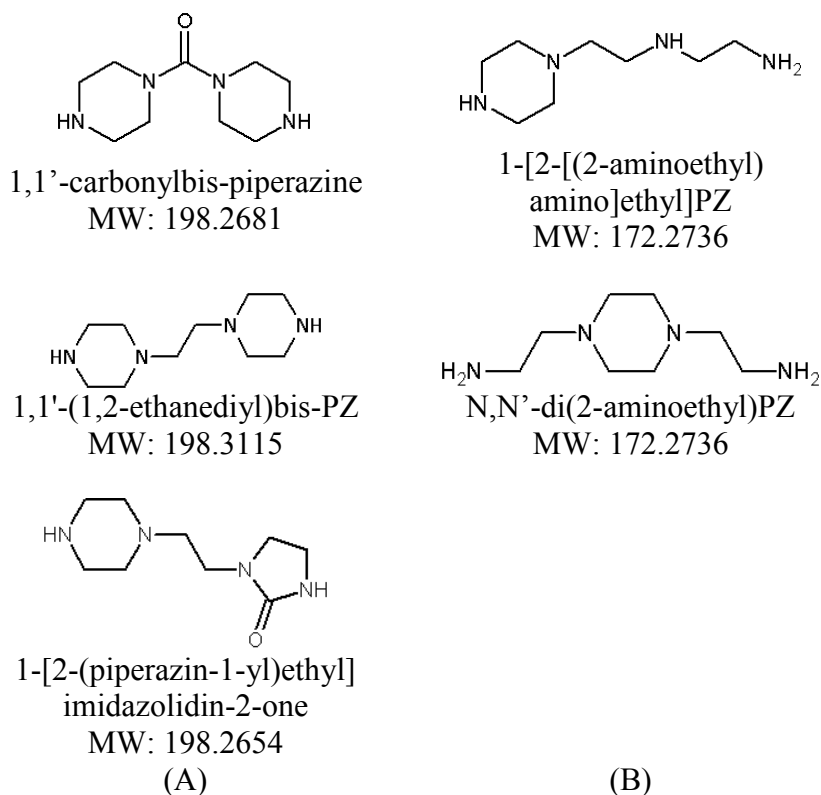


Figure 3.18: Examples of molecules which are difficult to distinguish with IC-MS

Another limitation was the presence of Na^+ and K^+ in our samples. The samples, glassware, and IC-MS systems were all constantly exposed to low levels of Na^+ and K^+ which could act as the ionizer in the ESI process. In this way, the m/z ratio found would have been much higher than if H^+ was the ionizer, as expected. This complicated the interpretation of results when the molecular weight of the parent amine was being determined. In a similar vein, some molecules had a tendency to bunch up and attach multiple molecules to a single H^+ producing a $(2\text{M}+\text{H})^+$ molecule instead of the expected $(\text{M}+\text{H})^+$. Again, this made interpreting results more challenging. Finally, the destructiveness of the type of ionization used was an issue. The ESI was not a gentle ionization technique and could break apart molecules so that fragments were being

analyzed as whole molecules. In general, this was not a large issue as there was still a significant portion of the parent molecule to analyze.

3.1.10 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

3.1.10.1 Apparatus description

Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was a method for measuring the concentration of elements in solution by quantifying the absorbance of a sample over specified wavelengths. A Varian 710-ES Axial ICP-OES (Varian Inc., Palo Alto, CA) was used for this analysis. The ICP-OES was effective at measuring the concentration of multiple analytes (heavy metals and other elements) simultaneously in a single dilution. The system was controlled through ICP Expert II[®] software. An autosampler held all the standards and samples to be run at a given time. When being analyzed, each sample was pumped to the glass, concentric spray chamber, or nebulizer, where an argon stream nebulized the sample to be sent directly to the plasma flame. The molecules broke down in the plasma into their atoms and lose electrons, giving off optical wavelengths characteristic to each element. The emitted wavelengths were then sent to the solid state CCD detector. The plasma was created by electromagnetic induction, or time-varying magnetic fields, and created energy that broke down argon, the carrier or rarefield gas, into plasma. The plasma flame was stable and maintained at 7000 K.

For each element of interest, the three to four wavelengths with the highest intensity of absorption were measured and one argon wavelength as a background measurement. A separate calibration curve was made for each wavelength and the final concentration reported for each element was the average of the calibrated concentration of all four wavelengths. ICP-OES allowed for quick analysis of multiple metals in

solution which was especially useful for samples that contain corroded stainless steel (Fe, Cr, and Ni) or oxidation experiments where multiple metals and tracers were added (Fe, Cr, Ni, Cu, V, K, or Na).

3.1.10.2 Analysis procedure

Varian's ICP Expert II[®] software was used to control the apparatus, set-up the analysis sequence, and store the data. For an analysis, the exhaust fan and advanced liquid cooling supply were first turned on and the valve from the argon Dewar to the system was opened to deliver a constant supply of argon. The front of the ICP-OES had a peristaltic pump head that was used for the sampling tube and the waste tube. The autosampler had a smaller peristaltic pump used to supply a rinse solution to the autosampler probe. The default when the machine was not in use was for the rinse solution to be water, but before a run this tube was transferred to 2% HNO₃ as the rinse solution. Acid was used to rinse the autosampler sampling probe between each sample injection. These three peristaltic tubes needed to be set in their respective pump heads before the ICP-OES was turned on. The final step for preparing the ICP-OES for a run is to light the plasma. The instrument panel of ICP Expert II[®] was used to light the plasma. The plasma usually did not light the first time as the argon had not fully purged oxygen gas (O₂) from the system accumulated since the previous run. The plasma ignited the second time it was lit since the argon has had a chance to fully purge the system.

ICP Expert II[®] required a method to establish the parameters to use during the analysis and a schedule of samples. In the method, the wavelengths of interest were selected. The first wavelength of argon was always selected as a background reference. Then, for each element the three or four wavelengths that registered the most intense absorbance were selected. ICP Expert II[®] allowed the user to view which wavelengths of

the elements of interest overlap in the spectrum. If this occurred, the most intense wavelengths may not have been chosen for the analysis due to interference. The first four wavelengths for Fe, Cr, and Ni did not interfere with each other. The total time required for each sample increased with the total number of wavelengths chosen. When analyzing for stainless steel metals (Fe, Cr, and Ni), the first four wavelengths were selected while programs with more than three elements of interest had only the first three wavelengths selected to minimize sample volume needed and analysis time.

The ICP-OES used an autosampler containing three racks of 60 samples and one rack for 10 calibration standards. Samples were prepared by first making the desired dilution (10 – 1000X) in DDI water with 2% HNO₃. Samples were between 5 and 10 mL and stored in plastic, 15 mL falcon tubes that fit in the autosampler racks. The sample volume required depended on the total number of wavelengths to be analyzed for each sample. Calibration standards contained between 0.1 and 100 ppm of each of the metals being analyzed for and were made in DDI water with 2% HNO₃ to match sample preparation. Standards were made from commercially available 2000 ppm metal standards containing 3% HNO₃ (Fisher Scientific). Additional calibration standards were placed every 10-20 samples as a check of the system performance. A 5 or 10 ppm standard containing all the metals of interest was used for this purpose.

After a run was completed, the program automatically turned off the plasma flame and pump head for the sample and waste lines. The autosampler rinse was then transferred from 2% HNO₃ to DDI water to rinse the autosampler probe. After a few minutes of rinsing, the autosampler pump was turned off manually in ICP Expert II[®]. The samples were removed from the autosampler racks and the three peristaltic tubes (sample, waste, and autosampler rinse) were removed from the pump heads so they were

not stretched out and weakened in between uses. Lastly, the cooling system was turned off and the argon valve was shut in.

3.1.10.3 Limitations and expected error

ICP-OES was a fast, effective way to quantify multiple elements in solution. The primary error occurs from using a calibration curve that extended over two orders of magnitude (0.1 to 100 ppm). Gravimetric error could have occurred in preparing these standards from the 2000 ppm stock which lead to error in the predicted concentrations using the calibration curve. Another major source of error was precipitation issues frequently encountered with thermal degradation experimental samples. Also, the concentrations of metals in samples that have corroded their metal container are not known ahead of time. Therefore, knowing the appropriate dilution was difficult and the insolubility of material in the sample was used to gauge the appropriate dilution. The oxidation state of the metals was not known and some appeared to be very insoluble despite the presence of 2% HNO_3 . Some solutions that had significant precipitation requiring additional dilution ended up having low concentrations of the metals of interest. The presence of solids could have damaged the ICP-OES spray chamber used to introduce the samples into the plasma. Therefore, when additional dilution was necessary to eliminate solids, the concentration of metals was at the very low end of the calibration curve.

The technology itself was considered very accurate for a multi-element solution and was designed to decrease interference from other elements. On the other hand, other methods, such as Atomic Absorption Spectroscopy (AA), were considered more accurate for a single element analysis. Since chromium, iron, and nickel were known to interact

and interfere in AA measurements, the ICP-OES was considered sufficient for the purposes of this project for a quick multi-component analysis of complicated solutions.

3.1.11 Nuclear Magnetic Resonance spectroscopy (NMR)

3.1.11.1 Background on NMR

Nuclear magnetic resonance (NMR) spectroscopy is a technique used to obtain information on the molecular structure of species in solution. NMR is used to detect molecules with non-zero spin. Stable isotopes with an odd number of protons and neutrons have an overall non-zero spin and, therefore, have a non-zero magnetic moment and angular momentum and can be detected by NMR. The most commonly used isotopes for NMR are ^1H and ^{13}C which are very useful for describing organic molecules.

During an NMR analysis, the sample of interest is subjected to a magnetic field and electromagnetic pulses and the result is a spectrum of peaks that are associated with individual atoms in the molecule. All molecules that are uniquely positioned within a molecule produce a separate response. Each individual atom can be assessed for the atoms it is directly connected to and what those molecules are connected to. If multiple atoms have the same relative position, they are all represented by one response on the NMR spectrum. For example, if a molecule is symmetric like PZ, there was only one unique position for all the carbons and one unique position for all the hydrogens (Figure 3.19). Each carbon in PZ is connected to another carbon, a nitrogen atom, and two hydrogen atoms. All the carbons in PZ are the same based on atomistic connectivity. In an asymmetrical molecule like PZCOO^- , there are 3 different types of hydrogen and carbon atoms because the presence of the carbamate changes the connectivity associated with the two carbons (labeled C_2 in Figure 3.19) connected to the nitrogen that has the

carbamate (labeled C₃ in Figure 3.19). PZCOO⁻ would, therefore, have three separate responses on the ¹H and ¹³C spectrum to represent the molecule.

The unique responses on the spectrum are represented as shifts in the peaks from a reference standard, usually dioxane. Specific functional groups have common areas of the spectrum where their peaks usually shift to. It is possible, therefore, to use tables of standard peak shifts to identify the type of functional group associated with an unknown peak. For example, the C=O in a carboxylic acid or carboxylate ion has a traditional shift in the region of 10 to 13 ppm on a ¹H NMR spectrum. The details of NMR analysis has been described previously in detail (Hilliard, 2008).

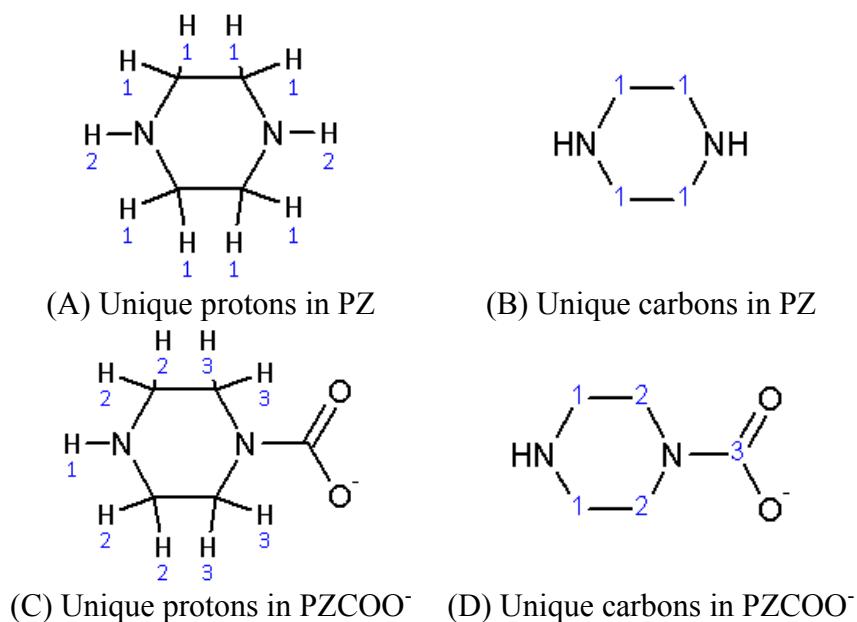


Figure 3.19: Identification of the unique protons and carbons in PZ (panels A and B) and PZCOO⁻ (panels C and D)

Aqueous, loaded PZ solutions are complicated compared to other amines because of the speciation that exists (Section 2.1). The ¹³C NMR spectrum for an undegraded, loaded PZ solution contains seven primary peaks associated with seven unique carbons

that are identified in Figure 3.20. In solution, equilibrium between protonated and unprotonated species occurs rapidly and ^{13}C NMR cannot differentiate between the two species. Therefore, the carbons of the protonation pairs of PZCOO^- and H^+PZCOO^- or CO_3^{2-} and HCO_3^- are not unique and are represented by a single peak (Figure 3.20, panels B and D). The four types of carbon on the backbone of the PZ (C_1 , C_2 , C_3 , and C_6) have a small downfield shift in the range of 40 to 45 ppm while the three carbons that are part of the carbonyl moiety (C_4 , C_5 , and C_7) have a large downfield shift and are detected in the range of 160 to 165 ppm.

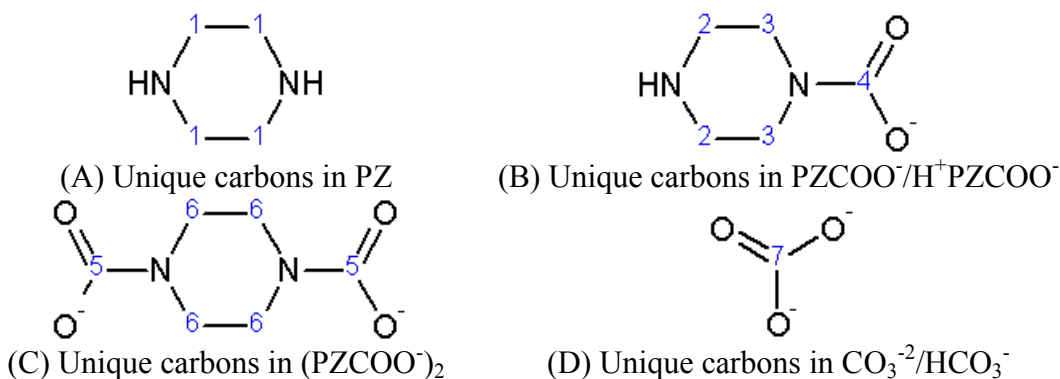


Figure 3.20: Unique carbons found in CO_2 loaded PZ solutions

In reference to this dissertation, NMR was used for two different purposes. First, NMR was used to screen for new degradation products. PZ degradation was sometimes difficult to accurately determine due to the large concentration of PZ and the detection limits of the analytical methods. NMR was used to determine if a sample only contained peaks representing PZ or if other, unidentified peaks existed. In this way, degradation of PZ could be confirmed in samples that were difficult to analyze using the other techniques described above. Secondly, ^{13}C analysis was used to analyze degradation

samples containing $^{13}\text{CO}_2$ to determine which, if any, degradation products contained the ^{13}C from $^{13}\text{CO}_2$.

3.1.11.2 Sample preparation and analysis

Samples for NMR analysis were prepared according to previous work and the recommendations of the staff of the University of Texas at Austin NMR Laboratory in the Department of Chemistry (Hilliard, 2008; Wallin and Storey, 2010). A solution was made with 10 wt% D_2O and 1 wt % dioxane with the balance being the sample of interest. Then, 2 to 3 mL of solution was carefully transferred to a 5.0 mm OD x 4.2 mm ID x 7 in NMR tube (Item No. 507-PP-7, Wilmad Glass, Vineland, NJ). When working with sensitive samples containing ^{13}C labeled CO_2 , the end of the tube was sealed by Mike Ronalter of the chemistry glass shop (Ronalter, 2009).

Samples were then submitted to the NMR laboratory for analysis. NMR measurements for ^1H and ^{13}C NMR were performed at the NMR laboratory at the University of Texas at Austin Department of Chemistry (Wallin and Storey, 2010). The NMR laboratory used a 500 MHz Varian Inova for ^1H NMR, or proton NMR (Agilent Technologies, Santa Clara, CA). The NMR laboratory used the same instrument ^{13}C NMR, or carbon NMR, but at 125 MHz.

For all samples, both ^1H and ^{13}C analysis were performed for all samples with correlation spectroscopy (COSY). COSY results assisted during data analysis to identify which specific atoms were responsible for each peak on both spectrums.

3.1.12 High Pressure Liquid Chromatography (HPLC) and LC-MS

HPLC was used to identify and quantify nonionic species in solution. In this dissertation, the HPLC was used to quantify 2-imidazolidone (2-Imid) and look for other unidentified peaks. The same HPLC method and column described here were also

applied to the LC-MS system attached to the same MS used for IC-MS, as in Section 3.1.9. The description of the MS, ESI system, and operation of Xcalibur[®] in Section 3.1.9 applied to the operation of the LC-MS, except that the flow path exiting the LC separation column was fed direction into the ESI chamber during analysis. LC-MS was used in an attempt to identify the unknown peaks found during the HPLC analysis of degraded PZ samples.

3.1.12.1 Apparatus description

HPLC was performed using a Dionex UltiMate 3000 LC unit with LPG-3400SD quaternary analytical pump, WPS-3000SL analytical split-loop autosampler, TCC-3000SD thermostatted column compartment, and VWD-2100 single channel variable wavelength detector (Dionex Corporation). Separation was achieved in an Acclaim[®] Polar Advantage II (PA2) reversed-phase analytical column with guard column (C18, 5 μ m, 120Å, 4.6 x 250 mm, Dionex Corporation). The eluent contained a gradient of acetonitrile, methanol, and water during a 30 minute analysis. Samples were diluted 10-20 times in analytical grade DDI water and analyzed directly. The method was optimized for maximum separation of complicated samples. The variable wavelength ultraviolet (UV) detector scanned at 210 nm for this method and detected a variety of organic compounds that had UV responses in this range. The system also fed the flow exiting the UV detector to the evaporative light scattering detector (ELSD) for additional quantification of semi-volatile and non-volatile compounds. In the ELSD, the eluent stream containing the sample was heated and nebulized in a heated nitrogen flow. The nebulization of non-volatile and semi-volatile compounds left a particle cloud that scattered light in the detector and created the positive response. Highly volatile compounds, such as the solvent and eluent, were nebulized to a vapor phase that only

minimally scattered light. Responses on the ELSD were not been high compared to the UV detector and were not used.

3.1.12.2 Analysis procedure

The operation of the HPLC was very similar to that described previously for the anion IC operation. Chromeleon[®] software (Dionex Corporation) controlled the system and directed the analysis of multiple samples through the use of a sequence and by applying the appropriate method, “PA2-MeOH-ACN-2.pgm” in this case. The method contained the information regarding the injection of the sample and eluent gradient. The same 1.5 mL vials with plastic snap caps used for anion IC also fit the WPS-3000SL autosampler of the UltiMate 3000. The details of the gradient method used for HPLC analysis is shown in Figure 3.21.

The flow path for HPLC was similar to other chromatography described previously. The quaternary analytical pump was used to produce the desired concentrations and flow rate of liquid indicated by the method at a given moment. The sample was injected into the flow path of the eluent that then reached the guard column and analytical column, where the separation occurred. After exiting the analytical column, the flow brought the sample to the UV detector where the UV absorbance of a given sample in solution at 210 nm created a response. This response was recorded to produce the analytical chromatograph from which concentrations were inferred. The flow exited the UV detector and then entered the ELSD. The signal from the ELSD was also recorded for each sample. Finally, the flow exited the ELSD and any remaining condensed phase stream was sent to waste.

As with IC, calibration curves were created in order to quantify the concentrations of species in the original sample. At least four or five calibration standards were made

for each molecule of interest. The detection limit of the UV is slightly higher than with anion IC or cation IC and standards used were in the range of 0.01 to 1 wt % of the desired molecule. The calibrations were fit with quadratic regressions. The calibration curve for 2-Imid created from 0.01 to 1 wt % of the compound routinely had an r^2 value of 0.999. The calibration and quantification was performed using the quantification wizard in the Chromeleon[®] software. The output at the end of analysis was a weight percent of each analyte in the dilute sample. This weight percent was adjusted using the dilution factor and then converted to mmole per kg for reporting.

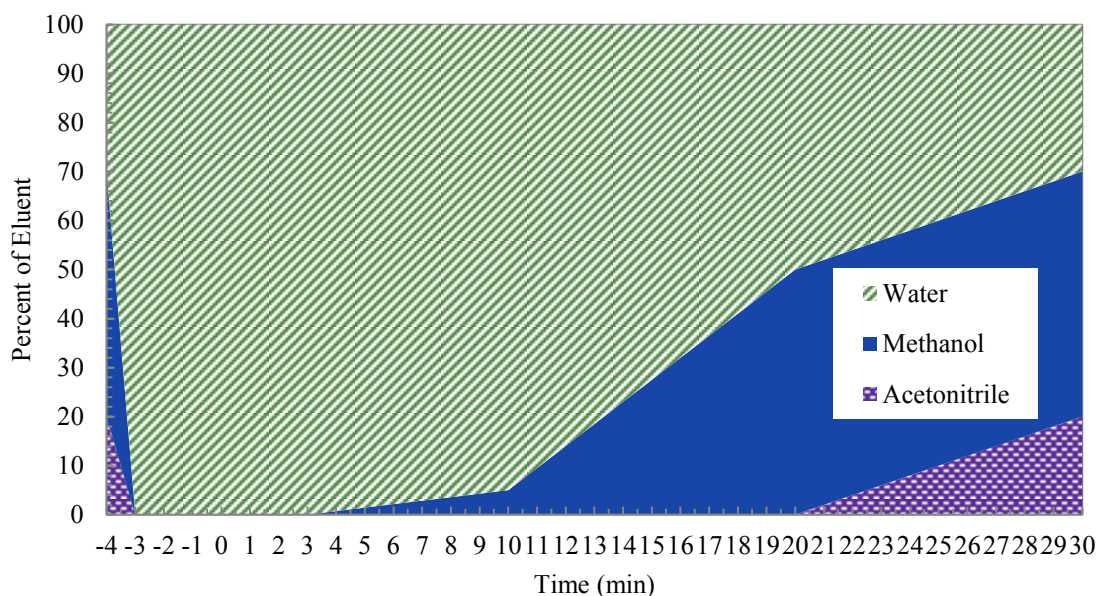


Figure 3.21: Water/methanol/acetonitrile gradient in HPLC method

3.1.12.3 Limitations and expected error

The largest sources of error in HPLC were the presence of unknown compounds, the unknown absorbance of many molecules on the UV scale, and the difficulty in optimizing the separation method. The samples analyzed were usually 10X dilutions which contained a large variety of unknown compounds. This resulted in a large number

(sometimes >30) unknown peaks that were never identified. When attempting to quantify one or more that have been identified with retention time matching of standards, the presence of so many unidentified compounds complicated the procedure. Also, the UV absorbance spectra of many of the molecules of interest were not available in literature, so it was difficult to predict or determine the identity of the unknown molecules. Finally, many variables can affect an HPLC separation and it was a challenge to fully optimize the system. For example, the flow rate, column type, guard column type, type of eluent, percentage of each eluent, dilution factor, injection amount, and temperature all affect the separation and quantification in varied ways. The system was extremely complex while the samples analyzed were more complex than standard organic chemistry lab samples. In the end, an acceptable method was found that yielded a good separation of the major compounds using a straightforward column and method. Although every variable was not exhaustively optimized, the separation was satisfactory for this analysis.

3.1.13 Total Organic Carbon (TOC) and Total Nitrogen (TN) analysis

Analysis for total organic carbon (TOC) and total nitrogen were performed using an Aurora 1030 Combustion TOC analyzer with total bound nitrogen (TN_b or TN) module (OI Analytical, College Station, TX). The TOC function is capable of quantifying 100 ppb to 30000 ppm C with precision of 1.5% relative standard deviation. Combustion of organic carbon is performed in an O₂-rich furnace where carbon is converted to CO₂ and intermediates. The gas stream then enters a catalyst chamber containing with platinum catalyst where the intermediates are converted to CO₂. The sample is sent through a scrubber to remove other contaminants and a dryer before reaching the infrared detector. For TOC, a sample size of 1 mL was used and a

calibration curve was developed from 3 to 11 mmole C per kg requiring 3000 to 4000X dilutions of the 8 m PZ samples analyzed.

For TN analysis, the same combustion chamber used for TC is used where all bound nitrogen in a liquid sample is reacted into NO_x (nitrogen trioxide (NO₃), nitrogen dioxide (NO₂), and nitric acid (NO)). After combustion in the TC combustion chamber, the gas stream is sent to a NO_x converter which contains catalyst that decreases NO_x to NO, which is then detected in the combustion analyzer. A sample size of 0.2 mL was used and a calibration curve was developed from 0.9 to 2.3 mmole N per kg requiring 8000 to 9000X dilutions of the 8 m PZ samples analyzed.

3.1.14 Amino Acid Liquid Chromatography (AA-LC)

Amino acid liquid chromatography (AA-LC) was used to observe and identify amino acids generated as degradation products. A Dionex ICS-3000 modular Dual RFIC Ion Chromatography System with AS autosampler was used (Dionex Corporation, Sunnyvale, CA). The eluent contained varying concentrations of sodium hydroxide (NaOH) and sodium acetate in analytical grade water. The separation occurred using an AminoPac PA10 guard column (4 x 50 mm) and an AminoPac PA10 analytical column (4 x 250 mm). Both columns contained hydrophobic, polymeric, pellicular, anion exchange resin according to the manufacturer. The analysis used an electrochemical detect with Ag/AgCl reference electrode that works through gold catalyzed oxidation of amino acids. Chromeleon[®] software analyzed the detector output and controlled the entire system.

The AA-LC analysis ran in parallel on the ICS-3000 with the anion IC technique and shared an AS autosampler. The AA-LC technique was used for screening of new compounds for this project and no specific amino acids were successfully identified or

quantified. The method was used to control the various components of the system was “Voice-1.pgm”, which is provided in Appendix C. In this program, various constraints and settings were used, as shown in Table 3.7.

Table 3.7: Settings and constraints for the AA-LC

Setting	Value	Units
Pressure.LowerLimit	200	Psi
Pressure.UpperLimit	3900	Psi
pH.LowerLimit	10	-
pH.UpperLimit	13	-
Column_TC	30	°C
Compartment_TC	30	°C
Flow	0.25	mL/min

In this method, there was one minute before each sample, indicated as negative time, which allowed the system to equilibrate to the starting gradient, set the flow rate at 0.25 mL/min, and to prepare for the injection. At time zero, the sample was injected and data acquisition from the electrochemical detector (ECD) was turned on. The eluent contains water and sodium hydroxide to for the first 11 minutes. Then, sodium acetate is added until a maximum concentration of 70%, where it remained for 20 minutes. After 44 minutes, data acquisition is concluded and the flow and gradient remained constant for 30 minutes to equilibrate the cell. The eluent concentration gradient over the course of “Voice-1.pgm” is shown in Figure 3.22. At the end of each run of samples, there was a final sample with the “Shutdown.pgm” method.

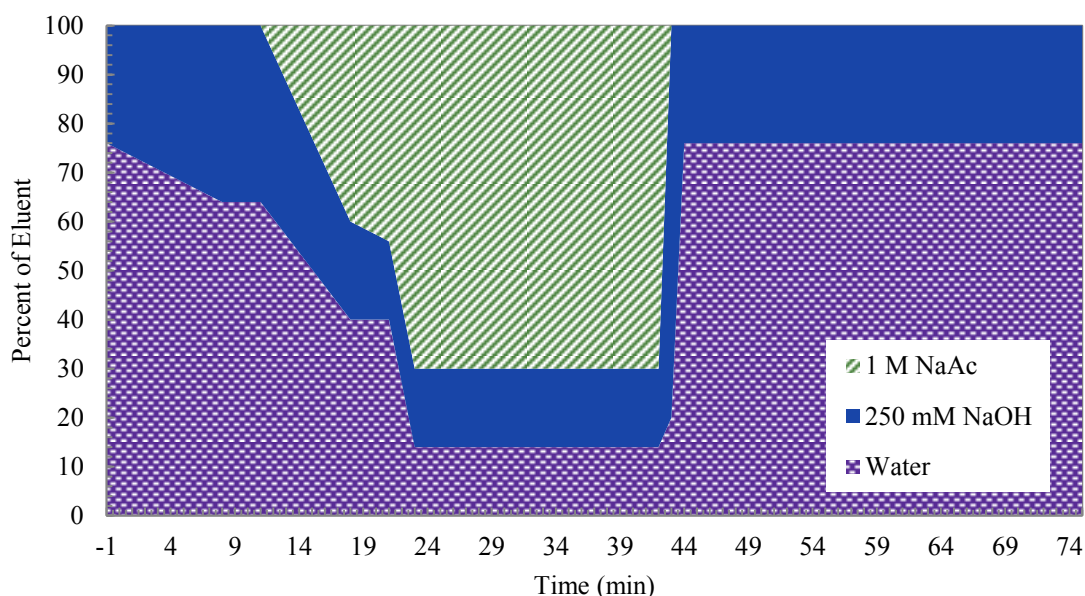


Figure 3.22: Sodium hydroxide and sodium acetate gradient in AA-LC method

3.2 EXPERIMENTAL EQUIPMENT

3.2.1 Thermal cylinders

Thermal degradation of amines was studied using thermal cylinders, formally referred to as thermal bombs (Davis, 2009). This experimental design allowed a high sample throughput due to the simple design and the Swagelok[®] seals maintained the solution pressure even during high temperature experiments.

3.2.1.1 Apparatus description

The thermal cylinders used were small, simple containers that sealed completely to allow amine solutions to be exposed to high temperatures under pressure. Thermal cylinders were constructed of five inches of ½-inch OD 316 stainless steel tubing with 316 stainless steel Swagelok[®] endcaps. The Swagelok[®] connection using ferrules provide an airtight seal that is rated to hold up to 2000 psi of pressure (138 bar). The simple nature of the cylinders allowed a high throughput of thermal degradation

experiments as hundreds of cylinders were constructed in a relatively short period of time and inexpensively. Cylinders were reused after the completion of each experiment but the end caps were married to a specific cylinder using engraved labeling.

3.2.1.2 Experimental procedure

Thermal degradation experiments were performed in forced convection ovens that maintain a steady high temperature. Before preparing the experimental cylinders, the oven was turned on and at the desired experimental temperature and allowed to stabilize.

The thermal cylinders all had engraved markings that indicate the cylinder number and each end separately, as indicated by the “A” and “B” in Figure 3.23. Different sets of cylinders were used that had different kinds of markings, such as “A” and “B” ends, “+” and “-” ends, or “●” and no marking ends. In each case, the sets are numbered consecutively and reused.

A group of clean thermal cylinders are prepared at the beginning of the experiment by sealing either the “B”, “-”, or no marking end of each cylinder, depending on the cylinder set used. The cylinders were preferably in numerical order to simplify the experiment and in order to quickly know which experiments were in each oven at one time. Each empty cylinder was weighed with both end caps and the mass is recorded. Next, 10 mL of the amine solution being tested was pipetted into the empty cylinder through the open “A”, “+”, or “●” end. That end was then sealed following the instructions provided by Swagelok[®] (one-quarter turn past finger-tight). Each sealed cylinder was then weighed again and the full mass was recorded.



Figure 3.23: Thermal cylinder with “A” end and cylinder number (39) labeled

All of the cylinders were placed in the oven and the start time of the experiment was recorded. At each sampling time point, usually every 1 to 4 weeks, one cylinder was removed from the oven. This cylinder was allowed to cool on the bench top and then the unopened cylinder was weighed and the mass was recorded to determine if the cylinder failed. At this point, the cylinder was opened and the sample was poured into a glass sample storage vial.

The thermal cylinders failed if the seal was not properly made before placing in the oven. Once the cylinders heated up the first time, an improperly sealed cylinder would have allowed amine vapor to leave the cylinder. This usually resulted in a distinct hot amine odor and the leaking liquid left burned, black residue on the outside of the cylinder. Cylinders that lost less than 20% of their initial amine solution weight were deemed to be successful cylinders. The failing of cylinders was very dependent on temperature where high temperature experiments (175 °C) lost anywhere from one-third to half of the initial cylinders while lower temperature experiments (150 °C) usually only had one or two failures. In a typical PZ experiment, a cylinder would either lose 1-3% of its mass or completely fail with losses of 80-100% so the failures were easy to pinpoint. Any completely empty cylinders were not analyzed as part of the experimental samples. However, partially failed cylinders (0 to 80% loss) were analyzed in case the liquid still

represented the experiment well. In the experimental design, extra cylinders were prepared to allow for possible failures.

3.2.1.3 Data analysis

The main analysis performed on samples from thermal degradation experiments was liquid phase analysis for amine concentration and the production of degradation products. All thermal degradation samples were analyzed for total alkalinity, CO₂ concentration, PZ concentration (or parent amine concentration if PZ is not the parent amine), amine degradation product concentrations (cation IC), and heat stable salts or carboxylate ion concentrations (anion IC). The mass change of each cylinder was analyzed as well to ensure that each cylinder did not lose a significant amount of mass during the experiment. For most experiments, the amount of iron, nickel, and chromium was analyzed to understand the leaching of metals from the cylinders during the course of the experiment.

3.2.1.4 Special considerations – solid solubility

Numerous thermal degradation experiments were performed on amine solutions that were not aqueous solutions at room temperature or had solubility issues after degradation. Special procedures were required to properly prepare the thermal cylinders for the experiment, remove the samples at the end of the experiment, or perform dilutions for liquid analysis. Hot water was used to warm the container holding the solution, either a bottle, vial, or thermal cylinder, in nearly every case where solubility was an issue. Solutions that were insoluble at room temperature were prepared as usual and maintained on a hot plate while filling the thermal cylinders. The cylinders were then sealed as normal and the experiment started. When the experiments were complete, the cylinders were removed from the oven and allowed to cool down to room temperature in order to

measure the post experiment mass. Then, the cylinders were warmed in a beaker of water to approximately 40-50 °C. The cylinders were then removed from the hot water, excess water was removed from the outside, the cylinders were opened, and finally the solution was poured directly into a sample vial. Once the solution cooled to room temperature, it again solidified in the sample vial. When dilutions and titrations were being performed, the small sample vial was placed in a small beaker of hot water again to solubilize the solution for analysis at 40-50 °C.

A few experimental solutions were soluble at room temperature and when emptying the cylinders but then crystallized in the sample vial when analysis was needed. It was assumed that the degradation products now present in the solution contributed to the insolubility. Another phenomena observed was that solutions that should be insoluble at room temperature and pressure were able to be transferred from the cylinders to a sample vial before any crystallization. The solution is exposed to high pressure in the cylinders and even when opened, do not crystallize immediately after being exposed to atmospheric pressure. For example, the 8 m PZ experiment with a loading of 0.1 mole CO₂ per mole alkalinity (TE21) exhibited this behavior. The cylinders were filled with warm solution and degraded. When the cylinders were opened after degradation they were soluble enough to pour into the sample vials. Once in the vials, they solidified after approximately 20 minutes. The viscosity of PZ solutions helps to delay crystallization slightly. The thermal degradation experiments that had solubility issues were treated in the way indicated in Table 3.8.

3.2.2 Low gas flow reactor – Original Oxidation Reactor (OOR)

Oxidation, or oxidative degradation, of amines was studied using low gas flow reactors. The original design of the oxidation reactor has been described previously in

great detail (Goff, 2005; Sexton, 2008). In this thesis, this design is known as the original oxidation reactor (OOR).

Table 3.8: Heat requirement in preparing, sampling and analyzing thermal experiments

Expt.	Solution	Heat Requirement at Each Experimental Step		
		Filling Cylinders	Emptying Cylinders	Making dilutions
TE21	8 m PZ, $\alpha=0$	Heat	Heat	Heat
TE23	8 m PZ, 0.15 mol H ⁺ /mol alk	None	Slight heat	Heat
TE24	8 m HomoPZ, $\alpha=0.3$	None	None	Heat
TE25	8 m Pyr, $\alpha=0.3$	None	Slight heat	Heat
TE26	8 m PD, $\alpha=0.3$	None	Slight heat	Heat
TE27	8 m HMI	None	None	Heat
TE34	8 m PZ, $\alpha=0.1$	Slight heat	None	Heat
TE36	8 m HMDA, $\alpha=0.3$	Slight heat	High heat	Heat
TE46	8 m PZ, $\alpha=0$	Heat	Heat	Heat
TE47	8 m PZ, $\alpha=0.1$	Slight heat	None	Heat
TE48	8 m PZ + 0.15 mol H ⁺ /mol alk	None	Slight heat	Heat
TE52	8 m PZ, $\alpha=0$	Heat	Heat	Heat
TE53	8 m PZ, $\alpha=0.2$	Heat	Heat	Heat
TE55	8 m PZ + 0.1 mol H ⁺ /mol alk	None	Slight heat	Heat
TE57	20 m PZ, $\alpha=0.3$	None	Slight heat	None
TE58	20 m PZ, $\alpha=0.3$	None	Slight heat	None
TE61	4 m PZ + 0.15 mol H ⁺ /mol alk	Heat	Heat	Heat
TE62	12 m PZ + 0.15 mol H ⁺ /mol alk	Heat	Heat	Heat
TE63	8 m PZ + 0.3 mol H ⁺ /mol alk	Heat	Heat	Heat
TE65	8 m PZ + 0.1 KHCO ₃	Heat	Heat	Heat

The OOR consists of a glass, jacketed reactor, recirculating water bath (Lauda-Brinkmann, Delran, NJ), gas pre-saturator, and mechanical agitator as shown in Figure 3.24. The reactor is a 600-mL jacketed, flat-bottomed reactor with internal diameter of 80 mm (Ace Glass, Vineland, NJ). The water bath was maintained at 55 °C for most experiments and water was circulated through the reactor jacket. The saturator was a two-piece, glass, vacuum trap placed in the 55 °C bath where the inlet gas was sparged through a column of water in order to saturate the gas at the reactor temperature. This

original design used a black, rubber stopper as the lid of the reactor. It had a central hole for the agitator and two holes near the outer edges for the inlet gas and for sampling.



Original Oxidation Reactor (OOR)

Teflon Oxidation Reactor (TOR)

Figure 3.24: Overall set-up for the OOR and TOR including a water or oil bath, pre-saturator, gas inlet line, and overhead agitator

This reactor design was used successfully for many years when oxidizing amines that readily oxidize such as MEA, blends of MEA and PZ, and EDA (Goff, 2005; Rochelle, 2010b; Sexton, 2008; Zhou et al., 2010). Unfortunately, with amines that oxidize slowly, such as PZ or MDEA, the degradation of the amine was overshadowed by errors caused by the reactor design. The water balance has always been the largest issue. Water easily escapes with gas exiting the reactor through the open annular space around

the agitator shaft. A secondary issue was the use of rubber as the lid material. PZ readily absorbed into this rubber lid further confounding degradation with mechanical issues with the reactor. After oxidation experiments, the stopper would commonly be swollen with the amine and water it had absorbed. The stopper edges were also hot because of their contact with the glass reactor, adding to the swelling concern. A total of 16 oxidation experiments were performed in the OOR. The results are presented alongside those achieved with the new oxidation reactor. The reactor used was indicated to allow for interpretation of the results.

3.2.3 Low gas-flow reactor – Teflon[®] Oxidation Reactor (TOR)

The Teflon[®] Oxidation Reactor (TOR) was design specifically with PZ degradation in mind. The TOR was based on the overall design and dimensions of the OOR, but adaptations were made with the goal of achieving a more precise measurement of PZ oxidation. The main reactor body was made out of glass by Mike Ronalter of the Glass Shop at the University of Texas at Austin (Ronalter, 2009).

3.2.3.1 Reactor design

The design elements that were maintained from the OOR to the TOR were:

Internal Dimensions: The internal dimensions of the OOR were maintained in an effort to ensure that the data captured from each reactor was comparable. The ID of 80 mm and jacketed height of 160 mm were maintained.

Inlet gas: The inlet gas configuration was maintained in both reactors. The gas flow of 100 mL/min was still pre-saturated at the reactor temperature in the water bath and then fed to the top of the agitation vortex. This was kept the same primarily to have data comparability between reactors.

Jacket heating: The heating of the reactor through a water jacket was maintained. This heating method did not seem to cause any problems with the OOR operation and allowed a water bath for the inlet gas to be pre-saturated at the reactor temperature.

The major modifications over the OOR design include:

Teflon[®] lid: The black, rubber stopper lid of the OOR was replaced with a Teflon[®] (Polytetrafluoroethylene, PTFE) lid with 7 pre-drilled openings with NPT fittings. The lid required the use of a Schott-style flange connection to attach to the reactor (shown in Figure 3.25). The flange connection was O-ring grooved to accept a PTFE coated O-ring in between the flange and the smooth bottom of the lid. A stainless steel Schott-style flange clamp was used to keep the pieces together.

Dimensional Differences: The use of a flange for the new lid required some additional height to be built into the overall height of the reactor. The jacketed portion was maintained at 160 mm, but the flange added approximately 65 mm of height, making the reactor 225 mm tall overall. This provided 65 mm of cooler glass surface and more overall gas headspace compared to the OOR. This was not ideal, but a necessity that came out of the way the glass TOR reactor body was constructed. The extra glass surface at the top of the reactor likely acted as a small condenser which helped control some vapor losses. Mike Ronalter, who constructed the glass TOR, attempted to minimize the overall height addition due to the flange.

Fritted Pre-Saturator: The vacuum trap used to saturate the inlet gas was modified with the addition of a fritted sparger rather than the open tube that originally was used. This decreased the size of the gas bubbles, hopefully achieving a better degree of saturation for a given water column height.

Oil Bath Conversion: A portion of experiments performed in the TOR were done at temperatures higher than 55 °C. To achieve these temperatures, the water bath was converted to an oil bath using dimethyl silicone oil as the circulating fluid. The tubing between the bath and reactor was changed to Tygon[®] silicone tubing since the original PVC tubing is not compatible with dimethyl silicone oil (Fisher Scientific Worldwide). Caution was used when adding water to the saturator since it was immersed in a bath of hot oil.

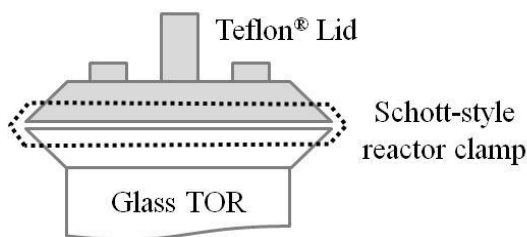


Figure 3.25: Schematic of TOR closure with Teflon[®] lid and Schott-style flange

3.2.3.2 Reactor set-up

The overall operation of the TOR was very similar to that of the OOR. The operation of the TOR will be described in detail since that of the OOR has been described previously (Goff, 2005; Sexton, 2008; Zhou et al., 2010).

The jacket of the reactor body was connected to the inlet and outlet lines of the recirculating portion of the water or oil bath. The lines were secured with hose clamps, even though the jacket has ringed hose connectors, because once hot fluid was flowing through the jacket, the hoses may have slipped off the connectors if not secured. The hoses were connected so that the inlet from the water bath was at the hose connection on the bottom of the reactor. This allowed fluid to fully fill the reactor jacket, rather than leaving the top portion with air.

The inlet gas to the reactor was typically 2% CO₂/ 98% O₂, except for a few experiments performed at different concentrations of CO₂ and O₂. Two sources were used for the gas: mixing the gas using flow controllers or a pre-mixed cylinder. The preferred method was to use two Brooks flow controllers connected to separate CO₂ and O₂ cylinders and connected to a controller unit. Each flow controller was sized for the appropriate flow and the controller unit was calibrated using a soap bubble flowmeter to achieve flows of 2 and 98 mL/min of CO₂ and O₂, respectively. After exiting the flow controllers, the two gas streams were combined using a 1/4" Swagelok[®] T-union and fed into the inlet of the pre-saturator (Arthur Fluids System Technologies). When the flow meters were malfunctioning, being repaired, or otherwise unavailable, pre-mixed cylinders were used. These cylinders were blended gases containing 2% CO₂ by volume with the balance O₂ (Matheson Tri-Gas, Basking Ridge, NJ). These cylinders were used when mixing gases was not possible due to the unavailability of flow controllers. The gas line from the cylinder was sent through a rotameter and then on to the pre-saturator. The rotameter was first calibrated with the soap-bubble flowmeter to achieve a total flow of 100 mL/min to the reactor. Calibrations were performed with the presence of water in the saturator to simulate the reactor conditions as closely as possible during calibration.

A two-piece vacuum trap was used as the air saturator to allow the pieces to be separated and the water column to be refilled. The bottom piece was secured to a ring stand using a clamp and placed into the water bath. The vacuum trap was taller than the standard size of Lauda water or oil bath so only the bottom 75% of the trap was actually under fluid. DDI water was added to fill the vacuum trap and the top was placed inside. The two-piece traps had a ground glass joint that provided a secure connection upon slight heating. The inlet gas line from the flowmeters was attached using Teflon[®] Swagelok[®] connections to the smooth tube connection of the trap (top center port)

(Arthur Fluids System Technologies). The outlet (side) of the trap was then connected to the tube that enters the reactor.

There were seven predrilled holes in the Teflon[®] lid that accepted NPT fittings ranging from ¼ to ¾ inch (Item: 12860-18, AceGlass, Vineland, NJ). The central hole was fitted with a Teflon[®] ¾" male NPT to 24/40 standard taper adapter (Item: CG-1945-T-21, ChemGlass, Vineland, NJ). Then, a 10 mm Teflon[®] stirring bearing with 24/40 male end with an O-ring was placed in the central hole (Item: CG-2077-H-01, ChemGlass). This central hole then accepted the 8 mm agitator shaft connected to the overhead agitator (Fisher Scientific Worldwide). One of the ½" NPT openings in the lid was fitted with the same ¾" male NPT to 24/40 standard taper adaptor. A hollow Teflon[®] 24/40 stopper was then placed in the adaptor and secured with a 24/40 joint clip (CG-3002-05, ChemGlass). This stopper port was used for addition of water to the reactor and sampling. Two of the ¼" NPT predrilled holes were fitted with straight Teflon[®] ¼" male NPT to ¼" Swagelok[®] fittings for the inlet and outlet of the gas (Arthur Fluids Systems Technologies). The inlet fitting was bored through to allow the gas inlet ¼" OD plastic tube to be fed through the lid and positioned at the top of the agitation vortex. The outlet fitting was a Teflon[®] Swagelok[®] 90° elbow open to the environment in an attempt to direct the outlet gas, if needed, away from just leaving the reactor through the annular space surrounding the agitator. The remaining openings in the lid were not used during operation and were filled with ¼" and ¾" male NPT Teflon[®] solid plugs (Items: 12867-04 and 12867-18, AceGlass).

A ring stand was used with two chain clamps to keep the reactor secure and completely vertical. The alignment of the agitator was a major concern during the experimental set-up and reactor operation. The additional height of the TOR compared to the OOR added to the vibration problems traditionally experienced in oxidation

experiments. The agitator shaft was not as far inside the body of the agitator during the TOR experiments because of the increased reactor height, allowing for more vibrations. Also, the design of the TOR intentionally allowed for a smaller annular space around the agitator, making alignment and vibration of the agitator shaft an even more crucial element of the reactor set-up. The agitator shaft was placed as far inside the agitator to allow that the propellers were approximately one inch above the bottom of the reactor, as with OOR experiments. The agitator body itself was also placed very close to the top of the stirring bearing, within 0.5 cm. Experiments were all constantly monitored to ensure that the agitator did not make contact with the stirring bearing. When it did occur, some Teflon[®] was shaved off and ended up in the reactor solution. This was avoided when possible.

Once all the major elements of the reactor system were in place, an experiment could begin. The circulating bath was first turned on to allow the fluid to heat to the experimental temperature and begin to heat the reactor body and pre-saturator. As it heated, the hose connections were checked for leaks. Experiments in the TOR were conducted with 350 mL of amine solution, as with the OOR experiments. This volume was measured in one 100 mL and one 250 mL volumetric flask. The amine was added to the reactor either with the lid off, or through the sampling port. The mass of the amine actually entering the reactor was recorded by weighing the full flasks and the flasks containing some residue after the PZ was added to the reactor. The overall mass balance of the experiment was recorded in terms of mass entering or exiting the reactor, so all additions were recorded in terms of mass. If additives such as metals or inhibitors were to be used, they were then added to the amine solution in the reactor through the sampling port. The solution was stirred briefly at low speed to incorporate the additives. The solution itself was allowed to heat up in the reactor for approximately 10 to 20

minutes with slow agitation (<300 rpm) while other parts of the experiment set-up were completed. Once all the solution elements were added to the reactor, the top was affixed with the Teflon[®] O-ring in place using the stainless steel flange clamp. The clamp was made very tight to discourage water collection in between the glass flange and Teflon[®] lid.

Before the experiment was started, an initial sample was taken through the sampling port. Liquid samples of 3 to 5 mL were extracted through the port using a long, 5 mL glass pipet or manual pipetter with a long 10 mL tip. A piece of laboratory tape was placed vertically on the side of the reactor and the initial level (after sampling) was marked. This mark was important in order to visually observe the water balance each day. It was used as a gauge to ensure that the water level was being maintained throughout long term experiments. The temperature of the solution was taken for higher temperature experiments as well before the experiment was started. To begin the experiment, the agitator was set at 1400 rpm and the gas flow was turned on. The start time of the experiment, officially, was when the gas flow was turned on.

3.2.3.3 Reactor sampling and analysis

Daily monitoring of the TOR was required due to the delicacy of the agitator vibration and stirrer bearing set-up. Each day, the water bath was refilled to make-up for evaporation if water was the circulating fluid. The circulating bath was programmed to turn itself off when a pre-determined low liquid level was achieved. At 55 °C and with water as the circulating fluid, it took approximately 36 hours to evaporate enough liquid to initiate the automatic shut off of the bath. The alignment of the agitator in the lid was also checked daily to ensure smooth operation.

Experiments were sampled every 3 days, although some were sampled every 2 or 4 days, depending on the experimental design. The sampling procedure performed was designed to maintain the mass balance of the reactor contents as closely as possible. There were three main parts of sampling: replacing water evaporated since the last sample, taking the sample, and remarking the level. Additional steps taken on certain experiments include measuring the temperature of the reactor contents or refilling the saturator.

The first step in all sampling was to add water to the reactor to replace what has evaporated since the previous sample. Water was added to the reactor through the sampling port to reach the previous line marked on the level indicator. The exact mass of water added to the reactor was recorded. The TOR generally needed 0.15 to 0.30 gram of water per hour at 55 °C or 0.40 to 0.60 gram of water per hour at 70 °C. After the water was added, the agitator was turned on for a few seconds to mix in the newly added water. Then, the 5 mL sample was withdrawn through the sampling port using a long glass pipet and pipet bulb or a manual pipetter with a long 10 mL pipet tip. The exact mass of sample withdrawn was recorded by weighing the sample vial before and after the sample was taken. Then, the new liquid level was drawn on the level indicator on the side of the reactor. Finally, the stopper was replaced on the sampling port on the lid and the agitator was restarted.

The crucial part of the sampling procedure was that water was replaced before the sample was taken. This was done to try to make the sample as representative as possible, excluding the water evaporation since the last sample was taken. The sample should represent what has happened if no evaporation occurred, an ideal situation that cannot be yet achieved by this oxidation reactor.

One advance made in the sampling procedure was to record the amount of water added to the pre-saturator during the sampling. The loss in liquid level in the pre-saturator was assumed to be the amount of water added to the gas stream and, therefore, to the reactor itself. This liquid should be taken into account in the mass balance. In all experiments past OE20, the amount of water add to the saturator was included in the sampling procedure and included in any mass balance calculations. Previous to OE20, the saturator was topped off with water daily during the daily check and the amount was not recorded.

Chapter 4 – Density, Viscosity, and Solubility of Concentrated, Aqueous PZ and PZ Blends

The physical properties of PZ solutions that are the most important to understand for CO₂ capture systems are discussed in detail in this chapter, such as density, viscosity, and physical solubility or solid-liquid equilibrium. A majority of this chapter is excerpted from a publication that focuses on density and viscosity of PZ and the application to online monitoring of PZ based CO₂ capture systems (Freeman and Rochelle, 2011). Another previous publication also briefly touched viscosity of PZ in relation to other amine systems of interest (Freeman et al., 2010b). This chapter also includes an additional section discussing the physical solubility of PZ in aqueous solution which includes some work from a review article on PZ as a solvent (Freeman et al., 2010b). Solubility data are especially useful when operating large scale PZ systems

where insolubility anywhere in the system could be catastrophic. Finally, density and viscosity measurements for PZ blended with substituted PZs (1-MPZ, 1,4-DMPZ, and 2-MPZ) are reported over a range of conditions.

4.1 INTRODUCTION TO PHYSICAL PROPERTIES OF PZ

Amine based absorption-stripping for CO₂ capture from coal-fired power plant flue gas will be an important technology to address global climate change. Concentrated aqueous piperazine (PZ) has been identified as an attractive solvent for this process (Freeman et al., 2010a; Freeman et al., 2010b). The density and viscosity data for this solvent are needed for design calculations of fluid flow and heat transfer. Because high viscosity interferes with mass transfer and increases the size of heat exchangers, the maximum concentration of PZ in the solvent may be determined by its viscosity. Furthermore, on-line instrumentation makes it attractive to use density and viscosity measurements to infer the amine concentration and CO₂ loading. Chen and Dugas demonstrated that on-line density measurements were useful in inferring CO₂ loading of potassium carbonate promoted by PZ and monoethanolamine (MEA) solutions during pilot plant operations (Chen, 2007; Dugas, 2009).

PZ has been investigated as a CO₂ rate promoter in solvents primarily consisting of aqueous methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), or potassium carbonate (Bishnoi and Rochelle, 2000a; Bishnoi and Rochelle, 2000b; Bishnoi and Rochelle, 2002a; Bishnoi and Rochelle, 2002b; Cullinane and Rochelle, 2004; Cullinane and Rochelle, 2005; Cullinane and Rochelle, 2006; Derks et al., 2008; Liu et al., 1999; Oyekan and Rochelle, 2009; Paul and Mandal, 2006b; Plaza et al., 2009; Samanta and Bandyopadhyay, 2009; Sun et al., 2005; Yang et al., 2010; Zhang et al., 2001). Concentrated PZ (40 wt %) has also been explored as a standalone solvent for

CO₂ capture (Freeman et al., 2010a; Freeman et al., 2010b; Rochelle, 2009). PZ has a low solubility in water which can prove detrimental in a large scale system and discouraged research into the solvent. The solubility of the PZ + H₂O system has been investigated previously (The Dow Chemical Company, 2001; Bishnoi and Rochelle, 2000a; Hilliard, 2008; Muhammad et al., 2009), but the effect of adding CO₂ to the system has only been researched recently (Freeman et al., 2010b; Hilliard, 2008). Large-scale CO₂ capture systems will contain a wide range of CO₂ concentrations throughout the absorber, stripper, and other unit operations; therefore, a full understanding of the effect of CO₂ concentration on the physical properties of a solvent is crucial. Previous literature on the density and viscosity of PZ solutions avoided insoluble solutions and includes data only at very low PZ concentrations (Cook and Lowe, 1976; Derks et al., 2005; Muhammad et al., 2009; Samanta and Bandyopadhyay, 2006). The concentrations of PZ studied, less than 14 wt % at 20 °C, are not useful for CO₂ capture applications since they cannot compete with the capacity of a baseline MEA solvent.

Recently, the addition of CO₂ to an aqueous solution of PZ was found to alleviate solubility concerns as PZ carbamate (PZCOO⁻) is more soluble than anhydrous PZ itself (Freeman et al., 2010b; Hilliard, 2008). Concentrated solutions can be made without solids precipitation and have been shown to have very advantageous properties for CO₂ capture such as fast rate of CO₂ absorption, high capacity, and resistance to thermal and oxidative degradation (Freeman et al., 2010a; Freeman et al., 2010b). Physical property studies that include PZ in the presence of CO₂ report on a blended solution with another amine, such as MDEA or AMP, where PZ is added as a kinetic promoter (Derks et al., 2008). In the few studies where the PZ + H₂O + CO₂ system is investigated alone, the only properties measured and reported are CO₂ solubility, N₂O solubility, Henry's constants and diffusivities (Hilliard, 2008; Samanta et al., 2007). Literature data for the

density and viscosity of PZ solutions in the presence of CO₂ are not available outside of the author's previous work (Freeman et al., 2010b).

This study provides density and viscosity data over ranges of PZ and CO₂ concentrations applicable to CO₂ capture applications. To match with previous CO₂ capture solvent literature, solutions are analyzed at 2 to 20 molal (m) PZ and a CO₂ loading of 0 to 0.47 mole CO₂ per mole alkalinity. The data for density and viscosity are reported in SI concentration units (mole per kg), but other common units are also provided (i.e. m and CO₂ loading) for clarity to the readers in this field. The data are not all inclusive across a range of CO₂ concentrations for a given PZ concentration and are absent where PZ precipitation or CO₂ evolution occurred.

4.2 EXPERIMENTAL NOTES

PZ solutions were prepared as described in Section 3.1.1 of this dissertation for analysis of their physical properties. Alkaline titration was used to determine the PZ concentration in these samples as described in Section 3.1.2 and was determined to be within 2% of the gravimetric preparation in all cases. TIC was used to analyze for CO₂ concentration in all samples as described in Section 3.1.3.

A few modifications were made to the standard analysis procedures in order to accurately assess these properties. First, dilution series were created by making a solution of the desired PZ concentration with high loading ($\alpha=0.45$) and zero loading. Intermediate loadings were created from these two CO₂ concentrations in order to have a range of loadings. Next, the 100X dilutions for TIC were made immediately after each analysis in order to capture the CO₂ concentration accurately. For a set of density or viscosity measurements, all of the loadings were analyzed at the same time and the dilutions were done immediately afterward.

The loading analysis is the most imprecise part of this study. The loading of amine solutions can change greatly due to handling, opening of bottles, or age of samples. All samples were handled carefully and analyzed immediately, but the loading of solutions inherently changed during the course of density and viscosity measurements. The error of the density and viscosity measurements is very low compared with the error in the measurement of CO₂ concentration. The estimated error in the TIC measurement is 4.0 %. Instrument errors are reported for the density meter and viscometer, but the error in CO₂ concentration overshadows them and has the most impact on the data regressions.

For both density and viscosity measurements, data are missing at low CO₂ concentration where solutions could not be analyzed due to PZ precipitation. When precipitation occurred in the rheometer, the shear stress during the 10 measurements was non-linear, producing scatter in the calculated viscosity. The shear stress was high as the samples were essentially a slurry. Data are also missing at high CO₂ concentration where CO₂ evolved from the sample. The higher temperatures of these measurements caused an increased CO₂ partial pressure leading to CO₂ evolution and instability in the measurement. This was evidenced by the production of bubbles visible in the u-tube of the DE40 or bubbles visible on the surface of the sample in the MCR 300.

For the viscosity measurements, a total of 10 measurements were taken every 10 seconds for each sample. Values reported are an average and standard deviation of these 10 instances. Percent error represented by the calculated standard deviations ranged from 0.13 % to 4.6 %. Errors were higher at higher temperatures where the value of viscosity was smaller, amplifying the standard deviation value when calculated as a percent.

Solubility or solid-liquid equilibrium measurements were based on visual observations. Aqueous solutions were prepared to cover the desired solution properties

and were allowed to equilibrate at each condition with stirring before solubility observations were made. Solutions were deemed insoluble based on the presence of any solid crystal or slurry in a given solution. The transition temperature is the temperature at which a liquid solution will first precipitate when cooled slowly. In measuring this property, a liquid solution at room temperature was heated to approximately 50 °C. For lean loadings, this caused any precipitate to melt. The temperature at which this melting occurred was noted as the approximate transition temperature and then the solution was cooled slowly. While cooling slowly, the temperature at which the solution first began to crystallize or precipitate was noted as the crystal temperature. Finally, the solution was heated again to carefully observe the temperature when the crystals fully melt and this was noted as the melting temperature. The crystal and melting temperatures demonstrated a hysteresis that was likely caused by the high viscosity of the liquid and an extended equilibrium time need to create crystals or fully melt a slurry or solid precipitate. The approximate temperature ramp for all transitions was 1 °C or less every 5 minutes.

4.3 DENSITY OF CONCENTRATED PZ

The experimental values for the density (ρ) of aqueous (PZ + CO₂) solutions as a function of PZ concentration (C_{PZ}), CO₂ concentration (C_{CO_2}), and temperature (T) are listed in Table 4.1. C_{PZ} is provided in units of m (molal, mole per kg water) and mole per kg solution. C_{CO_2} concentrations are given in units of mole CO₂ per mole alkalinity and mole per kg. Raw density data are provided with the units of kg per m³, but the ratio of density to the density of water (ρ_{water}) is used throughout the proceeding discussion, which is unit less. Values for ρ_{water} over the range of 20 to 60 °C were taken from the DIPPR Database (DIPPR, 2010).

Table 4.1: Density (ρ) of Aqueous (PZ + CO₂) Solutions from 20 to 60 °C

C _{PZ} molal	C _{PZ} mol/kg	C _{CO2} mol/mol alk	C _{CO2} mol/kg	Density, ρ (kg/m ³)		
				T = 20 °C	T = 40 °C	T = 60 °C
2	1.67	0.00	0.000	1006.7	999.4	989.1
	1.64	0.05	0.186	1014.6	1007.2	997.4
	1.64	0.11	0.366	1022.2	1014.8	1004.9
	1.63	0.16	0.545	1029.9	1022.4	1012.9
	1.61	0.22	0.728	1037.3	1029.9	1020.2
	1.61	0.25	0.894	1044.1	1036.5	1027.0
	1.59	0.32	1.080	1051.5	1043.8	1034.4
	1.58	0.38	1.246	1058.1	1050.5	1040.7
	1.57	0.44	1.416	1064.4	1056.7	-
	1.55	0.47	1.516	1068.8	1060.7	-
5	3.36	0.11	0.753	1049.3	-	-
	3.33	0.15	0.991	1062.2	1052.6	-
	3.25	0.22	1.433	1074.9	1065.5	1054.8
	3.21	0.28	1.780	1087.4	1078.2	1067.6
	3.16	0.35	2.216	1099.2	1090.2	1079.9
	3.11	0.40	2.504	1111.1	1102.1	1092.0
	3.06	0.46	2.822	1122.3	1113.3	1103.1
	3.03	0.50	3.023	1127.8	1118.8	1108.1
	3.01	0.53	3.182	1136.9	1127.6	-
7	4.11	0.16	1.281	1076.9	1066.1	-
	4.01	0.21	1.726	1092.3	1082.1	1070.7
	3.93	0.26	2.091	1106.1	1096.1	1085.2
	3.86	0.32	2.495	1120.6	1110.9	1100.4
	3.81	0.37	2.815	1134.1	1124.6	1114.3
	3.72	0.40	3.023	1147.3	1137.9	1127.7
	3.68	0.46	3.397	1159.6	1150.1	-
8	4.28	0.20	1.722	1100.7	1090.0	1078.5
	4.26	0.25	2.150	1116.2	1105.9	1094.9
	4.12	0.31	2.563	1130.8	1121.3	1110.7
	4.11	0.35	2.917	1145.7	1136.0	1125.7
	3.98	0.41	3.297	1160.1	1150.4	1140.2
	3.90	0.45	3.617	1173.4	1163.8	-

**Table 4.1: Density (ρ) of Aqueous (PZ + CO₂) Solutions from 20 to 60 °C
(Continued)**

C _{PZ} molal	C _{PZ} mol/kg	C _{CO2} mol/mol alk	C _{CO2} mol/kg	Density, ρ (kg/m ³)		
				T = 20 °C	T = 40 °C	T = 60 °C
9	4.68	0.15	1.453	1090.9	-	-
	4.59	0.20	1.879	1107.0	1096.1	1084.3
	4.52	0.26	2.347	1123.4	1112.8	1101.7
	4.41	0.30	2.714	1137.2	1127.0	1116.3
	4.33	0.36	3.169	1155.2	1145.3	1134.9
	4.24	0.40	3.471	1168.7	1158.9	1148.7
	4.14	0.44	3.695	1181.6	1171.7	-
10	4.80	0.25	2.436	1132.3	1121.2	1110.0
	4.73	0.31	2.875	1149.0	1138.7	1127.8
	4.69	0.36	3.343	1165.0	1154.9	1144.6
	4.41	0.41	3.726	1180.7	1170.8	1160.5
12	5.23	0.20	2.650	1121.9	1110.1	1097.8
	5.07	0.26	2.697	1139.8	1128.3	1116.7
	4.96	0.31	3.169	1156.9	1146.2	1135.3
	4.85	0.36	3.620	1173.6	1163.2	1152.7
	4.73	0.41	3.985	1189.5	1179.3	1169.0
20	6.96	0.10	1.338	1100.6	1084.7	1069.3
	6.70	0.16	2.123	1125.6	1110.8	1096.2
	6.53	0.20	2.577	1145.3	1131.3	1118.8
	6.47	0.25	3.137	1166.4	1153.7	1141.0

The ratio ρ/ρ_{water} is used to eliminate the temperature dependence of the data. At a given temperature, this ratio does not affect the trends observed. However, over a range of temperature the data collapse and the effect of C_{CO2} in relation to the effect of temperature on density is amplified. To demonstrate this effect, the temperature dependence of density and ρ/ρ_{water} are shown in Figure 4.1 for 2 and 8 m PZ (1.6 and 4.1 mole PZ per kg solution). The advantage of reporting ρ/ρ_{water} rather than density is that the effect of temperature can be minimized to focus on the effect of CO₂ concentration. This is a critical observation because the intent is to use on-line density meters in a CO₂

capture process to monitor CO₂ concentration. With regressions that eliminate the effect of temperature, the CO₂ concentration can be directly related to the density of the solution, allowing easy, inexpensive, on-line monitoring of CO₂ loading throughout a process.

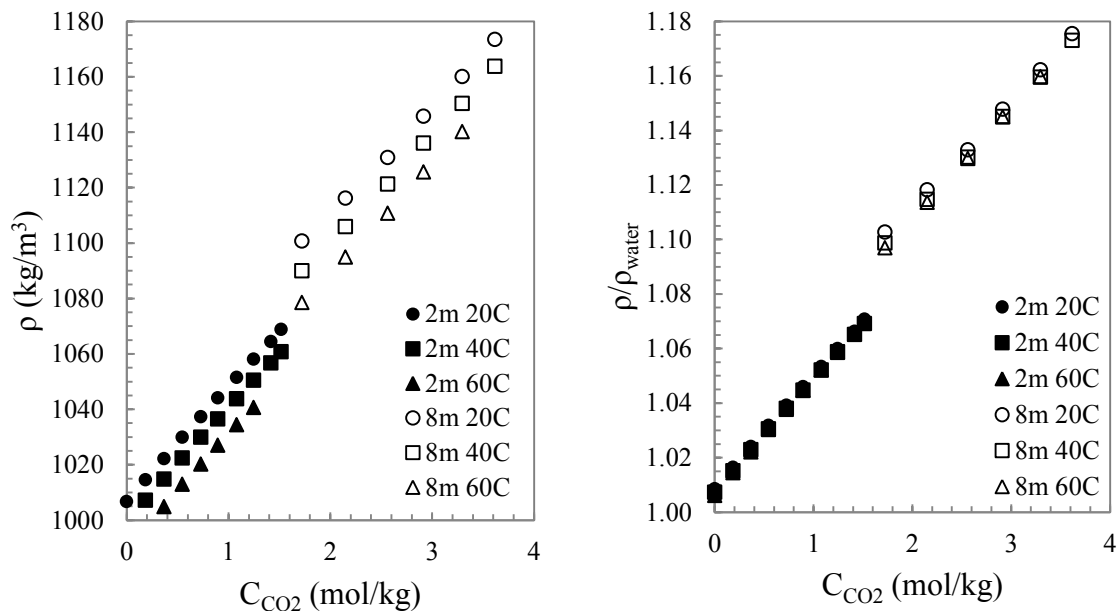


Figure 4.1: Density (ρ) (left panel) and ρ/ρ_{water} (right panel) as a function of CO₂ Concentration for aqueous PZ solutions.

All previous literature data reports density in the absence of CO₂ and only the 2 m PZ solution of this study does not precipitate in the absence of CO₂. All other density data reported in this manuscript contain CO₂. The density of 2 m PZ without CO₂ is shown along with previous literature data in Figure 4.2 (Derks et al., 2005; Muhammad et al., 2009; Samanta and Bandyopadhyay, 2006). The data of this study agree with literature values at 40 °C. At 60 °C, the data of Samanta and Bandyopadhyay (2006) appears to deviate at their highest PZ concentration while the data presented in this study agrees with that of Muhammed and colleagues (Muhammad et al., 2009).

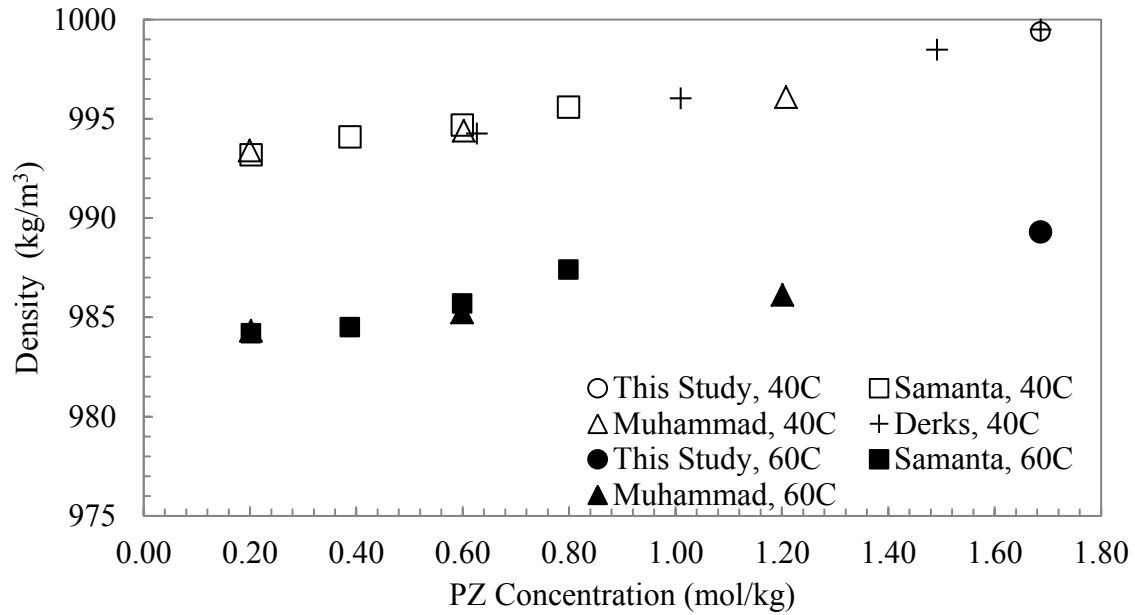


Figure 4.2: Comparison of density data for PZ without CO₂

The ρ/ρ_{water} of 2 to 20 m PZ at 40 °C are shown as a function of CO₂ concentration in Figure 4.3. Ignoring the 2 and 20 m PZ data, there is not a significant difference in the ρ/ρ_{water} of 5 to 12 m PZ when plotted in these units. The data collapse when observed in terms of ρ/ρ_{water} and C_{CO_2} in units of mole per kg, rather than density (ρ) and C_{CO_2} in units of mole per mole alkalinity.

The values for ρ/ρ_{water} for 5 to 12 m PZ were regressed over 20 to 60 °C using the least squares method as a function of C_{CO_2} and C_{PZ} , both in terms of mole per kg. The resulting regression is

$$\frac{\rho}{\rho_{\text{water}}} = 0.0407 \cdot C_{\text{CO}_2} + 0.008 \cdot C_{\text{PZ}} + 0.991 \quad (4.1)$$

where the standard error in the two coefficients and intercept were 0.00048 kg per mole CO₂, 0.00057 kg per mole PZ, and 0.002, respectively. The average error of the total data set was 0.24 % and the maximum error was 0.78 %. The regression predicts ρ/ρ_{water}

with similar accuracy across all three temperatures as the maximum error was 0.78 %, 0.60 %, and 0.49 % for data at 20, 40, and 60 °C, respectively. The error in predicting density rather than ρ/ρ_{water} is the same given the nature of the ratio used in the regression. The average absolute deviation (AAD) of a data set is defined as

$$AAD = \frac{1}{N} \sum_{i=1}^N \frac{|y_{\text{calc},i} - y_{\text{exp},i}|}{y_{\text{exp},i}} \quad (4.2)$$

where $y_{\text{calc},i}$ and $y_{\text{exp},i}$ are the calculated, or predicted, and experiment values of the dependent variable of interest, y , and N is the total number of data points. Using Equation 4.2, the AAD of Equation 4.1 with the density data for 5 to 12 m PZ at all temperatures was 0.0024, indicating that Equation 4.1 represents the data well.

The experimental ρ/ρ_{water} data at 40 °C are compared with the regression (Equation 4.1) in Figure 4.3. The prediction of Equation 4.1 is shown for 5, 8, and 12 m data to demonstrate the fit without cluttering the figure. The data for 2 and 20 m PZ were excluded from this regression but still appear in Figure 4.3 for reference. Although the regression is not intended for these PZ concentrations, a prediction for 2 and 20 m PZ yields an average error of 0.57 % and a maximum error of 1.48 %. The robustness of Equation 4.1 is demonstrated in the low error obtained when predicting data outside of the concentration ranges of data that were included in the original regression.

Only data at 40 °C are shown in Figure 4.3 for clarity and because of the importance of this temperature in the absorber side of an absorber/stripper CO₂ capture system. To encompass the entire data set, a parity plot comparing the experimental data to the predictions of ρ/ρ_{water} from Equation 4.1 for 20 to 60 °C and all PZ concentrations is shown in Figure 4.4. The data for 2 and 20 m PZ are highlighted with open points since they were not included in the regression of Equation 4.1.

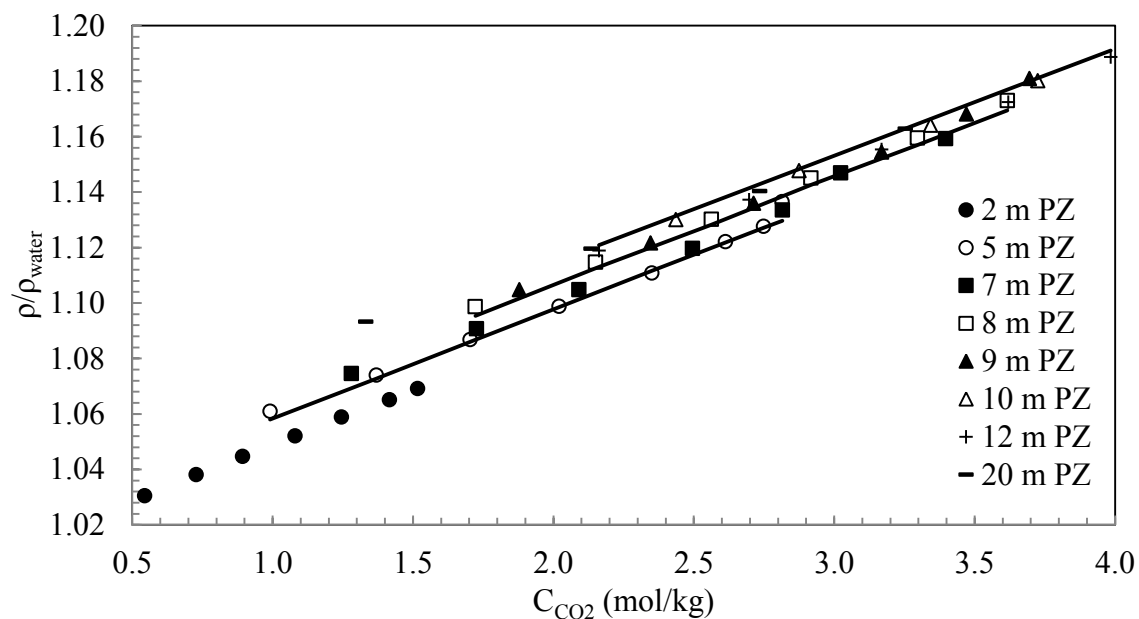


Figure 4.3: Comparison of ρ/ρ_{water} to the prediction of Equation 4.1 (solid lines; predicted for 5, 8, and 12 m PZ) at 40 °C

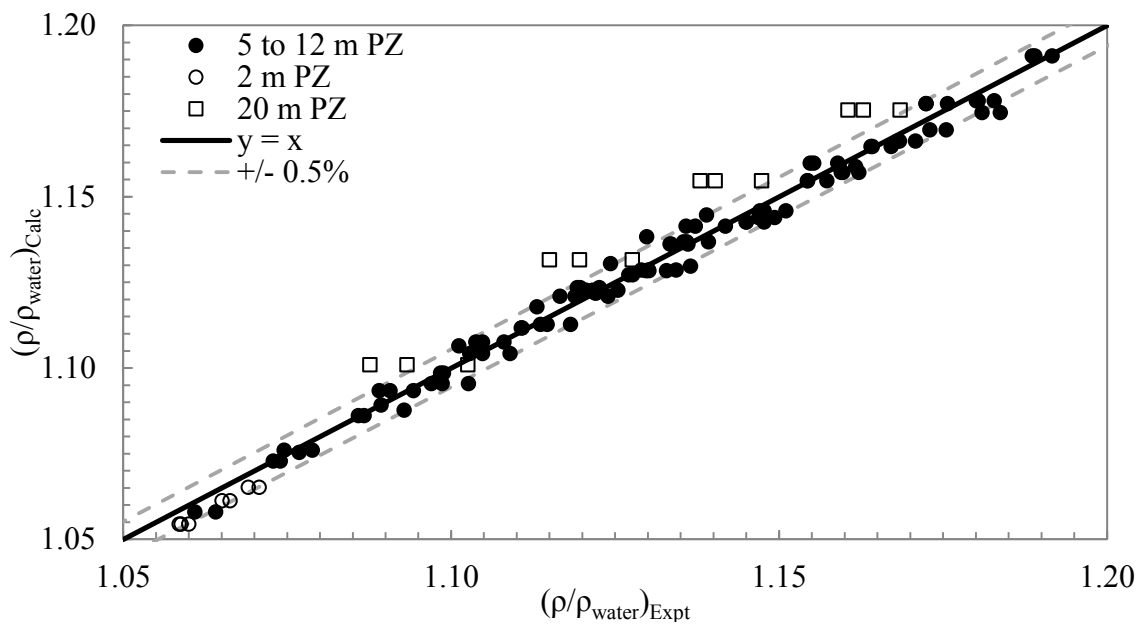


Figure 4.4: Parity plot demonstrating the accuracy of Equation 4.1 for predicting ρ/ρ_{water} from 20 to 60 °C

4.4 VISCOSITY OF CONCENTRATED PZ

The measured viscosity (μ) of aqueous (PZ + CO₂) as a function of C_{PZ} , C_{CO_2} , and temperature is given in Table 4.2. As with density measurements, previous literature has only reported viscosity of aqueous PZ solutions at low concentration without CO₂. Therefore, the only data from this study that are comparable to literature is a 2 m PZ solution in the absence of CO₂. The viscosity of this solution is compared with previous data in Figure 4.5 as a function of C_{PZ} in terms of mole per kg (Derks et al., 2005; Muhammad et al., 2009; Samanta and Bandyopadhyay, 2006). The viscosity data at 40 °C are in agreement with literature values. At 60 °C, the data of Muhammed and colleagues (Muhammad et al., 2009) appear to predict lower viscosity (μ) in comparison with the current study at higher C_{PZ} . There is no literature data at 60 °C above a C_{PZ} of 1.25, so it is not clear if the literature data or the current study predicts the more correct trend. The previous section demonstrated that the current study matched the results of Muhammed and colleagues (Muhammad et al., 2009) while that of Samanta and Bandyopadhyay (Samanta and Bandyopadhyay, 2006) appeared to deviate with increasing PZ concentration at 60 °C (Figure 4.2).

An extended set of viscosity data for 8 m PZ was obtained over a wider range of temperature than the other PZ concentrations and the data are shown in Table 4.3. The importance of 8 m PZ in planned and future industrial applications called for a wider range of data and a correlation to predict viscosity for this concentration. A correlation was created from the 8 m PZ data to relate the ratio of viscosity to the viscosity of water (μ/μ_{water}) to temperature (K), C_{CO_2} (mole per kg), and C_{PZ} (mole per kg), and has the form of

$$\ln\left(\frac{\mu}{\mu_{\text{water}}}\right) = a_1 + \Phi_1 + \frac{\Phi_2}{T} \quad (4.3)$$

Table 4.2: Viscosity (μ) of Aqueous (PZ + CO₂) Solutions from 25 to 60 °C

C _{PZ} m	C _{PZ} mol/kg	C _{CO2} mol/mol alk	C _{CO2} mol/kg	Viscosity, μ (mPa-s)					
				25 °C		40 °C		60 °C	
2	1.67	0.00	0.000	1.877	± 0.011	1.307	± 0.016	0.895	± 0.016
	1.64	0.05	0.186	1.896	± 0.007	1.334	± 0.014	0.906	± 0.020
	1.64	0.11	0.366	1.910	± 0.008	1.348	± 0.018	0.933	± 0.020
	1.63	0.16	0.545	1.917	± 0.008	1.371	± 0.015	0.942	± 0.018
	1.61	0.22	0.728	1.930	± 0.009	1.386	± 0.013	0.984	± 0.017
	1.61	0.25	0.894	1.952	± 0.006	1.414	± 0.018	0.984	± 0.018
	1.59	0.32	1.080	1.961	± 0.007	1.423	± 0.016	1.015	± 0.017
	1.58	0.38	1.246	1.971	± 0.010	1.439	± 0.011	1.021	± 0.017
	1.57	0.44	1.416	1.977	± 0.009	1.455	± 0.014	1.043	± 0.029
	1.55	0.47	1.516	1.968	± 0.013	1.468	± 0.041	-	-
5	3.25	0.22	1.433	-	-	3.231	± 0.012	1.946	± 0.018
	3.21	0.28	1.780	5.336	± 0.039	3.346	± 0.015	2.028	± 0.019
	3.16	0.35	2.216	5.457	± 0.022	3.464	± 0.007	2.144	± 0.021
	3.11	0.40	2.504	5.872	± 0.018	3.612	± 0.011	2.230	± 0.023
	3.06	0.46	2.822	5.927	± 0.015	3.689	± 0.014	2.309	± 0.019
	3.03	0.50	3.023	5.941	± 0.014	3.752	± 0.014	2.366	± 0.033
	3.01	0.53	3.182	6.010	± 0.018	3.751	± 0.010	2.502	± 0.022
7	4.01	0.21	1.726	10.85	± 0.053	6.347	± 0.039	3.543	± 0.050
	3.93	0.26	2.091	11.34	± 0.052	6.484	± 0.053	3.720	± 0.058
	3.86	0.32	2.495	11.60	± 0.000	6.929	± 0.070	4.218	± 0.057
	3.81	0.37	2.815	12.34	± 0.052	7.222	± 0.076	4.810	± 0.216
	3.72	0.40	3.023	12.60	± 0.047	7.617	± 0.082	4.849	± 0.104
	3.68	0.46	3.397	12.82	± 0.063	7.854	± 0.094	5.270	± 0.243
9	4.59	0.20	1.879	20.82	± 0.042	11.09	± 0.088	5.659	± 0.036
	4.52	0.26	2.347	22.03	± 0.048	12.09	± 0.120	6.318	± 0.060
	4.41	0.30	2.714	23.10	± 0.047	12.60	± 0.105	7.562	± 0.143
	4.33	0.36	3.169	23.99	± 0.032	13.90	± 0.115	8.442	± 0.186
	4.24	0.40	3.471	25.34	± 0.052	14.62	± 0.132	9.162	± 0.214
	4.14	0.44	3.695	26.72	± 0.079	15.21	± 0.110	10.24	± 0.466
10	4.80	0.25	2.436	31.37	± 0.189	16.92	± 0.253	9.084	± 0.069
	4.73	0.31	2.875	33.42	± 0.220	18.08	± 0.210	9.781	± 0.342
	4.69	0.36	3.343	35.45	± 0.227	19.89	± 0.407	11.06	± 0.237
	4.41	0.41	3.726	37.48	± 0.352	21.18	± 0.239	11.88	± 0.352

**Table 4.2: Viscosity (μ) of Aqueous (PZ + CO₂) Solutions from 25 to 60 °C
(continued)**

C _{PZ} m	C _{PZ} mol/kg	C _{CO2} mol/mol alk	C _{CO2} mol/kg	Viscosity, μ (mPa-s)					
				25 °C		40 °C		60 °C	
12	5.23	0.20	2.650	49.35	± 0.127	23.62	± 0.286	10.22	± 0.162
	5.07	0.26	2.697	52.68	± 0.181	26.01	± 0.213	11.78	± 0.294
	4.96	0.31	3.169	57.22	± 0.297	27.18	± 0.215	13.34	± 0.255
	4.85	0.36	3.620	60.17	± 0.236	31.42	± 0.413	15.11	± 0.213
	4.73	0.41	3.985	63.22	± 0.361	33.43	± 0.316	18.32	± 0.290
20	6.70	0.16	2.123	304.1	± 0.994	95.61	± 0.357	30.00	± 0.176
	6.53	0.20	2.577	373.1	± 0.994	120.3	± 0.483	40.88	± 0.286
	6.47	0.25	3.137	534.3	± 2.058	138.9	± 0.994	57.14	± 0.420

Table 4.3: Viscosity of 8 m PZ from 20 to 70 °C

C _{PZ} mol/kg	C _{CO2} mol/mol alk	C _{CO2} mol/kg	Temperature °C	Viscosity mPa-s		
4.26	0.24	2.150	20	20.30	±	0.09
4.12	0.29	2.563	20	20.93	±	0.08
4.11	0.35	2.917	20	22.21	±	0.10
3.98	0.40	3.297	20	22.78	±	0.12
4.26	0.24	2.150	25	16.50	±	0.17
4.12	0.29	2.563	25	17.14	±	0.13
4.11	0.35	2.917	25	18.19	±	0.13
3.98	0.40	3.297	25	18.76	±	0.12
4.26	0.24	2.150	30	12.93	±	0.11
4.12	0.29	2.563	30	13.54	±	0.13
4.11	0.35	2.917	30	14.56	±	0.13
3.98	0.40	3.297	30	15.24	±	0.21
4.26	0.24	2.150	40	9.460	±	0.14
4.12	0.29	2.563	40	9.988	±	0.17
4.11	0.35	2.917	40	10.79	±	0.17
3.98	0.40	3.297	40	11.37	±	0.19
4.26	0.24	2.150	50	6.586	±	0.06
4.12	0.29	2.563	50	7.072	±	0.07
4.11	0.35	2.917	50	7.580	±	0.04
3.98	0.40	3.297	50	8.322	±	0.08
4.26	0.24	2.150	60	5.351	±	0.06
4.12	0.29	2.563	60	5.769	±	0.06
4.11	0.35	2.917	60	6.466	±	0.06
3.98	0.40	3.297	60	6.905	±	0.07
4.26	0.24	2.150	70	3.919	±	0.05
4.12	0.29	2.563	70	4.509	±	0.05
4.11	0.35	2.917	70	4.683	±	0.05
3.98	0.40	3.297	70	5.152	±	0.05

where

$$\Phi_i = b_i \cdot C_{CO2} + c_i \cdot C_{PZ} + d_i \cdot C_{CO2} \cdot C_{PZ} \quad (4.4)$$

The values of the regressed parameters can be found in Table 4.4. Values for μ_{water} over the range of 20 to 70 °C were taken from the DIPPR Database (DIPPR, 2010). The resulting correlation (Equation 4.3) was able to fit all experimental μ/μ_{water} data within 2.4 %. The average absolute deviation (AAD) calculated using Equation 4.2 for the prediction of viscosity data was 0.028 indicating the data set is well represented by Equation 4.3.

Rearranging the above regression (Equation 4.3) leaves a relationship which predicts the viscosity of 8 m PZ with an average deviation of less than 3 % (maximum deviation of 6 %) (Equation 4.5).

$$\mu = \mu_{\text{water}} \cdot \exp\left(a_1 + \Phi_1 + \frac{\Phi_2}{T}\right) \quad (4.5)$$

The experimental viscosity data from Table 4.3 is compared to the prediction of Equation 4.5 in Figure 4.6. A parity plot comparing the experimental viscosity data to the values predicted using Equation 4.5 is shown in Figure 4.7 with 5 % deviation shown with dashed lines.

Table 4.4: Value of parameters in Equation 4.3

Parameter	i = 1	i = 2
a	1.723	-
b	2.63	-778
c	-1.019	355.2
d	-0.527	169.3

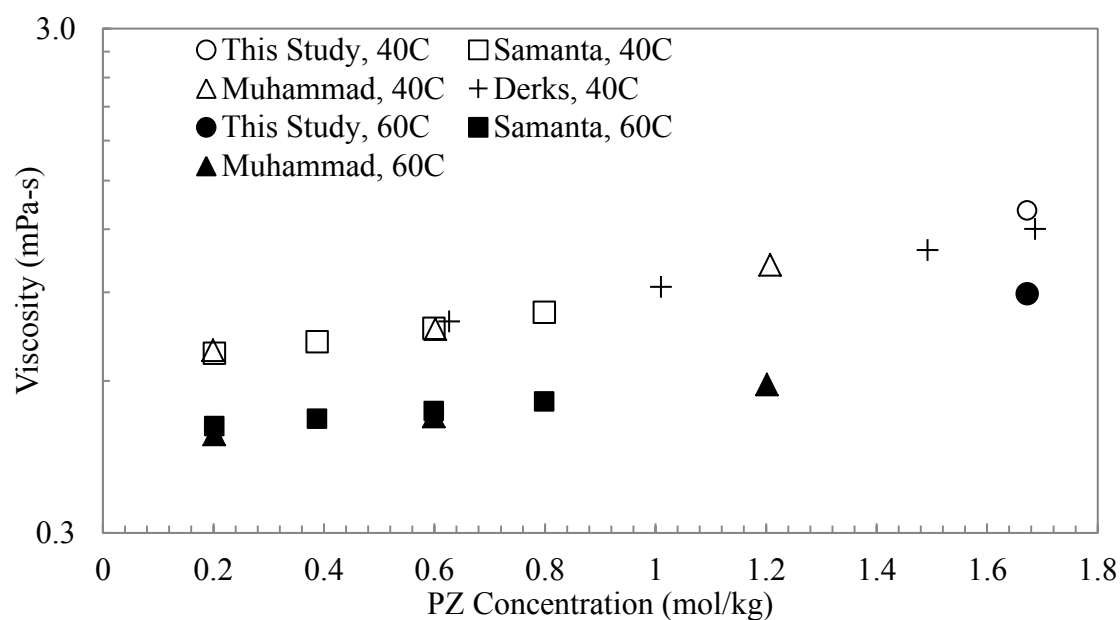


Figure 4.5: Comparison of viscosity data for PZ without CO₂

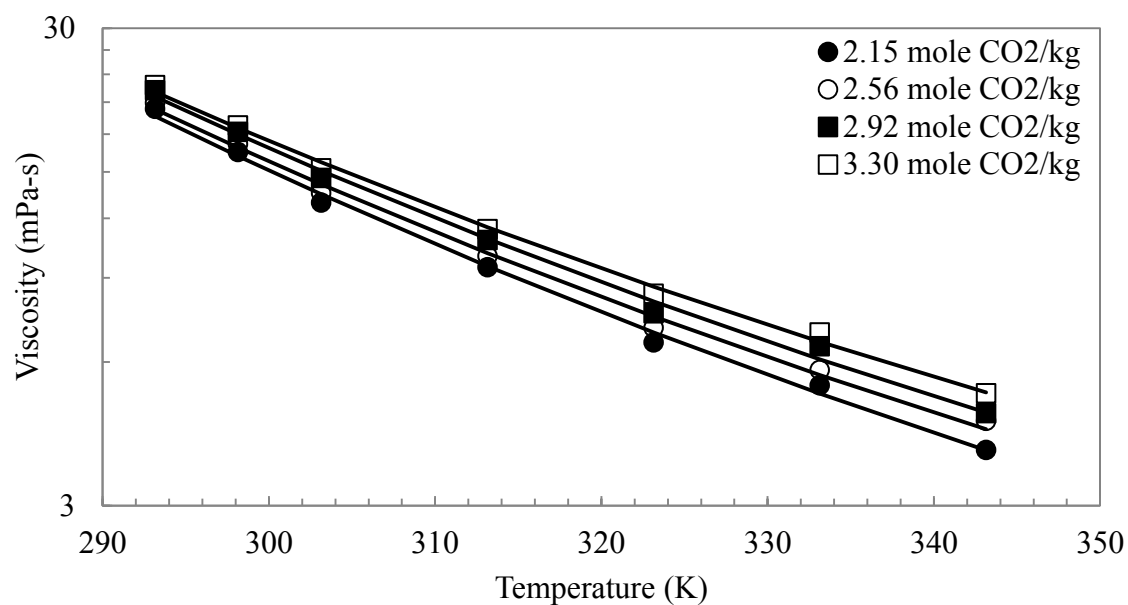


Figure 4.6: Comparison of the viscosity (μ) of 8 m PZ to the prediction of Equation 4.5 (solid lines) over a range of CO₂ concentrations

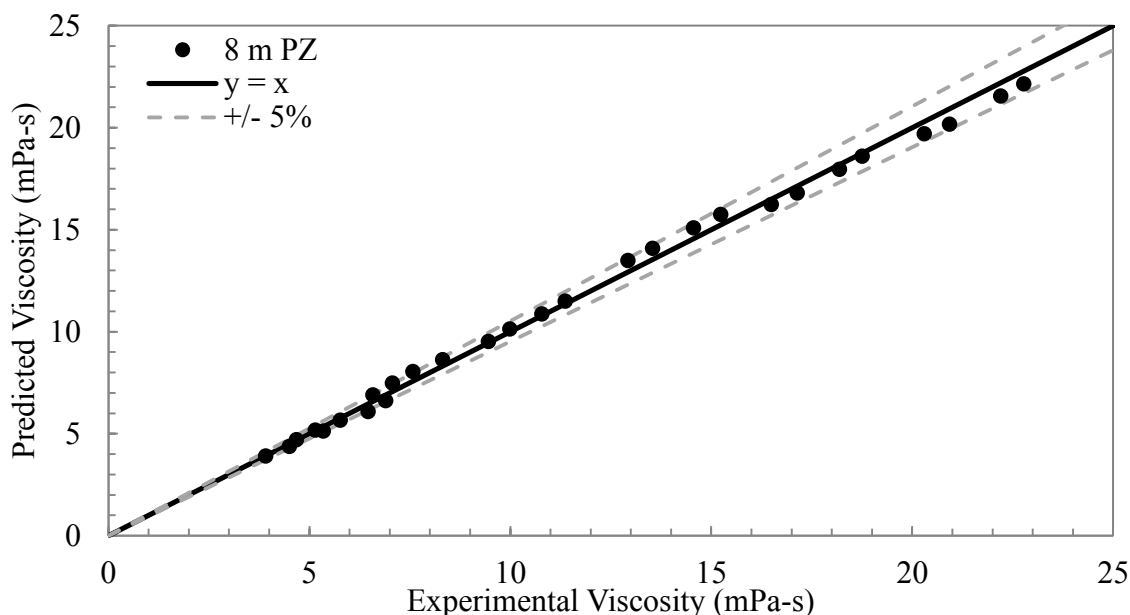


Figure 4.7: Parity plot demonstrating the accuracy of Equation 4.5 for predicting viscosity of 8 m PZ solutions at 20 to 70 °C

4.5.1 Choice of 8 m PZ based on viscosity

The viscosity of aqueous PZ increases rapidly with increased PZ concentration, as seen in the previous section. This high viscosity limits the PZ concentration applicable in CO₂ capture systems. The viscosity of 7 to 10 m PZ is compared with 7 to 13 m MEA, 7 m MDEA, 7 m MDEA / 2 m PZ, and 60wt% DGA[®] in Figure 4.8 (Huntsman Corporation, 2005; Closmann et al., 2009). The amine concentration is plotted in units of moles alkalinity per kilogram of water in order to compare mono- and diamines on a similar basis. All of the viscosities compared are at 40°C and at the rich loading of the system (0.3 mole CO₂ per mole alkalinity for MDEA and MDEA/PZ blend; 0.4 mole CO₂ per mole alkalinity for PZ and DGA; 0.5 mole CO₂ per mole alkalinity for MEA).

Comparison of the viscosity on this basis shows how the amine basic group affects overall viscosity. As the concentration of basic groups increases in a molecule, the viscosity increases. The viscosity of 8 m PZ is higher than that of 7 m MEA, but as

compared to 60 wt % DGA[®], the viscosity of PZ is lower for a higher alkalinity. Therefore, PZ has the advantage of having two amine functional groups without suffering an increase in viscosity over DGA[®]. DGA[®] solutions at 60 wt % are successfully used in natural gas treating, which indicates that a PZ solution of a similar viscosity value should be possible (Al-Juaied and Rochelle, 2006b; Al-Juaied, 2004). The viscosity value of 8 m PZ with 0.4 mole CO₂ per mole alkalinity is one reason for the choice of 8 m PZ as the best concentrated PZ system.

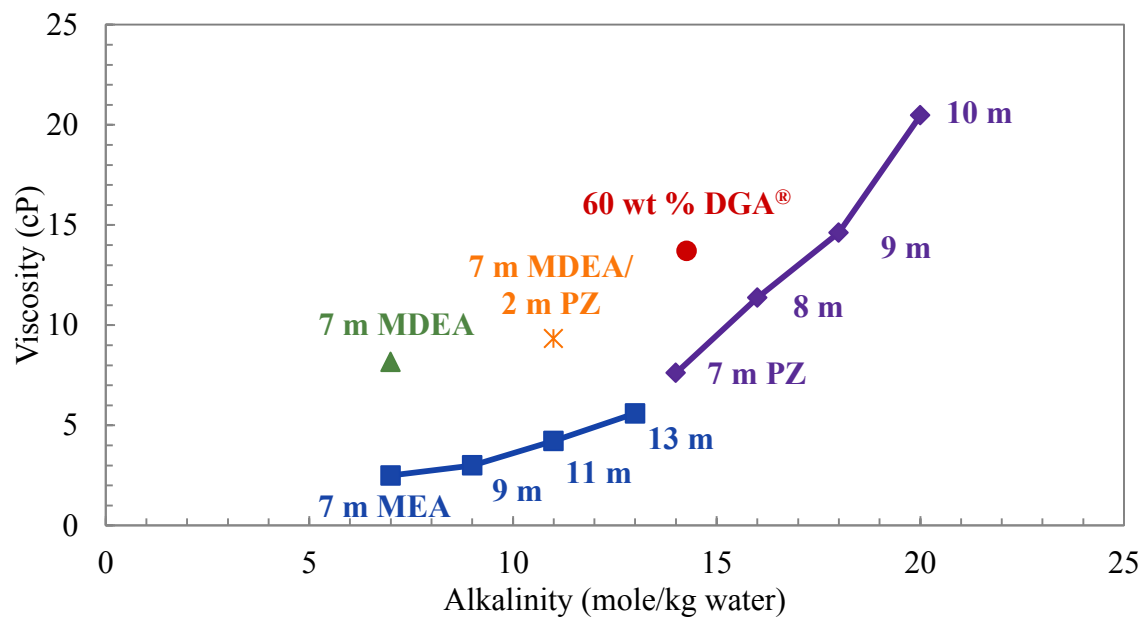


Figure 4.8: Viscosity of Amine Solutions at Typical Rich Loading and 40 °C

4.5 SOLID-LIQUID EQUILIBRIUM OF CONCENTRATED PZ

The solubility of PZ solutions is a crucial operational parameter for a concentrated PZ CO₂ capture system. In an effort to elucidate the solid-liquid equilibrium (SLE) behavior of PZ, two types of measurements were taken during this project. First, solutions with or without PZ precipitation were analyzed to understand the regions of insolubility. This was a more ‘shotgun’ approach to the issue of solubility by first

analyzing PZ solutions over a range of PZ concentration, CO₂ loadings (CO₂ concentrations), and temperatures. Second, transition temperatures were measured for a variety of solutions to accurately gauge the exact transition temperature for a given solution with a set PZ concentration and CO₂ loading.

4.5.1 Regions of insolubility for concentrated PZ

To examine the regions of insolubility for concentrated PZ, a database was created for all solutions that could be analyzed. Any PZ solutions that were analyzed for concentration and CO₂ loading were included in a database of solubility data. This included solutions used for other experiments (i.e. degradation experiments) or made in particular for solubility experiments. This database included only PZ solutions, no blends of PZ with other substituted PZ or other amines. Solutions were classified as soluble, where no evidence of precipitation was found, or insoluble where there was either complete precipitation, some precipitation on the bottom of the bottle, or a slurry existed. For insoluble solutions, the supernatant was generally analyzed for PZ and CO₂ concentration. This may have caused additional error since the supernatant may not accurately represent the overall solution characteristics that produced the precipitation. It would have been more accurate to heat each solution up that contained precipitate until it fully melted in order to measure the overall solution characteristics that led to insolubility. Measuring the supernatant likely led to the regions of solubility and insolubility to overlap on a few occasions.

The goal of this database was to quickly establish regions of insolubility within the typical operation range of a CO₂ capture system. The data are presented below in Figure 4.9, Figure 4.10, and Figure 4.11 as plots of CO₂ loading against PZ concentration for a given temperature. In each figure, soluble solutions are indicated with a filled point

(●) while insoluble solutions are indicated with an open point (○). The line on each figure is the prediction of the SLE for each temperature provided by the Aspen model of Hilliard (Hilliard, 2008). The data from Hilliard are provided to demonstrate that physical solubility of PZ was not correctly predicted with the early versions of PZ thermodynamic models.

The regions of insolubility for concentrated PZ are shown in Figure 4.9 at 21 °C or room temperature. The room temperature data demonstrate a few of the issues discovered when analyzing the supernatant versus the total solution. The point containing about 10 m PZ with a loading of 0.35 mole CO₂ per mole alkalinity, for example, is surrounded by soluble points and was likely analyzed with a large amount of error. The ability of the Hilliard model to predict solubility is demonstrated by the solid line in Figure 4.9. For low concentration PZ, the prediction is good but deviates with higher concentrations of PZ. This is expected since there was a dearth of high concentration PZ data available when Hilliard was modeling PZ thermodynamics.

In the insoluble regions at low loadings, the solid is predicted to be PZ hexahydrate (PZ·6H₂O) which represents the solution simply meeting the solubility limit of the anhydrous PZ·6H₂O used to make PZ solutions, but this was not confirmed with XRD. In this region, the speciation indicates low concentrations of H⁺PZ and PZCOO⁻ in comparison to free PZ. X-ray diffraction (XRD) analysis of a solution that was overloaded and precipitated at high CO₂ loadings indicated that the precipitated crystals were protonated PZ carbamate hydrate (H⁺PZCOO⁻·H₂O) (Xu, 2008). This is expected to occur in regions of rich CO₂ loading where the concentration of H⁺PZCOO⁻ is significantly higher than free PZ, H⁺PZ, or PZCOO⁻.

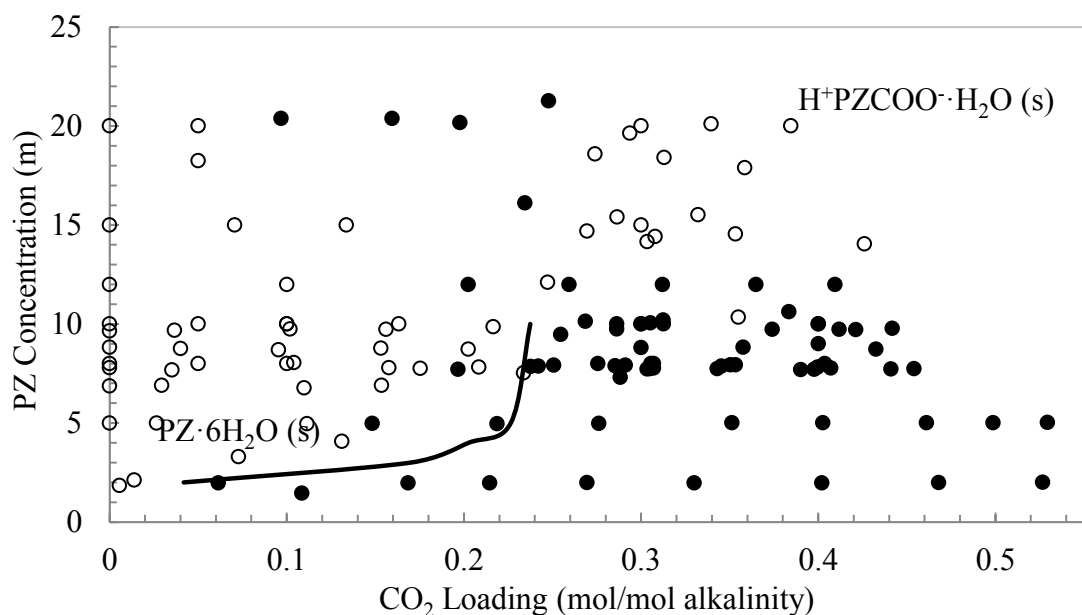


Figure 4.9: Regions of insolubility for concentrated PZ at 21 °C; data: ●, soluble solutions; ○, insoluble solutions; line: prediction of (Hilliard, 2008)

The regions of insolubility measured for 40 °C are shown in Figure 4.10. This data set includes solutions analyzed during the course of this thesis and those from the thesis of Hilliard during his measurement of vapor-liquid equilibrium (Hilliard, 2008). Hilliard performed a set of measurements at 40 °C on a variety of solutions and solutions without precipitation were required to get accurate results. Therefore, the solutions Hilliard analyzed are assumed to be free of insolubility. The predictions from Hilliard were not as extensive for 40 °C and only two points make up the predicted solubility curve in Figure 4.10. The lean loading region of insolubility at 40 °C is not as large as at room temperature, so an estimation of where $\text{PZ} \cdot 6\text{H}_2\text{O}$ is the likely precipitate is not indicated. It is still expected that rich precipitation will likely contain a majority of $\text{H}^+\text{PZCOO}^- \cdot \text{H}_2\text{O}$.

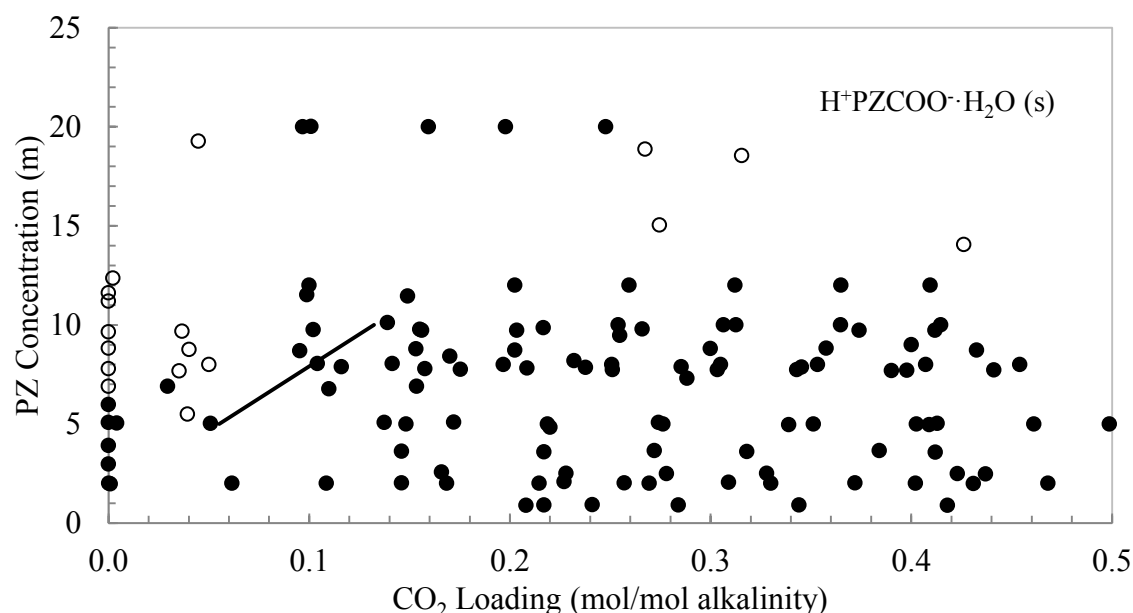


Figure 4.10: Regions of insolubility for concentrated PZ at 40 °C; data: ●, soluble solutions; ○, insoluble solutions; line: prediction of (Hilliard, 2008)

The solubility database also includes data at 60 °C which are shown in Figure 4.11. Most PZ solutions are soluble at this temperature, so there were few solutions found to be insoluble at this temperature. The Hilliard thermodynamic model did not predict SLE at this temperature so a model line is not included in Figure 4.11 (Hilliard, 2008). The solutions that were insoluble at 60 °C appear to indicate that some regions of high PZ concentration and rich loading will still not be soluble at this high temperature condition. This was not expected and would need to be investigated further to avoid precipitation in any real systems that may operate in this region. Solutions ranging from 0 to 12 m PZ were found to be completely soluble over a range of CO₂ loadings. This demonstrates that a concentrated PZ solvent will not likely experience insolubility during normal operation in a real CO₂ capture system if kept warm and not extremely rich in CO₂.

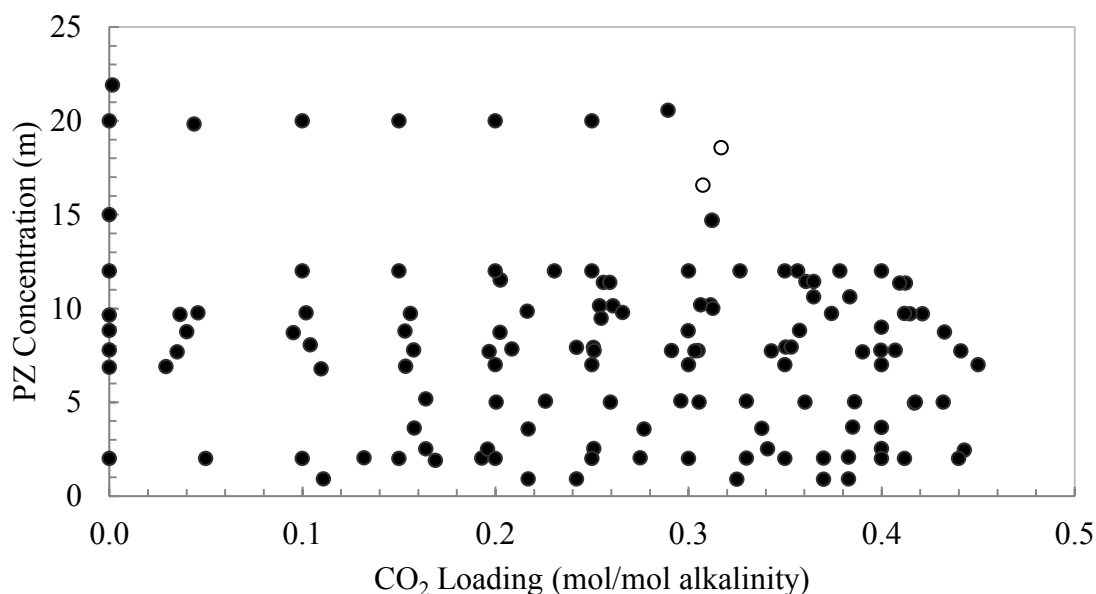


Figure 4.11: Regions of insolubility for concentrated PZ at 60 °C Data: ●, soluble solutions; ○, insoluble solutions

4.5.2 Transition temperature of concentrated PZ

One important characteristic of the SLE of concentrated PZ solutions is the transition temperature, or temperature at which a solution transitioned between liquid and solid for a given PZ concentration and CO₂ loading. This is a helpful parameter to understand in order to control a PZ solution in service and maintain a liquid solution when operating a CO₂ capture system. The transition temperature was measured as described previously and above in Section 4.2 and all values measured in this project are summarized in Table 4.5 (Freeman et al., 2010b). Provided PZ concentrations in molal are approximate while the PZ concentration in weight percent was determined from acid titration and CO₂ loading was measured with TIC.

Table 4.5: Transition temperatures for 3 to 25 m PZ

PZ Conc. m	PZ Conc. wt %	CO ₂ Loading mol/mol alk	Crystal Temp °C	Melting Temp °C
3	20.4	0	29.5	31
4	25.2	0	32.0	35.5
5	30.4	0	36.0	38.5
6	34.0	0	40.0	41
7	37.3	0	41.8	43.5
7	36.4	0.029	39.5	40.5
7	35.8	0.110	36.5	37.5
7	35.1	0.153	33	34.5
8	40.1	0	43.0	45
8	39.2	0.035	40.0	41
8	39.2	0.104	38.5	39.5
8	37.7	0.158	33.0	34.5
8	37.1	0.209	26.5	29
8	36.2	0.251	18.0	22.5
8	35.5	0.303	3.0	10
8	35.0	0.343	0.0	0
9	43.2	0	43.0	44
9	42.2	0.040	40.5	41.2
9	41.1	0.095	38.0	39
9	40.3	0.153	33.5	35
9	39.4	0.202	29.0	30.5
9	40.4	0.255	21.0	24
9	38.1	0.300	7.0	15
9	37.2	0.358	0.0	0
10	45.4	0	43	44
10	44.7	0.037	40.5	41.5
10	43.6	0.102	38.5	39.5
10	42.5	0.156	35.0	36
10	41.6	0.217	27.0	31
10	40.6	0.266	18.0	23
10	38.7	0.313	5.5	13
10	38.2	0.374	0.0	0
11	49.1	0	42.5	44
12	50.0	0	41.5	42.5
12	47.2	0.1	37.0	38.5
15	56.3	0	36.0	38.5
20	61.9	0	41.5	44
25	69.4	0	49.0	55.5

The transition temperature of unloaded PZ solutions ranging from 1.0 to 20 m PZ are compared to data available in literature with up to 80 wt% PZ in Figure 4.12 (The Dow Chemical Company, 2001; Bishnoi, 2000; Corporation, ; Hilliard, 2008; Muhammad et al., 2009). The data from this study show a eutectic point at 19 m PZ (60 wt %) that was also observed in the data from The Dow Chemical Company (2001) and Hilliard (2008). The solubility of anhydrous PZ at 20 °C, or room temperature, is 14 wt % PZ, which corresponds to 1.9 m PZ. The data from this study agrees with the data from the Dow Chemical Company. The data from Hilliard (2008) over predict the transition temperature between up to a mass fraction of PZ of 0.6. The method used to obtain this data, a Differential Scanning Calorimeter (DSC), used a temperature ramp of 5 °C per minute, would may not have allowed enough time for equilibrium and even heating of the sample to correctly predict the transition point. The measurements of both Bishnoi and Muhammed did not observe the eutectic point because their methods involved allowing a known quantity of PZ to reach equilibrium at a given temperature while any precipitation settled out (Bishnoi, 2000; Muhammad et al., 2009). Then, the supernatant liquid was analyzed to provide a solubility limit at that temperature condition. The eutectic point would not be able to be observed in this way because at a range of temperatures, there would be three possible compositions of PZ in the supernatant. The data outside of the range of the eutectic point agree nicely with the data from this study and that of The Dow Chemical Company (2001).

The transition temperature of 5, 7, 8, 9, 10, and 12 m PZ solutions over a range of CO₂ loading were measured and are shown in Figure 4.13. The shape and location of the transition temperature curve does not vary significantly over the concentration range of 7 to 12 m PZ. Also, the unloaded transition temperature is nearly identical over the range of PZ concentrations.

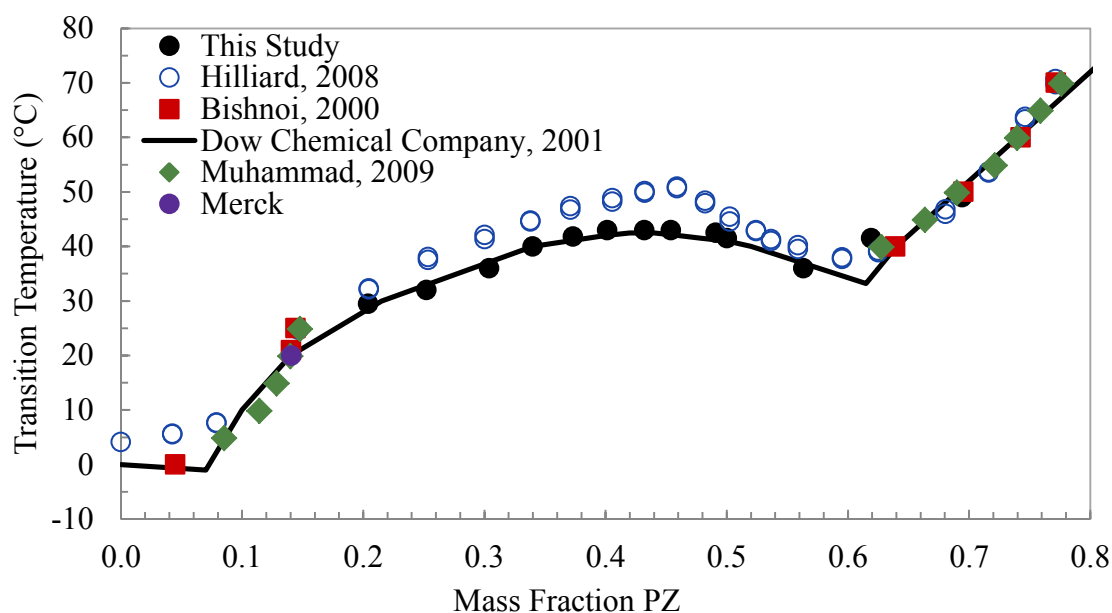


Figure 4.12: Comparison of transition temperatures of unloaded PZ

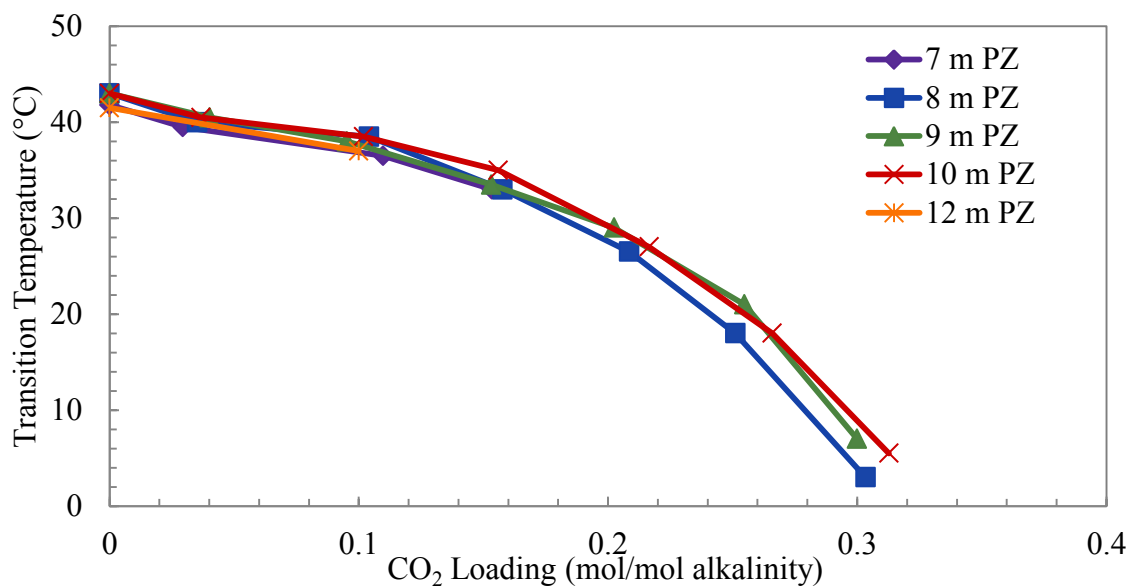


Figure 4.13: Crystal transition temperatures for 7 to 12 m PZ

As mentioned in section 4.2, two temperatures were recorded for each measurement, the crystal temperature and the melting temperature. The crystal temperature is the temperature plotted in Figure 4.13 since crystallization is the most likely concern for this system. An example of the hysteresis seen in the SLE of PZ is shown in Figure 4.14. In these measurements, the temperature at which a transition was visually observed was different depending on whether a liquid solution was cooled or a solid or slurry was heated.

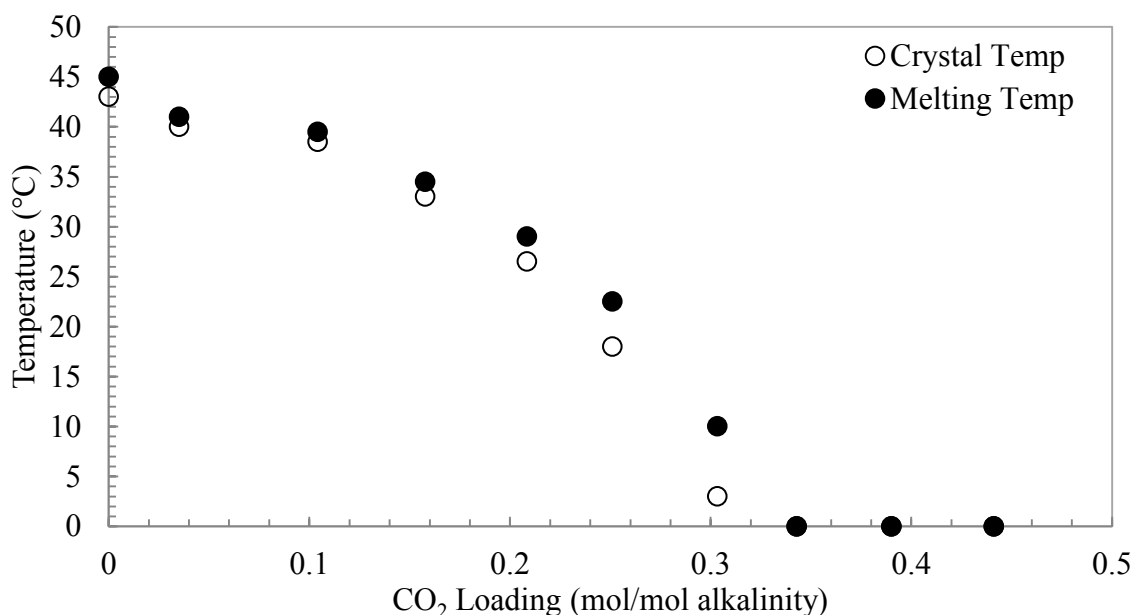


Figure 4.14: Example of hysteresis in SLE data for 8 m PZ

The solubility envelope for 8 and 10 m PZ is shown again in Figure 4.15 to highlight these two concentrations that are the most important for future industrial application. The two dashed lines at rich loadings in Figure 4.15 represent soluble PZ solutions indicating that the solubility envelope extends at least this high in CO₂ loading. These four data points represent the richest soluble solutions that were obtained at 0 and 40 °C during the solubility studies. Beneath the transition temperature line, at low

temperatures and lean CO_2 loading, a precipitate will likely be $\text{PZ} \cdot 6\text{H}_2\text{O}$ while rich loading precipitation, as shown in the figure, has been shown to be $\text{H}^+\text{PZCOO}^- \cdot \text{H}_2\text{O}$ (Xu, 2008). The envelope also demonstrates that for 8 m PZ a CO_2 loading of approximately 0.25 mole CO_2 per mole of alkalinity is required to maintain a liquid solution without precipitation at room temperature (20°C).

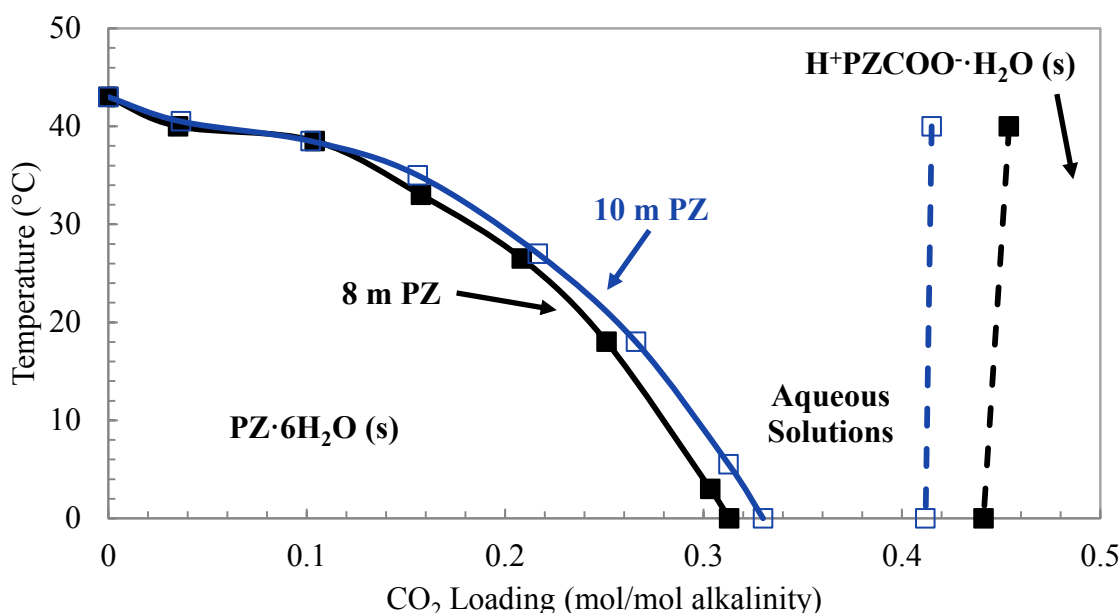


Figure 4.15: Solubility envelope for 8 and 10 m PZ

4.6 PHYSICAL PROPERTIES OF PZ BLENDS

A blend of PZ, 1-methylpiperazine (1-MPZ), and 1,4-dimethylpiperazine (1,4-DMPZ) was identified as potential novel amine system for CO_2 capture based on thermal degradation experiments. This blend is advantageous because 1-MPZ by itself was found to degrade to nearly equal parts PZ and 1,4-DMPZ, creating an equilibrium between the three molecules (see Section 7.3 for details). Because of this behavior, a blend of PZ, 1-MPZ, and 1,4-DMPZ was believed to be a good solvent because the equilibrium between the molecules would limit degradation to other amines and there was a potential cost

savings in the manufacturing of the amine blend due to decreased separation costs. One blend that was specifically identified as potentially useful was 5 m PZ / 2 m 1-MPZ / 1 m 1,4-DMPZ. The density and viscosity of this blend was measured in the same way described previously for concentrated PZ. In addition, the viscosity of 4 m PZ / 4 m 1-MPZ, 5 m PZ / 5 m 1-MPZ, and 4 m PZ / 1,4-DMPZ were each measured and are reported below. Blends of PZ with 2-MPZ were investigated as potentially favorable solvent systems as well. Densities over a range of loadings were measured for 4 m PZ / 4 m 2-MPZ and 5 m PZ / 5 m 2-MPZ.

4.6.1 Density of 5 m PZ / 2 m 1-MPZ / 1 m 1,4-DMPZ

The density of 5 m PZ / 2 m 1-MPZ / 1 m 1,4-DMPZ was measured over a range of CO₂ loadings from 0 to 0.39 and over a range of temperatures from 10 to 80 °C (283.15 to 353.15 K). Data were obtained for all solutions where precipitation and CO₂ evolution was absent. The raw data are shown in Table 4.6 while the data are plotted in Figure 4.16. The data demonstrate the expected trends of an increase of density with increasing CO₂ loading and decreasing temperature.

4.6.2 Viscosity of 5 m PZ / 2 m 1-MPZ / 1 m 1,4-DMPZ

The viscosity of a blend of 5 m PZ / 2 m 1-MPZ / 1 m 1,4-DMPZ was measured over a range of CO₂ loading from 0 to 0.39 and from 10 to 80 °C. Data were obtained for all solutions where precipitation and CO₂ evolution was absent. The raw data obtained are shown in Table 4.6 and Figure 4.17. The data demonstrate the expected trend that viscosity increases with increasing CO₂ concentration and decreasing temperature.

Table 4.6: Density and Viscosity of 5 m PZ / 2 m 1-MPZ / 1 m 1,4-DMPZ from 10 to 80 °C

CO ₂ Loading mol/mol alk	CO ₂ Conc. mol/kg	T °C	Density (ρ) g·cm ³	Viscosity (μ) mPa-s		
0.2	1.661	10	1.0937	42.320	±	0.042
0.23	1.900	10	1.1031	42.940	±	0.070
0.29	2.411	10	1.1221	44.240	±	0.070
0.33	2.680	10	1.1358	44.440	±	0.070
0.37	2.940	10	1.1490	44.390	±	0.088
0.39	3.105	10	1.1553	44.290	±	0.120
0.1	0.894	25	1.0553	18.030	±	0.082
0.15	1.286	25	1.0707	19.290	±	0.110
0.2	1.661	25	1.0856	20.540	±	0.178
0.23	1.900	25	1.0955	21.310	±	0.173
0.29	2.411	25	1.1147	22.790	±	0.242
0.33	2.680	25	1.1287	23.380	±	0.199
0.37	2.940	25	1.1421	23.870	±	0.200
0.39	3.105	25	1.1481	23.960	±	0.212
0	0	40	1.0117	7.420	±	0.095
0.05	0.478	40	1.0290	8.261	±	0.122
0.1	0.894	40	1.0457	9.154	±	0.148
0.15	1.286	40	1.0618	9.993	±	0.157
0.2	1.661	40	1.0772	10.900	±	0.226
0.23	1.900	40	1.0874	11.390	±	0.213
0.29	2.411	40	1.1073	12.570	±	0.206
0.33	2.680	40	1.1214	13.290	±	0.311
0.37	2.940	40	1.1347	13.680	±	0.319
0.39	3.105	40	1.1408	13.960	±	0.337
0	0	60	0.9957	3.666	±	0.125
0.05	0.478	60	1.0139	4.157	±	0.124
0.1	0.894	60	1.0317	4.698	±	0.180
0.15	1.286	60	1.0486	5.310	±	0.226
0.2	1.661	60	1.0644	5.900	±	0.243
0.23	1.900	60	1.0750	6.354	±	0.246
0.29	2.411	60	1.0951	7.045	±	0.293
0.33	2.680	60	1.1097	7.698	±	0.369
0	0	80	0.9786	2.035	±	0.051
0.05	0.478	80	0.9978	2.289	±	0.104
0.1	0.894	80	1.0165	2.628	±	0.123
0.15	1.286	80	1.0337	3.039	±	0.142
0.20	1.661	80	1.0511	3.277	±	0.160
0.23	1.900	80	1.0614	3.696	±	0.103
0.29	2.411	80	-	4.163	±	0.192
0.33	2.680	80	-	5.350	±	0.196

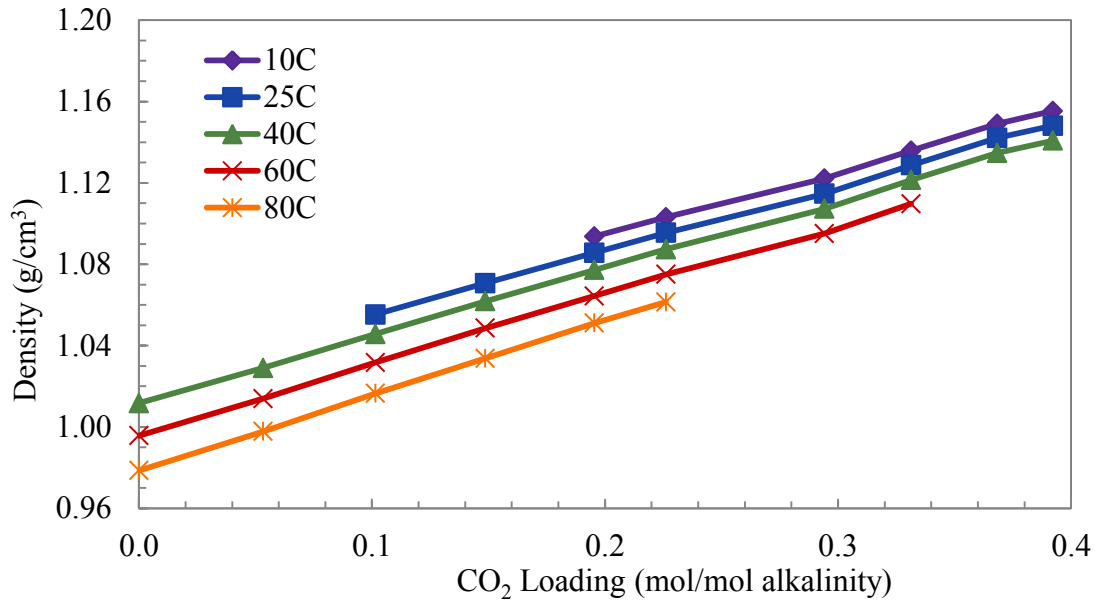


Figure 4.16: Density of 5 m PZ / 2 m 1-MPZ / 1 m 1,4-DMPZ from 10 to 80 °C

A correlation was created from the 5 m PZ / 2 m 1-MPZ / 1 m 1,4-DMPZ data to relate the ratio of viscosity to the viscosity of water (μ/μ_{water}) to temperature (K) and C_{CO_2} (mol/kg) and has the form of

$$\ln\left(\frac{\mu}{\mu_{\text{water}}}\right) = \Phi_1 + \Phi_2 \cdot T + \frac{\Phi_3}{T} \quad (4.6)$$

where

$$\Phi_i = a_i + b_i \cdot C_{\text{CO}_2} \quad (4.7)$$

The values of the regressed parameters can be found in Table 4.7. Values for μ_{water} over the range of 10 to 80 °C (283.15 to 353.15 K) were taken from the DIPPR Database (DIPPR, 2010). The resulting correlation (Equation 4.6) was able to fit all experimental μ/μ_{water} data within 5.1 % with an average error of only 2.0 %. The average

absolute deviation (AAD) calculated using Equation 4.2 for the prediction of viscosity data was 0.0012 indicating the data set is well represented by Equation 4.6.

Rearranging the above regression (Equation 4.6) leaves a relationship which predicts the viscosity of 5 m PZ / 2 m 1-MPZ / 1 m 1,4-DMPZ directly (Equation 4.8).

$$\mu = \mu_{\text{water}} \cdot \exp\left(\Phi_1 + \Phi_2 \cdot T + \frac{\Phi_3}{T}\right) \quad (4.8)$$

The experimental viscosity data from Table 4.6 is compared to the prediction of Equation 4.8 in Figure 4.17. A parity plot comparing the experimental viscosity data to the values predicted using Equation 4.8 is shown in Figure 4.18 with 5 % deviation shown with dashed lines.

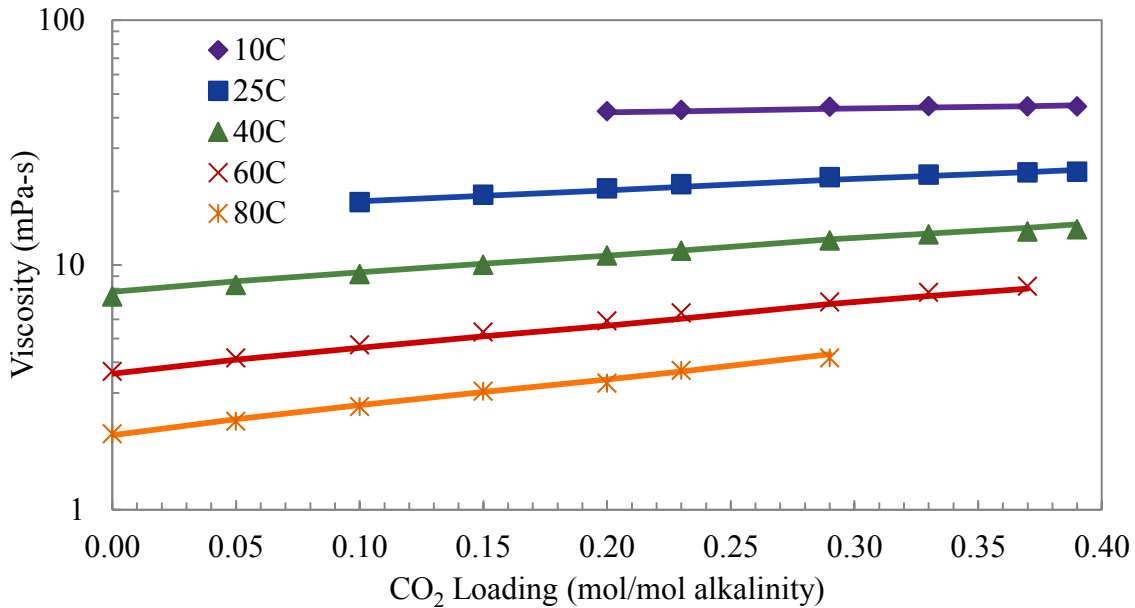
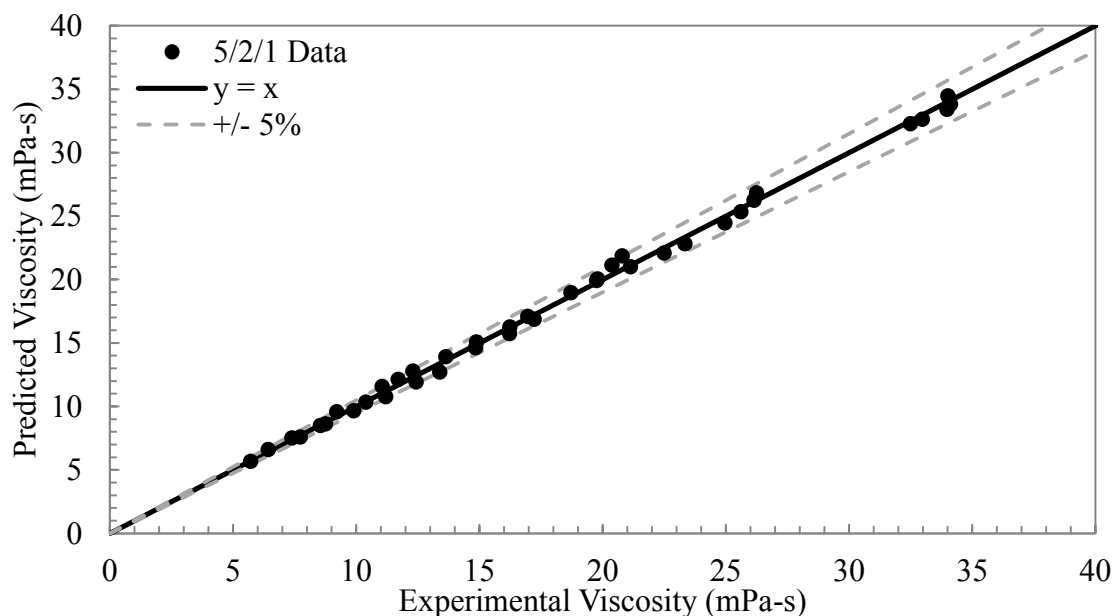


Figure 4.17: Comparison of the viscosity of 5 m PZ / 2 m 1-MPZ / 1 m 1,4-DMPZ to the prediction of Equation 4.8 (solid lines) over a range of CO₂ concentrations

Table 4.7: Value of parameters in Equation 4.6

Parameter	i = 1	i = 2	i = 3
a	-29.12	0.0379	6167.9
b	6.151	-0.00746	-1131.04

**Figure 4.18: Parity plot demonstrating the accuracy of Equation 4.8 for predicting viscosity of 5 m PZ / 2 m 1-MPZ / 1 m 1,4-DMPZ solutions from 10 to 80 °C**

4.6.3 Viscosity of 4 m PZ / 4 m 1-MPZ

The viscosity of the blend of 4 m PZ / 4 m 1-MPZ was measured by Cindy Tran as part of her student project that took place in the Rochelle lab. The raw viscosity data are shown in Table 4.8 while the data are shown plotted against CO_2 loading in Figure 4.19. The standard deviations in the measurement of viscosity for the data in Figure 4.19 are plotted as error bars, but the small size of the deviation is overshadowed by the data point itself in most cases. The 25 °C data set contains a large amount of error. It is likely that this error is a combination of possible solidification or the presence of slurries during measurements and the fact that an undergraduate student took these measurements while they were first learning how to use the rheometer. The higher loading samples

appear to have successful measurements for 25 °C, indicating it is likely that the low loading samples were suffering from slurries or solidification for the lower loading samples.

Table 4.8: Viscosity of 4 m PZ / 4 m 1-MPZ from 25 to 60 °C

CO ₂ Loading mol/mol alk	T °C	Viscosity (μ) mPa-s	
0.05	25	16.390	$\pm$ 0.357
0.10	25	15.330	$\pm$ 0.048
0.15	25	11.630	$\pm$ 0.048
0.20	25	17.320	$\pm$ 0.042
0.25	25	20.660	$\pm$ 0.107
0.30	25	21.420	$\pm$ 0.140
0.35	25	22.350	$\pm$ 0.178
0.40	25	22.710	$\pm$ 0.145
0.00	40	7.378	$\pm$ 0.095
0.05	40	8.004	$\pm$ 0.131
0.10	40	8.832	$\pm$ 0.155
0.15	40	9.883	$\pm$ 0.244
0.20	40	10.280	$\pm$ 0.169
0.25	40	11.040	$\pm$ 0.201
0.30	40	11.970	$\pm$ 0.231
0.35	40	12.760	$\pm$ 0.241
0.40	40	13.140	$\pm$ 0.255
0.05	60	3.092	$\pm$ 0.031
0.10	60	4.719	$\pm$ 0.159
0.15	60	5.243	$\pm$ 0.198
0.20	60	5.691	$\pm$ 0.170
0.25	60	6.387	$\pm$ 0.224
0.30	60	6.138	$\pm$ 0.084
0.35	60	7.139	$\pm$ 0.180
0.40	60	7.698	$\pm$ 0.157

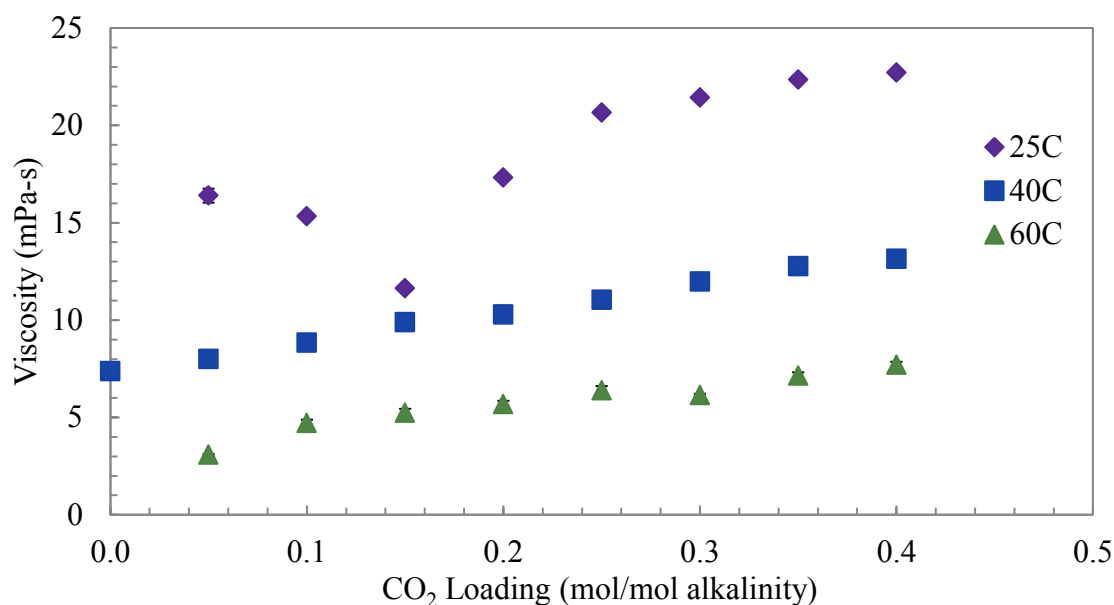


Figure 4.19: Viscosity of 4 m PZ / 4 m 1-MPZ from 25 to 60 °C

4.6.4 Viscosity of 4 m PZ / 4 m 1,4-DMPZ

The viscosity of the blend of 4 m PZ / 4 m 1,4-DMPZ was also measured by Cindy Tran as part of a student project within the Rochelle laboratory. The raw viscosity data is shown in Table 4.9 while the data are shown plotted against CO₂ loading in Figure 4.20. The standard deviation of the viscosity measurement for each data point is plotted as an error bar in Figure 4.20, but they are not visible compared to the data point itself. There are a few data points that appear to deviate from the expected trend. This is the result of basic experimental error because the measurements were performed by an undergraduate learning to use the apparatus.

4.6.5 Density of 4 m PZ + 4 m 2-MPZ

Blends of PZ with 2-MPZ were investigated as novel solvents that potentially had better solubility characteristics than concentrated PZ alone. The density of a blend of 4 m PZ + 4 m 2-MPZ was measured as part of this effort. The raw density data are shown in

Table 4.10 while the data are plotted against CO₂ loading in Figure 4.21.

Table 4.9: Viscosity of 4 m PZ + 4 m 1,4-DMPZ from 25 to 60 °C

CO ₂ Loading mol/mol alk	T °C	Viscosity (μ) mPa-s	
0.10	25	19.110	± 0.032
0.15	25	21.050	± 0.071
0.20	25	22.380	± 0.079
0.25	25	23.740	± 0.070
0.30	25	24.540	± 0.097
0.35	25	24.300	± 0.082
0.10	40	9.176	± 0.069
0.15	40	10.090	± 0.099
0.20	40	11.070	± 0.082
0.25	40	12.190	± 0.166
0.30	40	13.010	± 0.099
0.35	40	13.210	± 0.120
0.10	60	4.526	± 0.086
0.15	60	5.389	± 0.160
0.20	60	6.017	± 0.162
0.25	60	5.078	± 0.021
0.30	60	6.895	± 0.030
0.35	60	6.681	± 0.296

Table 4.10: Density of 4 m PZ + 4 m 2-MPZ from 20 to 60 °C

CO ₂ Loading mol/mol alk	CO ₂ Conc. mol/kg	Density, ρ (g/cm ³)		
		20 °C	40 °C	60 °C
0.15	1.289	1.0782	1.0651	1.0531
0.18	1.728	1.0938	1.0817	1.0703
0.25	2.173	1.1088	1.0974	1.0863
0.30	2.573	1.1227	1.1119	1.1012
0.34	2.980	1.1367	1.1265	1.1160
0.39	3.373	1.1506	1.1408	1.1303

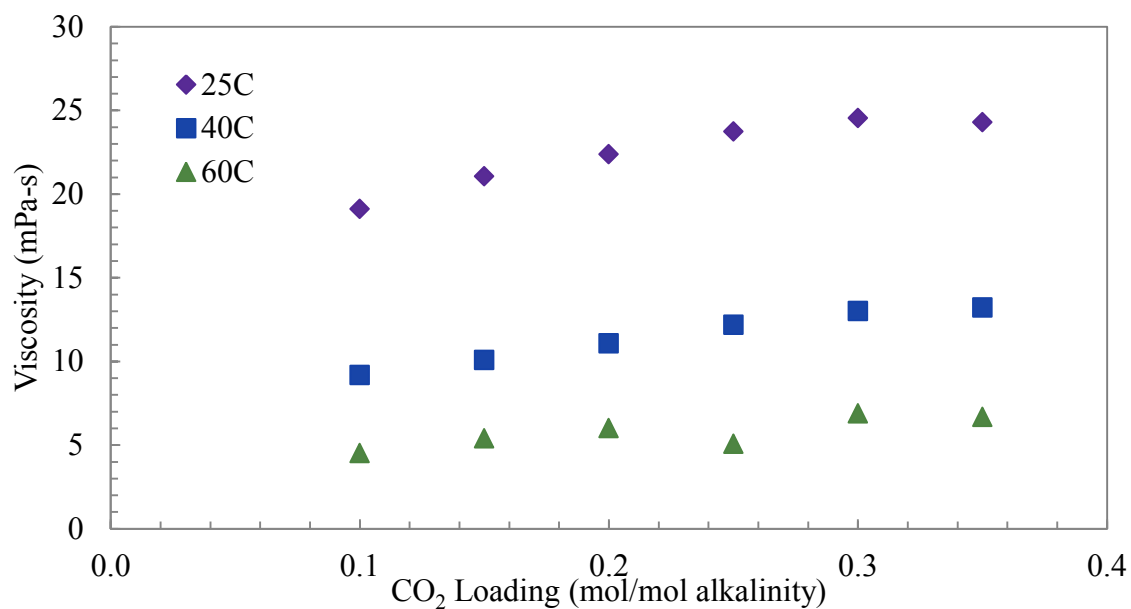


Figure 4.20: Viscosity of 4 m PZ + 4 m 1,4-DMPZ from 25 to 60 °C

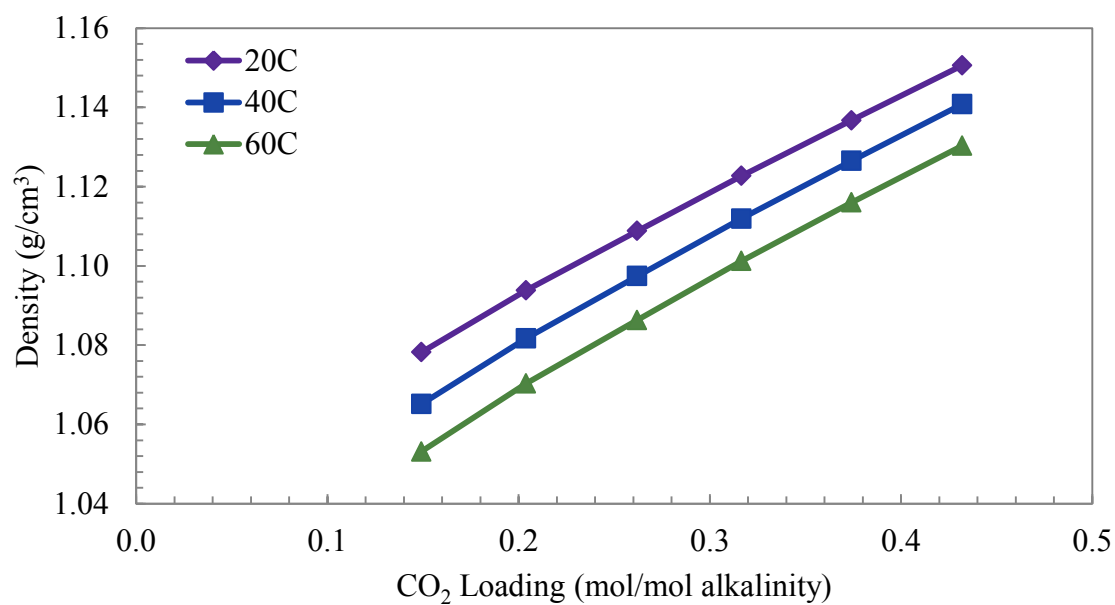


Figure 4.21: Density of 4 m PZ + 4 m 2-MPZ from 20 to 60 °C

4.6.6 Density of 5 m PZ + 5 m 2-MPZ

Another blend of interest was a 5 m PZ + 5 m 2-MPZ blend where the increased alkalinity would enhance kinetic rates of CO₂ absorption. The density of this blend was measured over a range of CO₂ loadings and temperatures. The raw density data are shown in Table 4.11 while the data are plotted against CO₂ loading in Figure 4.22.

Table 4.11: Density of 5 m PZ + 5 m 2-MPZ from 20 to 60 °C

CO ₂ Loading mol/mol alk	CO ₂ Conc. mol/kg	Density, ρ (g/cm ³)		
		20 °C	40 °C	60 °C
0.078	0.782	1.0544	1.0390	1.0254
0.116	1.141	1.0749	1.0607	1.0478
0.175	1.676	1.0959	1.0827	1.0704
0.233	2.184	1.1156	1.1034	1.0915
0.302	2.747	1.1346	1.1231	1.1117
0.349	3.120	1.1530	1.1421	1.1309
0.411	3.588	1.1708	1.1604	1.1494
0.469	3.997	1.1827	1.1727	1.1615

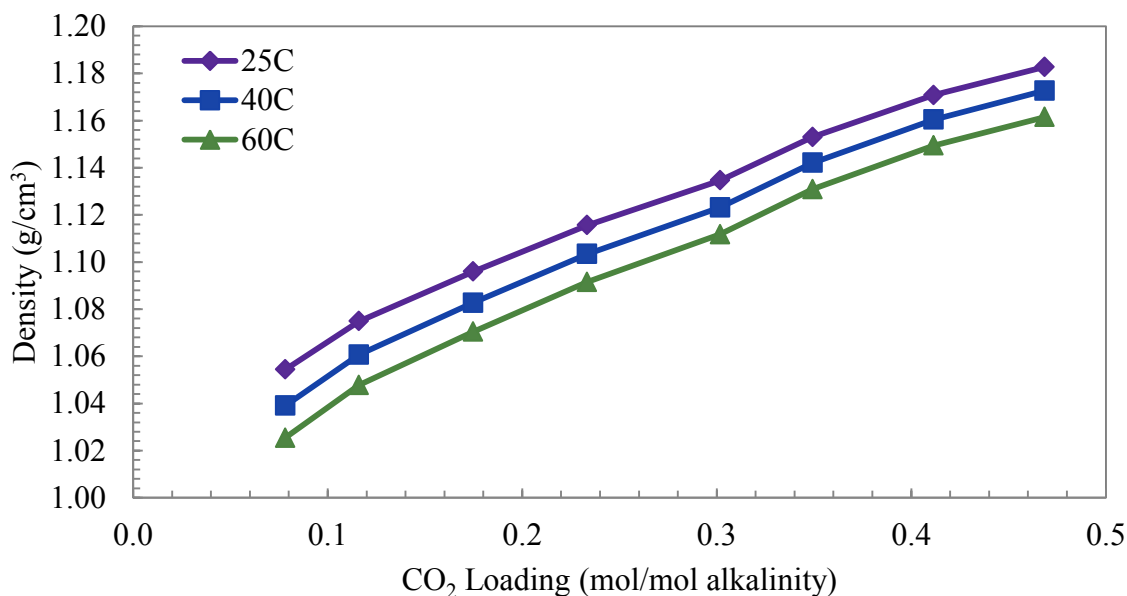


Figure 4.22: Density of 5 m PZ + 5 m 2-MPZ from 20 to 60 °C

4.6.7 Comparison of density data

The density of 4 amine solutions containing a total alkalinity of 16 m has been measured over a range of temperatures and CO₂ concentrations. A summary of the density data obtained is shown in Figure 4.23 where data for each blend at 40 °C are compared with a prediction of the density of 7 m MEA (Weiland et al., 1998). All of the PZ based solvent systems demonstrate similar density behavior and all have higher density than 7 m MEA. Density can affect pump work and fluid heat and mass transfer so a decreased density can be advantageous. On the other hand, if monitoring of CO₂ concentration through on-line density measurements is desired, the increased slope of the PZ density data can be advantageous to produce a more robust correlation where a larger and more accurate density measurement can be achieved for a given change in CO₂ loading.

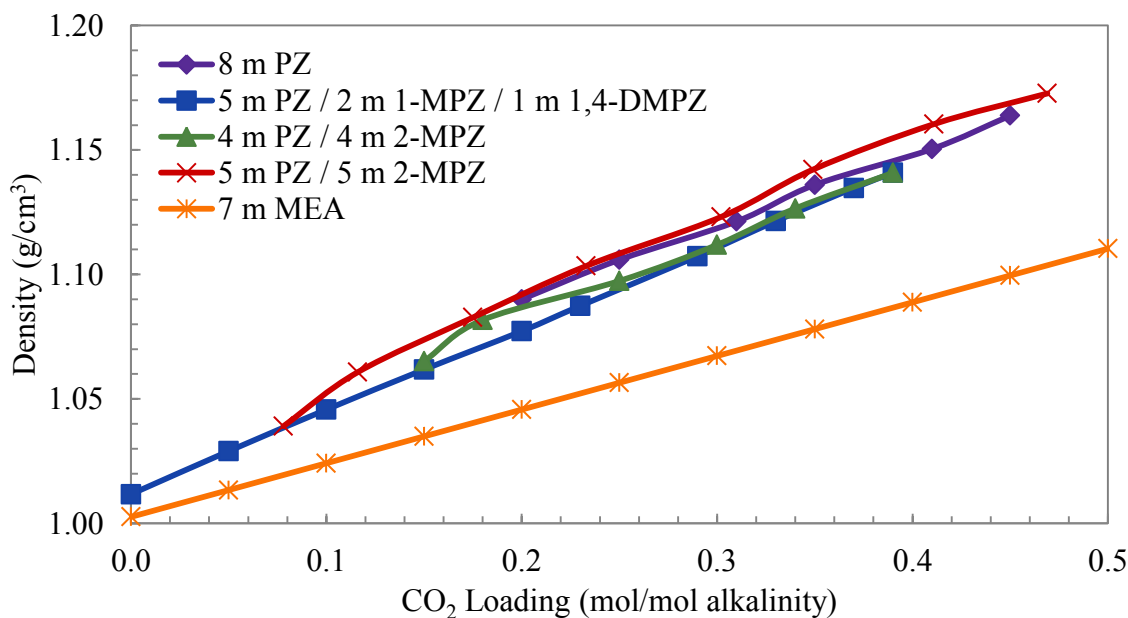


Figure 4.23: Comparison of density data for PZ based systems at 40 °C

4.6.8 Comparison of viscosity data

The viscosity of 4 amine solutions containing a total alkalinity of 16 m has been measured over a range of temperatures and CO₂ concentrations. A summary of the viscosity data obtained are shown in Figure 4.24 where data for each blend at 40 °C are compared with a prediction of the viscosity of 7 m MEA (Weiland et al., 1998). The baseline 8 m PZ solution has a lower viscosity than the three PZ blends but still significantly higher than that of MEA. This is advantageous for the concentrated PZ solvent compared to the blends, but MEA still has an advantage in this category since as increased viscosity leads to increased pumping work, decreased mass transfer, and decreased heat transfer. All of the PZ based solutions would suffer from these disadvantages compared to a MEA system.

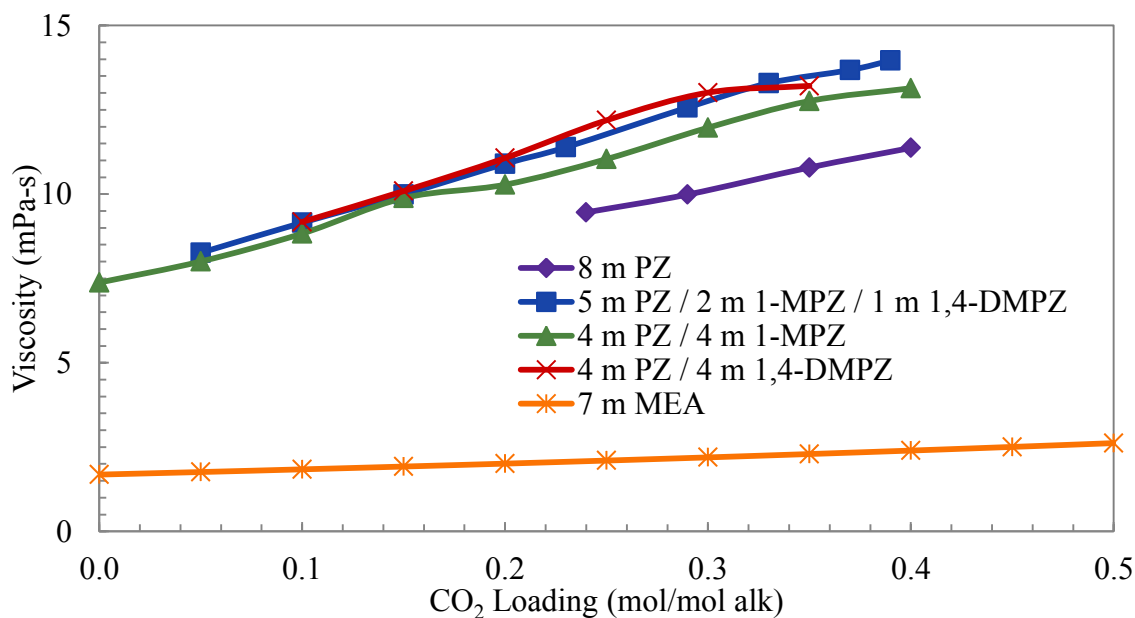


Figure 4.24: Comparison of viscosity data for PZ based systems at 40 °C

4.7 CONCLUSIONS

At 0 °C, 8 m PZ will not precipitate solids between 0.32 and 0.44 mole CO₂ per mole alkalinity. At an operating temperature of 40 °C, 8 m PZ will be an aqueous solution between 0.1 and 0.45 mole CO₂ per mole alkalinity. The room temperature (20 °C) solubility of unloaded PZ is 14 weight %, or 1.9 m PZ, while the soluble loading range is approximately 0.25 to 0.4 mole CO₂ per mole alkalinity at this temperature. Transition temperatures for concentrated PZ were measured over a range of CO₂ loading and hysteresis was observed in the temperature at which crystals formed when cooled or precipitation melted when heated.

The viscosity of 8 m PZ at 40 °C with 0.4 mole CO₂ per mole alkalinity is 11.4 cP, higher than that of 9 m MEA with 0.5 mole CO₂ per mole alkalinity (3 cP). Solutions of 60wt% DGA[®] with 0.4 mole CO₂ per mole alkalinity, a commercial gas treating solvent, has a viscosity 13.7 cP, even higher than PZ. The viscosity of 8 m PZ is given by Equation 4.9 in terms of the viscosity of water (cP), μ_{water} , concentration of CO₂ (mole per kg), C_{CO_2} , concentration of PZ (mole per kg), C_{PZ} , and temperature (K), T.

$$\ln\left(\frac{\mu}{\mu_{\text{water}}}\right) = 1.723 + 2.63 \cdot C_{\text{CO}_2} - 1.019 \cdot C_{\text{PZ}} - 0.527 \cdot C_{\text{CO}_2} \cdot C_{\text{PZ}} + \frac{-778 \cdot C_{\text{CO}_2} + 355.2 \cdot C_{\text{PZ}} + 169.3 \cdot C_{\text{CO}_2} \cdot C_{\text{PZ}}}{T} \quad (4.9)$$

Density of 5 to 12 m PZ solutions was regressed in terms of the density of water, ρ_{water} , C_{CO_2} , and C_{PZ} , and the resulting regression is shown in Equation 4.1. The effect of temperature on density was eliminated by including ρ_{water} at a given temperature.

$$\frac{\rho}{\rho_{\text{water}}} = 0.0407 \cdot C_{\text{CO}_2} + 0.008 \cdot C_{\text{PZ}} + 0.991 \quad (4.1)$$

Online measurement of density and viscosity will permit accurate on-line estimates of PZ concentration and CO₂ loading. On-line viscosity and density monitors can be employed in a pilot plant, demonstration plant, or full scale CO₂ capture application as an inexpensive, easy, and effective way to continually monitor the condition of a PZ solvent. Both PZ concentration and CO₂ loading have traditionally been offline analyses that take on the order of minutes or hours to complete. Online monitoring allows for instant feedback and constant monitoring of the solvent conditions where maintaining the solution within physical solubility windows is a crucial operational concern.

The regression for viscosity was developed with only 8 m PZ data and this limits its application. Viscosity of PZ solutions is complicated and regressions across large PZ concentration ranges generally contain unacceptable levels of error for online monitoring applications. The density regression should be very robust in applications centering around 8 m PZ, the most likely concentration of concentrated PZ systems.

A blend of 4 m PZ / 4 m 2-MPZ, being developed for its beneficial physical solubility, has density less than 1% higher than an 8 m PZ solution with the same alkalinity. On the other hand, a blend of 5 m PZ / 2 m 1-MPZ / 1 m 1,4-DMPZ has up to a 3% lower density but 23% higher viscosity. All blends of PZ with substituted PZ molecules had very similar density values to PZ itself, but up to 30% higher viscosity. Blends can have advantageous characteristics, but can also result in unfavorable changes to density and viscosity.

Chapter 5 – Thermal Degradation Rate of PZ

In order to assess the thermal degradation rate of PZ as it applies to CO₂ capture applications, a number of thermal degradation experiments were conducted on concentrated, aqueous PZ. Prior work had identified PZ as a thermally resistant amine (Davis, 2009). To further explore the thermal resistance of PZ, experiments were performed that investigated the effect of temperature, PZ concentration, CO₂ concentration, and additives on the degradation rate of PZ. A first order rate constant was calculated and compared for all conditions. Portions of this chapter are excerpted from previous work (Freeman et al., 2010a).

5.1 CONCENTRATED PIPERAZINE THERMAL DEGRADATION EXPERIMENTS

Thermal stability has been identified as a significant advantage of concentrated, aqueous PZ used for CO₂ capture applications. The temperatures chosen for PZ

degradation experiments reflect the ability of PZ to resist thermal degradation. Degradation of monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP), MEA blended with AMP, Morpholine (Mor), PZ, or diglycolamine[®] (DGA[®]) and other MEA structural analogs were previously studied over a range of 100 to 150 °C where significant degradation was observed at 150 °C in most cases (Davis, 2009). The screening experiment performed by Davis for 8 molal (m) PZ showed no amine loss at 135 °C after 4 weeks (Davis, 2009). Based on this data, initial experiments for PZ were performed at 150 and 175 °C. Although these temperatures are not representative of what is proposed for industrial CO₂ processes, PZ experiments were limited by time restrictions. Estimations for initial experiments showed that 72 weeks was required at 135 °C to shown measurable and significant PZ loss (10 to 15% amine loss). Any temperature less than 135 °C would have made the experiments over two years long.

The PZ concentration of interest for this dissertation is 8 m and was the focus of thermal degradation experiments. Four experiments were performed at 10 m PZ when this concentration was initially being investigated as well. Lower and higher concentrations (4 and 12 m PZ) were tested at two temperatures to determine the effect of PZ concentration on thermal degradation. Several high concentration experiments at 15 and 20 m PZ were performed to investigate the upper limit of PZ concentration and for use in thermal reclaiming modeling by other researchers. Solutions of 8 m PZ with 0 to 0.47 mole CO₂ per mole alkalinity were investigated to gauge the entire effect of CO₂ loading. A summary of the thermal degradation experiments on concentrated, aqueous PZ in the absence of other amines or additives is given in Table 5.1. Included in this table is the value of the first order rate constant, k_1 , for PZ loss for each experiment. The determination of this value is described in the following section.

Table 5.1: Summary of PZ Thermal Degradation Experiments

Temp (°C)	PZ Conc. (m)	CO ₂ Loading (mol/mol alk)	Experiment(s)	$k_1 \times 10^9$ (s ⁻¹)
135	8	0.3	TE10	1.0
	8	0.4	TE11	0.5
	10	0.3	TE1A	4.8
	10	0.4	TE1B	-
150	8	0.3	TE9, TE14	6.1
	8	0.4	TE15	7.9
	10	0.3	TE2A	8.9
	10	0.4	TE2B	6.0
	15	0.3	TE3A	-
	20	0.3	TE3B	24.2
165	4	0.3	TE49	35.5
	8	0	TE46	0.8
	8	0.1	TE47	18.4
	8	0.3	TE44	31.4
	8	0.4	TE45	40.9
	12	0.3	TE50	50.3
175	4	0.3	TE32	114
	8	0	TE21	7.0
	8	0.1	TE34	65.8
	8	0.2	TE53	78.8
	8	0.3	TE4, TE12, TE18	132
	8	0.4	TE13, TE19	171
	8	0.47	TE54	23.8
	12	0.3	TE33	156
	20	0.1	TE58	44.7
	20	0.3	TE57	168

This chapter as a whole highlights the effect of solution characteristics on the loss of PZ as the primary dependent variable. The production of degradation products will not be described in detail in each experiment in this chapter as a detailed discussion can be found in Chapter 6. Generation of formate, total formate, and ethylenediamine (EDA) will be used as representative compounds that are universally found during PZ thermal degradation. They will be used to represent the entire mix of degradation

products found in thermally degraded PZ without obscuring the main conclusions. A specific formyl amide, N-formyl PZ (FPZ), and N-(2-aminoethyl)piperazine (AEP) are generated during thermal degradation and account for a significant portion of the mass balance in many cases, but were not regularly quantified with cation IC until the end of the project. Therefore, there is not data for these compounds for all experiments. Comparisons of FPZ and AEP generation are made where data is sufficient. All of the quantified degradation products can be found in tabulated thermal degradation data contained in Appendix D

5.2 FIRST-ORDER RATE CONSTANTS ANALYSIS

It will be shown in the following section that the loss of PZ during thermal degradation is approximately first order in amine concentration at 175 °C (section 5.3.2). This observation is supported by the fact that most thermal degradation concentration profiles for PZ can be well characterized by an exponential regression. Provided the vast amount of thermal degradation data acquired in this project, an analysis was needed to investigate the PZ loss data in a simplified way in order to understand all of the data and draw meaningful conclusions that are applicable to real world situations. The method developed was the calculation and comparison of first order rate constants, k_1 , for thermal degradation experiments. The calculation of k_1 assumes a first order loss in PZ as shown by the following rate equation where C_{PZ} is the concentration of PZ in any appropriate units (Equation 5.1).

$$-\frac{dC_{PZ}}{dt} = k_1 C_{PZ} \quad (5.1)$$

Equation 5.1 can be translated directly into an equation relating the fraction of PZ at any point in time, F_{PZ} , because the initial concentration will always be used as the denominator of the ratio (Equation 5.2).

$$-\frac{dF_{PZ}}{dt} = k_1 F_{PZ} \quad (5.2)$$

This assumed form of a rate expression for PZ is a differential equation that can be solved for F_{PZ} at any time point (Equation 5.3 and Equation 5.4).

$$\ln \frac{F_{PZ}}{F_{PZ,0}} = -k_1 \cdot t \quad (5.3)$$

$$F_{PZ} = F_{PZ,0} \cdot \exp(-k_1 \cdot t) \quad (5.4)$$

Each set of thermal degradation data was regressed with an exponential trendline that matched this form of the rate equation. As an example of this analysis, the PZ loss data for the degradation of 8 m PZ with 0.3 mole CO_2 per mole alkalinity at 175 °C is shown in Figure 5.1. These data are collated from multiple experiments performed with the same conditions and an exponential regression has been fit for the entire set. The regression fits the data well as evidenced by the high coefficient of determination (r^2). Based on the form of Equation 5.4, the k_1 for this set of condition is $7.97 \times 10^{-2} \text{ wk}^{-1}$, or $1.32 \times 10^{-7} \text{ s}^{-1}$. Raw thermal degradation data, as shown in the figure, are reported in weeks in this dissertation (Appendix D), but the k_1 will be calculated in inverse seconds (s^{-1}) for consistency with standard reaction rate reporting and previous work (Cullinane and Rochelle, 2006; Freeman et al., 2010a; Rochelle et al., 2001). The k_1 was calculated in s^{-1} for all experimental data sets obtained in this dissertation.

The rate constant, k_1 , was predicted to have an Arrhenius temperature dependence with the form shown in Equation 5.5 where k_1 and the pre-exponential factor, A , have units of inverse time, the activation energy, E_A , is in kJ per mole, R is the universal gas constant, and the temperature, T , is in Kelvin. A linearized form of Equation 5.5 is shown in Equation 5.6.

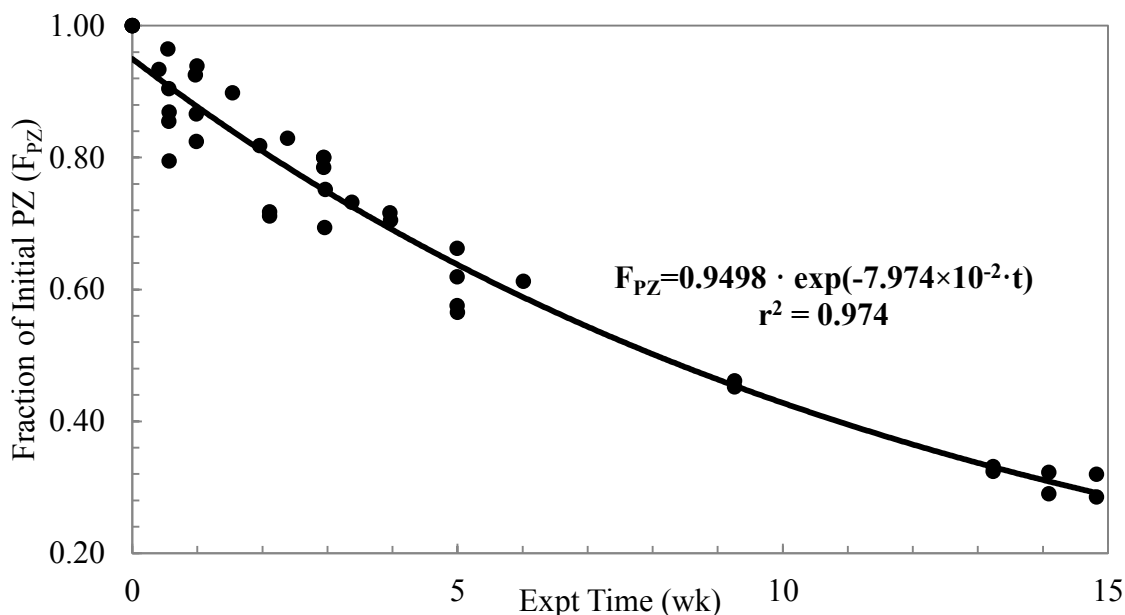


Figure 5.1: An example of the determination of k_1 value from thermal degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 175 °C

$$k_1 = A \cdot \exp\left(\frac{E_A}{R} \cdot \frac{1}{T}\right) \quad (5.5)$$

$$\ln(k_1) = \ln(A) - \frac{E_A}{R} \cdot \frac{1}{T} \quad (5.6)$$

The Arrhenius behavior of k_1 values for PZ degradation has been confirmed. The structure of Equation 5.6 suggests a linear relationship between $\ln k_1$ and T^{-1} . A plot comparing the calculated k_1 value on a logarithm scale and T^{-1} for experiments with 8 m PZ with 0.3 mole CO₂ per mole alkalinity is shown in Figure 5.2. The data are plotted using Kelvin temperature units, but Celsius units are shown for clarity. The linear behavior of the data confirm that thermal degradation of concentrated PZ can be estimated accurately with a first order rate constant with Arrhenius temperature behavior. The activation energy for thermal degradation can be calculated from the slope of the linear fit shown in Figure 5.2. The activation energy for this set of data is 183.5 kJ per mole. Arrhenius temperature behavior of k_1 is observed in nearly every set of PZ

conditions and in the data from amines. Activation energies vary slightly, but the overall trends seen in the k_1 value are maintained.

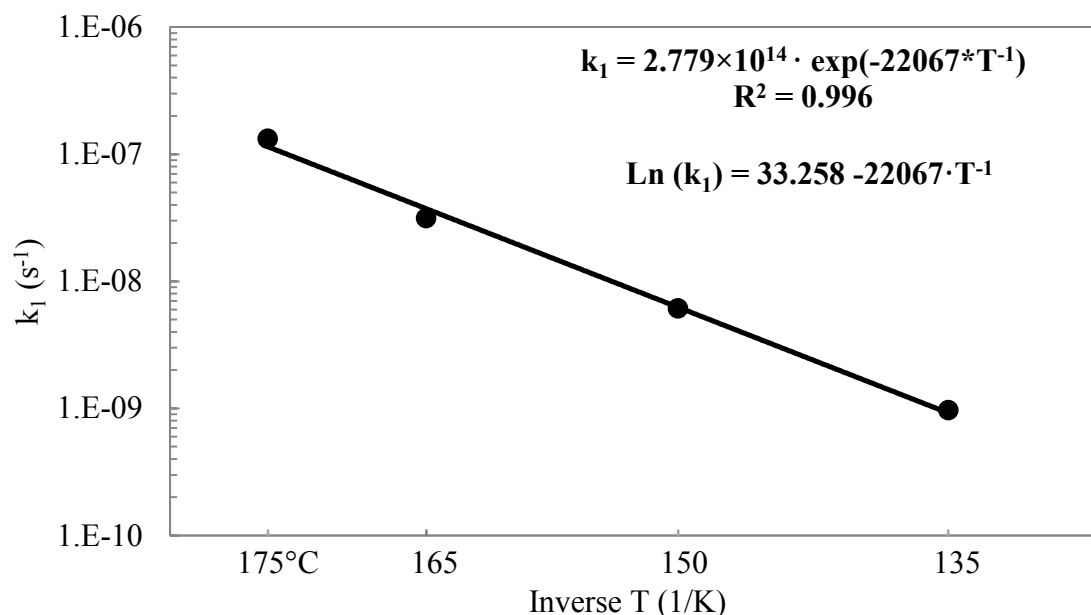


Figure 5.2: Demonstration of the Arrhenius behavior of the first order rate constant (k_1) for thermal degradation of 8 m PZ with 0.3 mole CO_2 per mole alkalinity

In chapter 7, PZ is compared with other CO_2 capture amines using this same analysis. For other amines, k_1 values are calculated using the same methodology, unless otherwise noted. For most amines discussed, the first order approximation fits well either because the data suggests the amine behavior is first order in amine loss, or because data is limited to only a few points. This overall approach allows an assessment of the tendency of an amine to degrade thermally without having to account for the length of experiment, which can vary from 4 to 72 weeks, and complex differences in degradation mechanism. This analysis is intended to be a tool to quickly assess the thermal stability of an amine in relation to other systems tested under similar conditions.

The k_1 calculation can be an oversimplification of systems where more complicated kinetics can take over beyond the initial periods of degradation. For example, this is true in the data shown in section 5.3.2.1 for rich loaded 20 m PZ. If a set of thermal degradation data demonstrated noticeably different behavior than first order in amine loss, an initial first order rate was determined and the constant was considered an apparent first order rate constant. Usually, this meant taking the first order rate using the first 10-50% of the data, based on the time scale.

For the concentrated PZ data discussed in this chapter, a first order approximation across the entire data set was used, except for aforementioned 20 m PZ experiment. The calculated k_1 values are indicated in each graph that shows PZ loss as a function of time along with exponential regressions. In this way, the derivation of k_1 for each experiment discussed is demonstrated.

5.2.1 Evaluation of error in regressed slopes and k_1 values

To assess the overall experimental error expected from the thermal degradation procedure, data from experiments with the same conditions were analyzed for repeatability and parallelism of regressed slopes used to determine k_1 values. The basis for the analysis was a student's t-test to determine if the regressed slope was the same with statistical significance for repeated experiments. For each experiment of interest, a data set was comprised of the time values (X variable) and natural log of the fraction of initial PZ ($\ln(F_{PZ})$, Y variable). Since first order behavior has been assumed for this analysis, a plot of $\ln(F_{PZ})$ against experiment time should be well fit with a linear regression. A linear regression of this nature was performed with all experimental data and k_1 values were calculated from the slope of the regression.

Three conditions during this project were repeated with multiple experiments. At 150 °C, TE9 and TE14 were both performed with 8 m PZ with 0.3 mole CO₂ per mole alkalinity. At 175 °C, TE4, TE12, and TE18 were all performed with 8 m PZ with 0.3 mole CO₂ per mole alkalinity. Finally, TE13 and TE19 were both performed with 8 m PZ with 0.4 mole CO₂ per mole alkalinity at 175 °C. The details of this statistical analysis will be shown for data from TE4, TE12, and TE18. The results will then be shown for the other two comparisons (TE9 and TE14; TE13 and TE19). The analysis performed in this section is based on the methods for comparing two straight lines using separate regression fits that has been described previously (Kleinbaum et al., 1988).

Each data set was treated separately and an independent, linear regression was made. The regressions were in the following form that relates the independent variable (X; experiment time) to the slope of the regression (m_i), the intercept (b_i), and the dependent variable (Y; $\ln(F_{PZ})$) (Equation 5.7).

$$Y = m_i X + b_i \quad (5.7)$$

A test was then performed to determine parallelism between the regressed slopes from two data sets of interest. This approach determined if two lines have the same slope with a given confidence. This translates to an estimation of the error in the calculation of k_1 , since this value is derived from the regressed slope of each data set. The null hypothesis, H_0 , therefore is that the slopes of two sets of data (m_1 and m_2) will be the same (Equation 5.8).

$$H_0 : m_1 = m_2 \quad (5.8)$$

A test statistic, T , for evaluating parallelism can then be defined as follows (Equation 5.9). This parameter can be used to determine if the null hypothesis is true or

false by comparing it with a t-value determined from the degrees of freedom (DOF) and desired confidence interval. Values of t are obtained from tables available in statistics literature (Kleinbaum et al, 1988). If the null hypothesis is false, the absolute value of T will be greater than the t-value based on a student's distribution (Kleinbaum et al., 1988).

$$T = \frac{m_1 - m_2}{S_{m_1 - m_2}} \quad (5.9)$$

In Equation 5.9, each slope (m_1 or m_2) is the least-squares estimate of the slope of the data while $S_{m_1 - m_2}$ is an estimate of the standard deviation of the estimated differences between the two slopes. This variable can be defined as follows (Equation 5.10).

$$S_{m_1 - m_2} = \sqrt{S_{P,Y/X}^2 \left[\frac{1}{(n_1 - 1)S_{X_1}^2} + \frac{1}{(n_2 - 1)S_{X_2}^2} \right]} \quad (5.10)$$

In this equation, the variance in the X variable for both sets of data is used ($S_{X_1}^2$ and $S_{X_2}^2$) as well as $S_{P,Y/X}^2$, a pooled (P) estimate of the variance based on the mean-square error of each of the two regressions (S_{Y/X_1}^2 and S_{Y/X_2}^2) and the number of data points in each set (n_1 and n_2). The pooled estimate of variance and the mean-squared error of each regression can be calculated using the following formulas (Equation 5.11 and 5.12) (Kleinbaum et al., 1988).

$$S_{P,Y/X}^2 = \frac{(n_1 - 2) \cdot S_{Y/X_1}^2 + (n_2 - 2) \cdot S_{Y/X_2}^2}{n_1 + n_2 - 4} \quad (5.11)$$

$$S_{Y/X_i}^2 = \frac{1}{n - 2} \sum_{i=1}^n (Y_i - Y_{i,\text{regression}})^2 \quad (5.12)$$

The assumptions of this analysis are that the test statistic will be distributed with a student's t regular probability curve with a number of degrees of freedom equal to $(n_1 + n_2 - 4)$ when the null hypothesis defined in Equation 5.8 is true (Kleinbaum et al., 1988).. A t-value will be used in this analysis that depends on the DOF $(n_1 + n_2 - 4)$ and has 95% confidence, or a significance level of 0.05, indicated as $t_{n_1+n_2-4, 1-\alpha/2}$. The two subscripts after t indicate the DOF and confidence level to use in each particular case.

An example can be shown where the data from TE4, TE12, and TE18 are analyzed in detail. The three data sets of interest are shown in Figure 5.3 along with least-squares linear regression and the coefficient of variance (r^2) for each regression. The slope, intercept, and other pertinent data from the linear regressions are shown in Table 5.2 for reference. The sample variance in X and the residual mean-square error was been calculated for each regression.

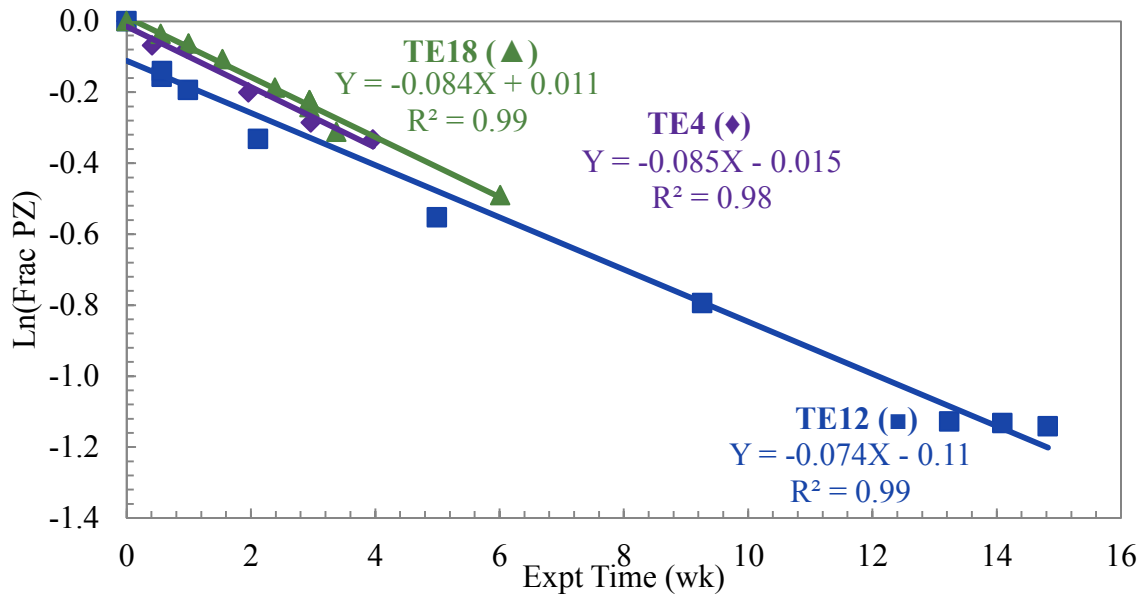


Figure 5.3: Linear regression of TE4, TE12, and TE18 for statistical analysis

Table 5.2: Details of linear regressions

Data set	Data points	Slope (wk ⁻¹)	Intercept	Mean of X	Sample variance ($S_{X_i}^2$)	Residual mean-square error (S_{Y/X_i}^2)
TE4	6	-0.085	-0.015	1.7	2.38	0.00051
TE12	10	-0.074	-0.111	6.1	38.07	0.00350
TE18	10	-0.084	0.011	2.4	2.97	0.00091

Using the linear regression and the analysis described above, the T value for a comparison of two data sets can be calculated from Equation 5.9. This procedure has been done for the three independent pairs of TE4, TE12, and TE18 and the results are shown in Table 5.3. In all three cases, the absolute value of T is not larger than the t-value, so H_0 is not rejected. This implies that the null hypothesis is accepted since there is not sufficient evidence to reject it. This implies that with the chosen confidence interval (95%), the slopes of the three data sets are the same and indicate the overall error of the thermal degradation experiment is likely less than 5% for a standard experiment.

Table 5.3: Results for statistical comparison of parallelism of PZ loss slope for TE4, TE12, and TE18 (8 m PZ, 0.3 mole CO₂ per mole alkalinity, 175 °C)

Data set 1	TE4	TE4	TE12
Data set 2	TE12	TE18	TE18
DOF	12	12	17
α	0.05	0.05	0.05
$t_{n1+n2-4, 1-\alpha/2}$	$t_{12,0.975}$	$t_{12,0.975}$	$t_{17,0.975}$
t value	2.179	2.179	2.110
$S_{P,Y/X}^2$	0.00251	0.000774	0.00221
$S_{m_1-m_2}$	0.0148	0.632	0.0094
T	-0.792	-0.00138	1.149
T	0.792	0.00138	1.149
H_0	True	True	True

The similarity of the slopes also indicates that the k_1 value derived from the data should not contain significant error when calculated from each experiment separately. To demonstrate this, the k_1 value was calculated from the regression shown in Figure 5.3 for

each of the three experiments (TE4, TE12, and TE18). These values are shown in Table 5.4 along with the average and standard deviation that results from the three separation regressions. Finally, the k_1 value that is a result of regressing all of the data together as one data set is shown in the final row of Table 5.4. The average k_1 value determined from separate experiments is $134 \pm 11 \text{ s}^{-1}$. The low standard deviation and agreement in the regression of all of the data agrees with the t-test analysis that showed all three sets had statistically similar slopes. It is expected that all of the thermal degradation experiments suffered similar levels of experimental error, even though repeated experiments could not be performed.

Table 5.4: Comparison of error between individual and average k_1 calculations (8 m PZ, 0.3 mole CO_2 per mole alkalinity, 175 °C)

Data set or expt.	$k_1 \times 10^9$ (s^{-1})
TE4	141
TE12	122
TE18	140
Average	134
Standard deviation	11
Regression of all data	130

The same data analysis to test for parallelism in the slope of PZ loss was performed for the two remaining sets of experiments performed under the same conditions. The results are shown in Table 5.5 and in the first case, a comparison of TE9 and TE14, the null hypothesis was found to be true indicating the slopes are statistically not different with a 95% confidence. For the second comparison, TE13 and TE19, however, the null hypothesis was found to be false and the slopes of the data were determined to be statistically different. Calculation of the k_1 value for each data set along with an average value is shown in Table 5.6. The k_1 value for TE9, TE14 and the value obtained when all of the data is regressed at the same time is within the expected

deviation when the values are calculated separately and averaged. For the k_1 value of TE13 and TE19, a large deviation between the values calculated individually and the regression for the overall group of data was observed. This was expected provided the results of the student t-test. For Table 5.1 and the analysis of k_1 values in section 7.4, the value obtained from regressing all of the data simultaneously was used for the two analyses of data at 175 °C. For the final set of data comparing TE13 and TE19, the k_1 value from TE19 was used due to the higher propensity for cylinder failures and other experimental concerns with the data from TE13.

Table 5.5: Results for statistical comparison of parallelism of PZ loss slope for TE9 and TE14 (8 m PZ, 0.3 mole CO₂ per mole alkalinity, 150 °C) and TE13 and TE19 (8 m PZ, 0.4 mole CO₂ per mole alkalinity, 175 °C)

Data set 1	TE9	TE13
Data set 2	TE14	TE19
DOF	25	18
α	0.05	0.05
$t_{n1+n2-4, 1-\alpha/2}$	$t_{25,0.975}$	$t_{18,0.975}$
t value	2.06	2.101
$S^2_{P,Y/X}$	0.000252	0.00219
$S_{m_1-m_2}$	0.000846	0.00933
T	0.610	2.921
T	0.610	2.921
H_0	True	False

Table 5.6: Comparison of error between individual and average k_1 calculations

8 m PZ, 0.3 mol/mol alk, 150 °C		8 m PZ, 0.4 mol/mol alk, 175 °C	
Data set or expt.	$k_1 \times 10^9$ (s ⁻¹)	Data set or expt.	$k_1 \times 10^9$ (s ⁻¹)
TE9	5.3	TE13	126
TE14	6.1	TE19	171
Average	5.7	Average	135
Standard deviation	0.6	Standard deviation	12
Regression of all data	6.2	Regression of all data	127

5.3 PZ DEGRADATION EFFECTS

The rate of PZ degradation was assessed in terms of three primary variables: temperature, PZ concentration, and CO₂ concentration or CO₂ loading. Each of these variables was investigated independently with a series of experiments that kept the other two variables constant. Isolating the effect of each variable separately was critical as all three are interconnected in terms of degradation rates. For all of the variables, multiple sets of experiments were performed at differing conditions.

5.3.1 Effect of temperature

The effect of temperature on PZ thermal degradation was examined by degrading solutions at constant PZ and CO₂ concentrations. A summary of the experiments performed to examine temperature is given in Table 5.7. In total, nine groups of experiments were performed under similar conditions that highlighted the effect of temperature. For simplicity and to avoid repetitive reporting of data, three of the groups shown in bold text in Table 5.7 will be discussed in detail while the remaining six will not be discussed. The raw data from all experiments are provided in Appendix D to allow the interested reader to reproduce any comparisons of interest that are not described in detail.

The high temperatures of all of the PZ experiments should be noted. The intention of the experiments was not to demonstrate degradation at stripper conditions currently used for less stable amines (i.e., MEA). The resistance of PZ to thermal degradation that was identified by Davis allows higher temperature stripping with expected energy savings (Davis, 2009). As noted above, the slow degradation rate of PZ also introduced time constraints so higher temperature experiments were performed, even if not representative of temperatures expected for PZ stripping in a CO₂ capture system. The activation energy, E_A , for thermal degradation, discussed in greater detail in section

7.4, was calculated from data sets that included three or more temperatures. The activation energies for PZ systems that were calculated are included in Table 5.7.

Table 5.7: Experiment series to investigate the effect of temperature

Solution Constants	Values Tested				E _A (kJ/mol)
4 m PZ, $\alpha=0.3$	-	-	165 °C	175 °C	-
8 m PZ, $\alpha=0$	-	150 °C	165 °C	175 °C	258.1
8 m PZ, $\alpha=0.1$	-	-	165 °C	175 °C	-
8 m PZ, $\alpha=0.3$	135 °C	150 °C	165 °C	175 °C	183.5
8 m PZ, $\alpha=0.4$	135 °C	150 °C	165 °C	175 °C	191.4
10 m PZ, $\alpha=0.3$	135 °C	150 °C	-	-	-
10 m PZ, $\alpha=0.4$	135 °C	150 °C	-	-	-
12 m PZ, $\alpha=0.3$	-	-	165 °C	175 °C	-
20 m PZ, $\alpha=0.3$	-	150 °C	-	175 °C	-

Previous work on the thermal degradation of numerous amines found that temperature strongly affects the degradation rate, as expected. In the case of MEA, an increase of 15 °C quadruples the loss of MEA (Davis, 2009). Arrhenius relationships between the rate constant of amine and degradation temperature were also observed for MEA, 3-amino-1-propanol, 4-amino-1-butanol, AMP, 2-amino-1-propanol, 1-amino-2-propanol, and blends of MEA with PZ, Mor, DGA, or AMP (Davis, 2009). Other degradation studies have not varied temperature so the effect on amine loss was not observed (Lepaumier et al., 2010; Lepaumier et al., 2009a; Reza and Trejo, 2006).

5.3.1.1 Effect of temperature for 8 m PZ with a lean loading (0.3 mol/mol alkalinity)

Solutions of 8 m PZ with 0.3 mole CO₂ per mole alkalinity were degraded at temperatures from 135 to 175 °C. The loss of PZ in each experiment as a fraction of the initial PZ is compared in Figure 5.4. The generation of formate, total formate, EDA, FPZ, and AEP are compared for the same experiments in Figure 5.5, Figure 5.6, Figure

5.7, Figure 5.8, and Figure 5.9, respectively. FPZ and AEP were not quantified at 150 °C.

As anticipated, thermal degradation is a strong function of temperature with the high temperature experiments at 165 and 175 °C producing significant losses of PZ. The highest temperature produced a loss of 68% of the initial PZ after 15 weeks. A decrease of 10 °C in the experimental temperature (165 °C) produced a loss of only 33% of the initial PZ, roughly half the rate. A further decrease of 15 °C in the experimental temperature (150 °C) lowers the loss to only 11% of the initial PZ. This is a 33% decrease in the loss rate of PZ for a change of 15 °C. This is a weaker temperature effect than observed for MEA where an increase of 15 °C quadrupled the loss of MEA (Davis, 2009).

The generation of degradation products in this comparison provides an example of what is typically seen with PZ thermal degradation. The generation of formate and total formate, or formyl amides, increases with temperature or PZ degradation rate. Ethylenediamine (EDA), on the other hand, seems to reach a maximum in the two high temperature experiments where even at higher degradation rates, the maximum EDA concentration does not exceed 50 to 65 mmole EDA per kg. This was observed throughout this project and is likely due to reaction of EDA into other products such as 2-imidazolidinone (2-Imid). In the low temperature experiments, the degradation rate is slower and the production of EDA has not reached its peak where further reactions of EDA limit its liquid phase concentration. FPZ and AEP are generated quickly at high temperatures, as is expected with fast thermal degradation. It is not clear why FPZ reaches a maximum value in the 175 °C. AEP was not produced at a significant rate at 135 °C.

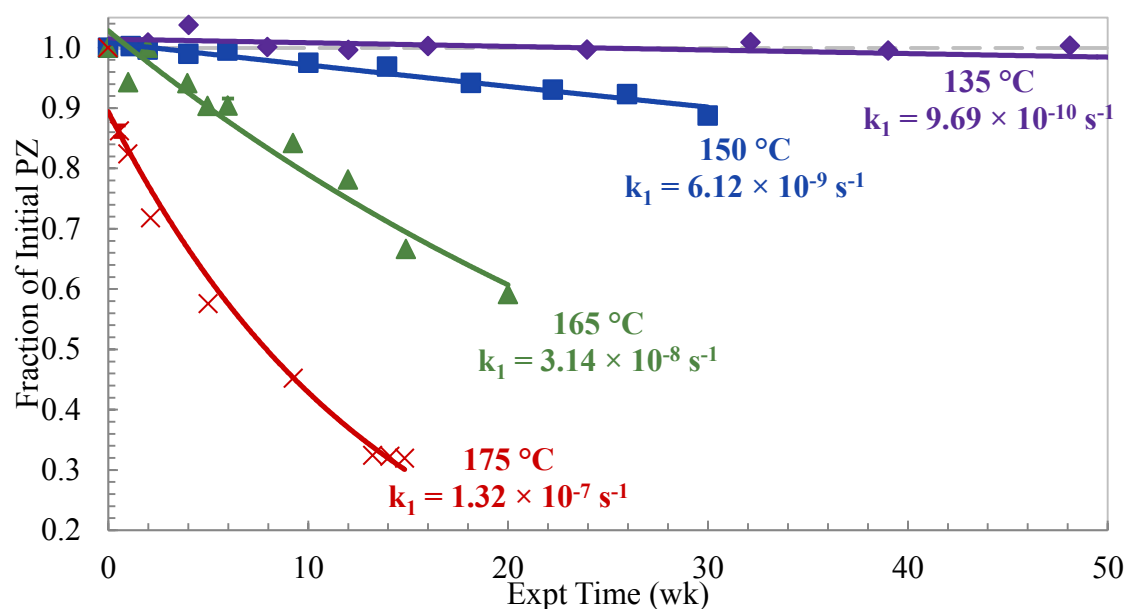


Figure 5.4: Comparison of PZ loss for 8 m PZ ($\alpha=0.3$) degraded at 135 to 175 °C ×

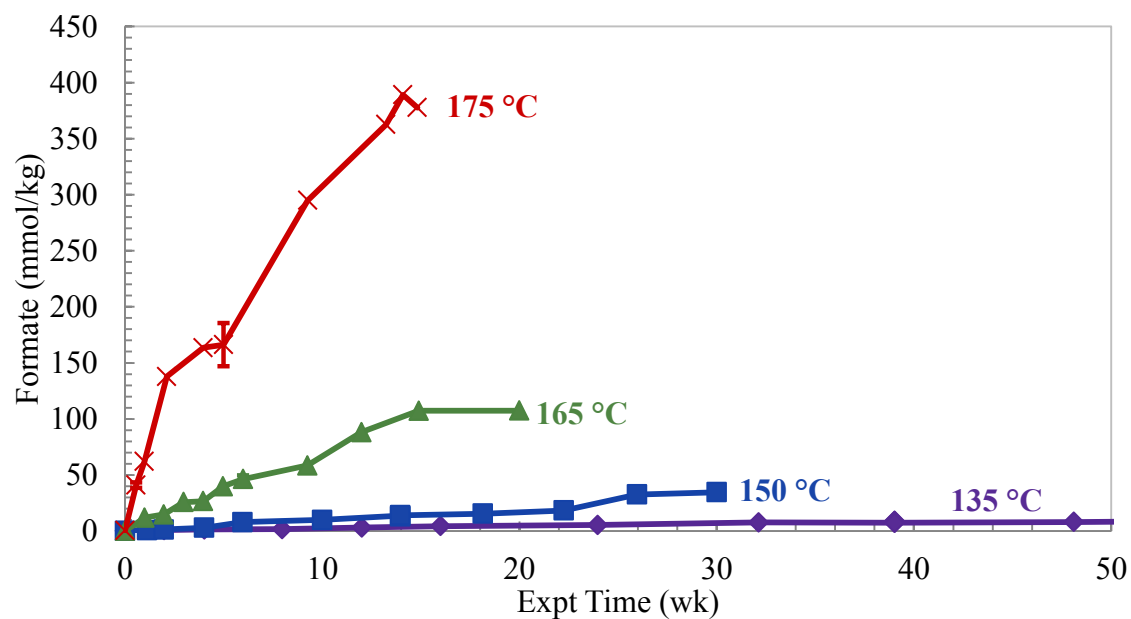


Figure 5.5: Comparison of formate generation for 8 m PZ ($\alpha=0.3$) degraded at 135 to 175 °C

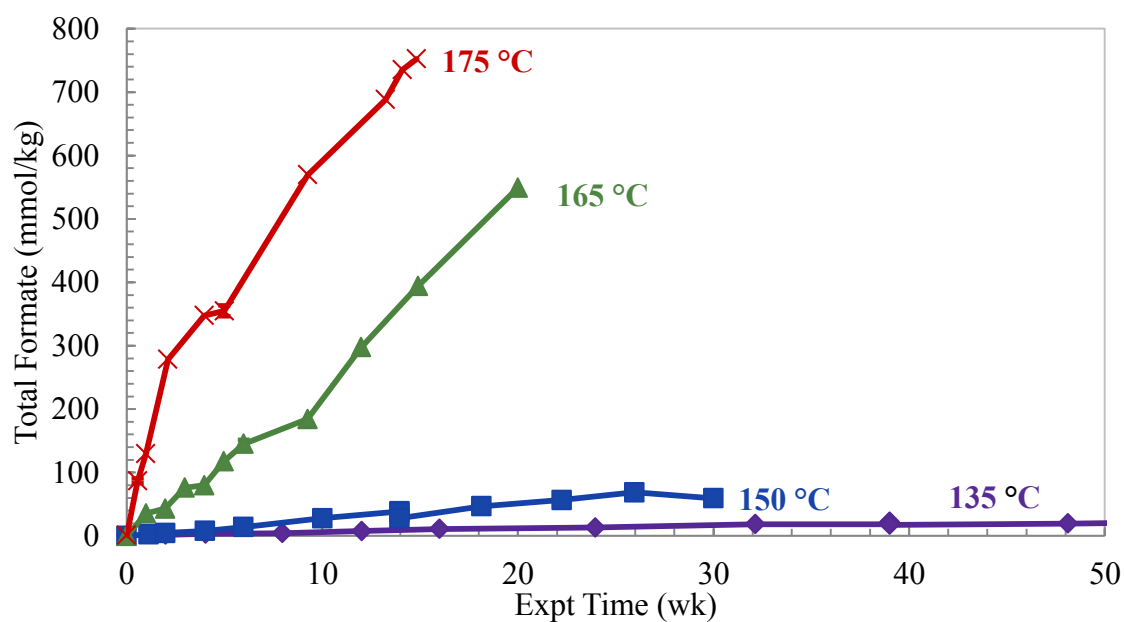


Figure 5.6: Comparison of total formate generation for 8 m PZ ($\alpha=0.3$) degraded at 135 to 175 °C

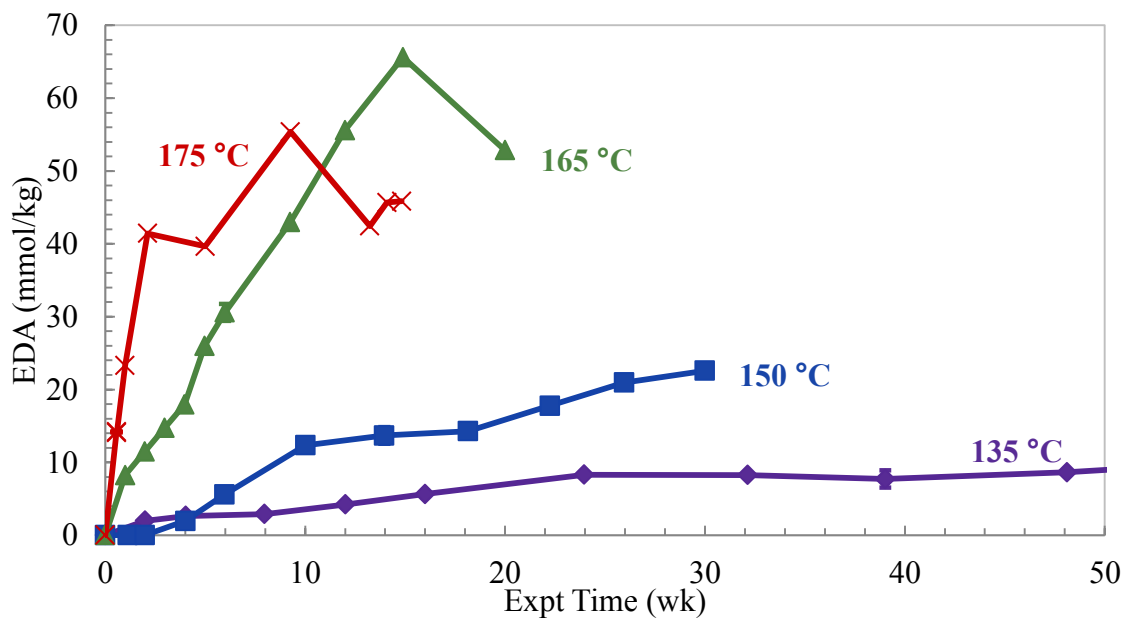


Figure 5.7: Comparison of EDA generation for 8 m PZ ($\alpha=0.3$) degraded at 135 to 175 °C

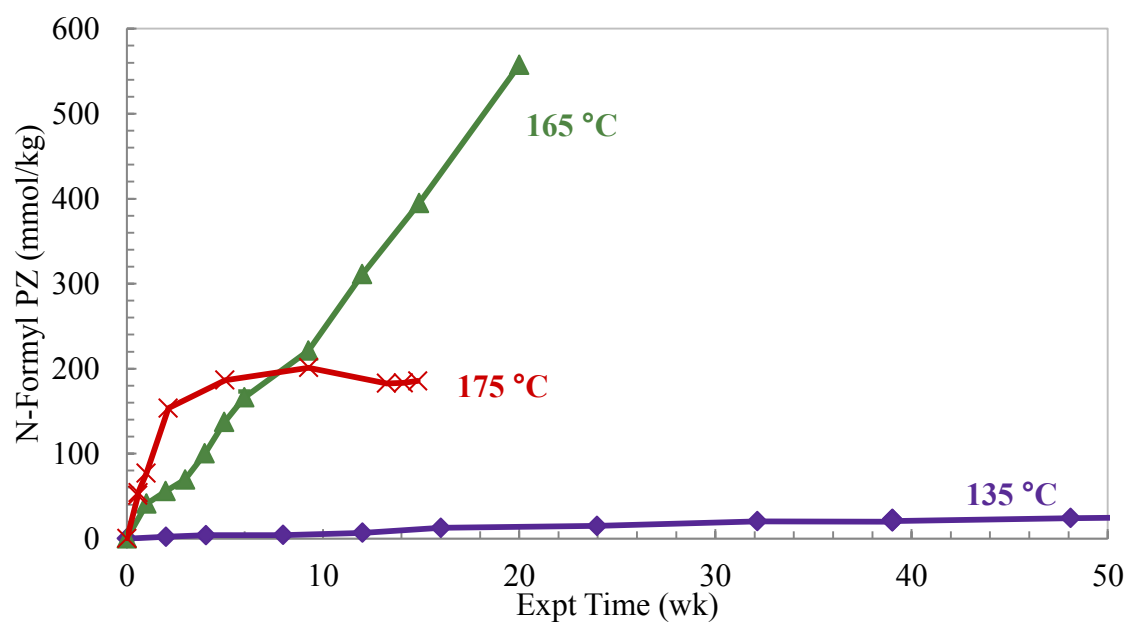


Figure 5.8: Comparison of FPZ generation for 8 m PZ ($\alpha=0.3$) degraded at 135 to 175 °C

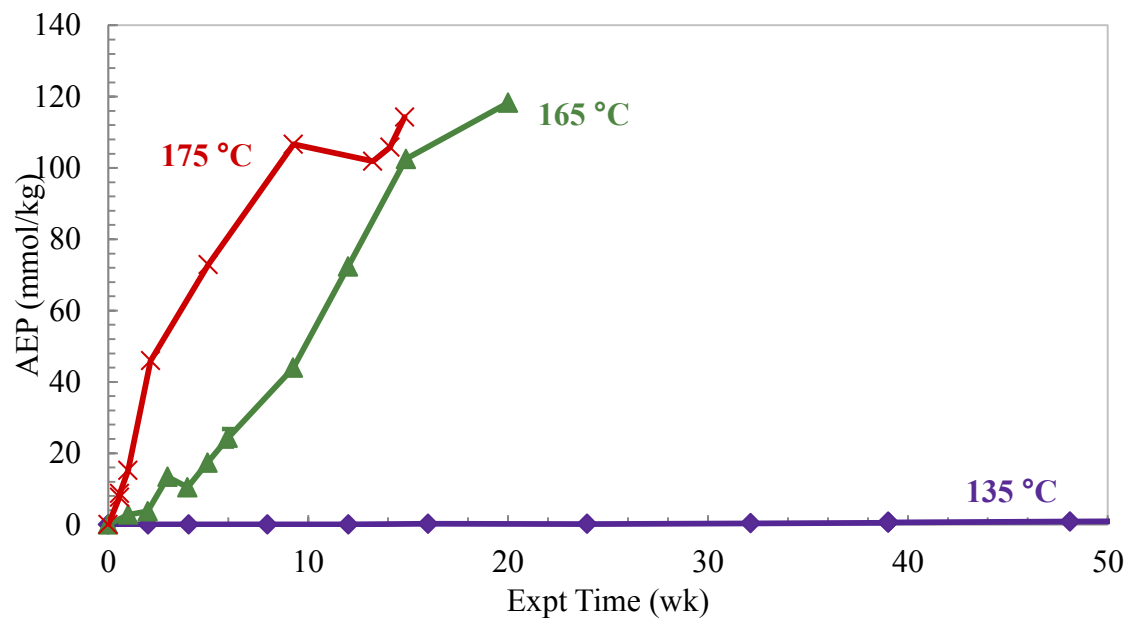


Figure 5.9: Comparison of AEP generation for 8 m PZ ($\alpha=0.3$) degraded at 135 to 175 °C

5.3.1.2 Effect of temperature for 8 m PZ with a rich loading (0.4 mol/mol alkalinity)

A solution of 8 m PZ with 0.4 mole CO₂ per mole alkalinity was degraded from 135 to 175 °C, the anticipated maximum range of temperatures for the stripping section of a concentrated PZ CO₂ capture unit. Previous experiments for MEA showed that thermal degradation rates increased with increased CO₂ loading, amplifying the importance of understanding degradation on the rich portion of the system (Davis, 2009). The loss of PZ for rich loaded 8 m PZ degraded from 135 to 175 °C is compared in Figure 5.10. The generation of formate, total formate, EDA, FPZ, and AEP are compared for the same experiments in Figure 5.11, Figure 5.12, Figure 5.13, Figure 5.14, and Figure 5.15, respectively.

As with the lean loaded solutions above, temperature strongly affected PZ loss in rich loaded solutions. The highest temperature, 175 °C, produced a loss of 70% of the initial PZ after 15 weeks of degradation. A decrease in 10 °C in the experimental temperature decreased the loss by approximately one-half as only 37% of the initial PZ was lost at 165 °C after 15 weeks. A further decrease of 15 °C showed a marked decrease of 5.3 times as only 7% of the initial PZ was lost at 150 °C. This enhancement is significantly higher than that seen in MEA solutions, demonstrating that the temperature effect in PZ is highly dependent on CO₂ loading. The generation of formate, total formate, EDA, and AEP behaved similarly to the lean loaded experiments. The maximum achieved in EDA concentration in the high temperature experiments is pronounced and indicate that EDA in the liquid phase is an intermediate product of PZ thermal degradation. For FPZ, the generation rate was nearly the same for 165 and 175 °C, indicating the mechanism may not be accelerated between these temperatures with rich loading. As with the lean loaded experiments, a maximum in FPZ concentration was observed at 175 °C, but not at 165 °C.

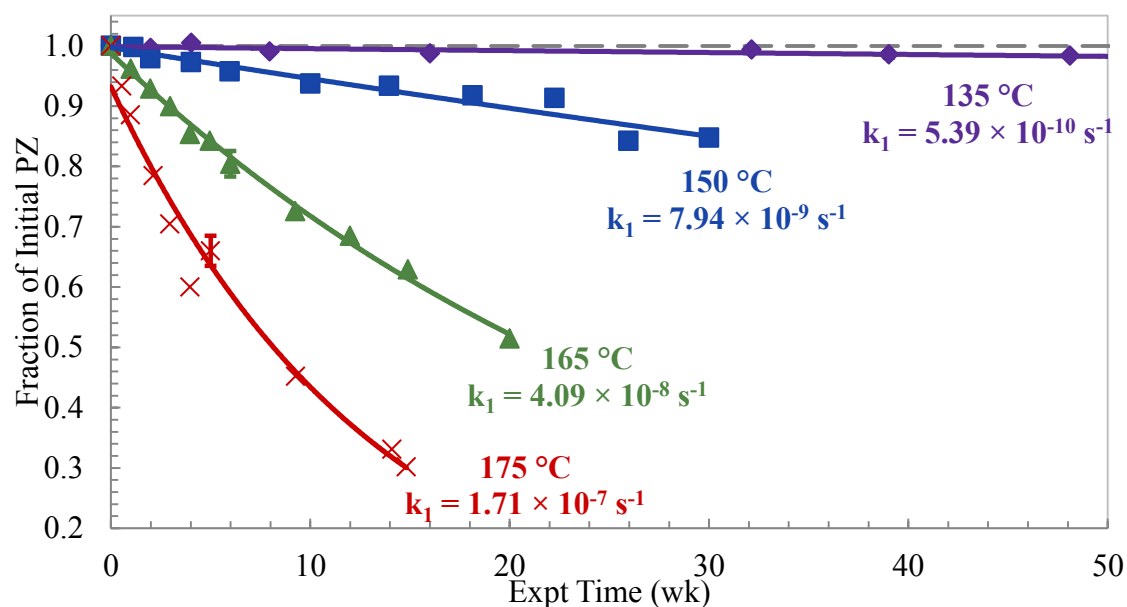


Figure 5.10: Comparison of PZ loss for 8 m PZ ($\alpha=0.4$) degraded at 135 to 175 °C

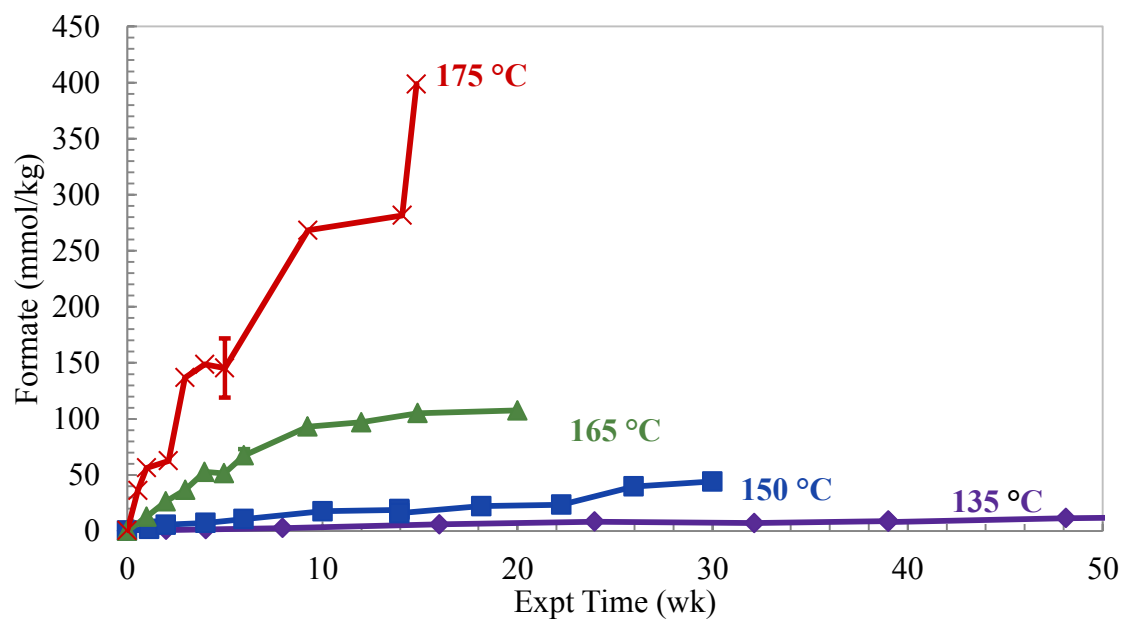


Figure 5.11: Comparison of formate generation for 8 m PZ ($\alpha=0.4$) degraded at 135 to 175 °C

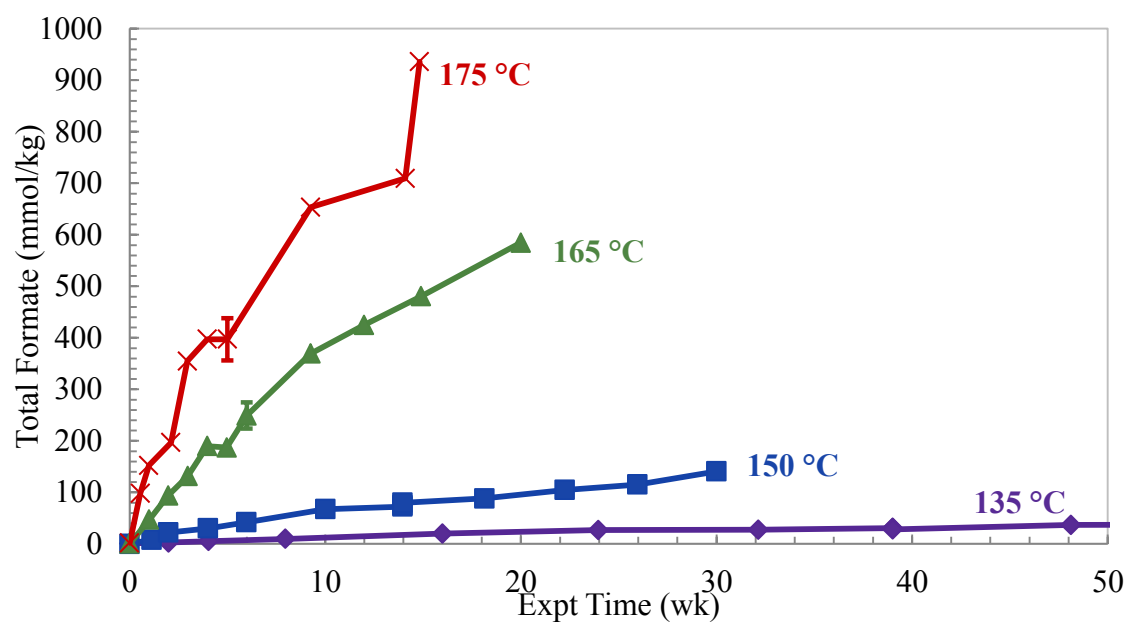


Figure 5.12: Comparison of total formate generation for 8 m PZ ($\alpha=0.4$) degraded at 135 to 175 °C

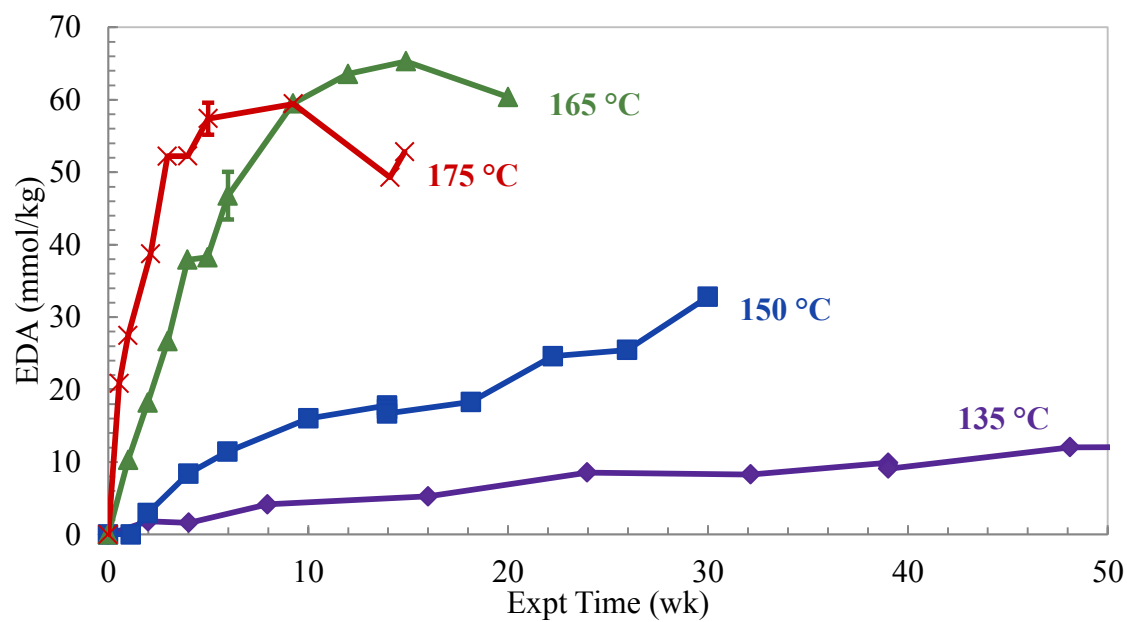


Figure 5.13: Comparison of EDA generation for 8 m PZ ($\alpha=0.4$) degraded at 135 to 175 °C

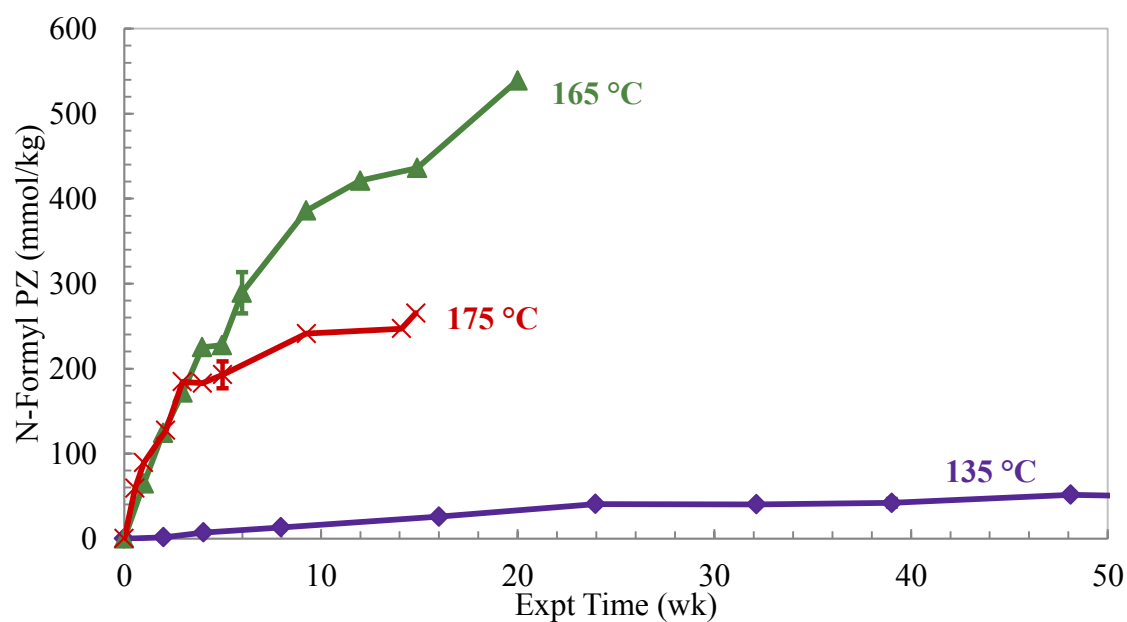


Figure 5.14: Comparison of FPZ generation for 8 m PZ ($\alpha=0.4$) degraded at 135 to 175 °C

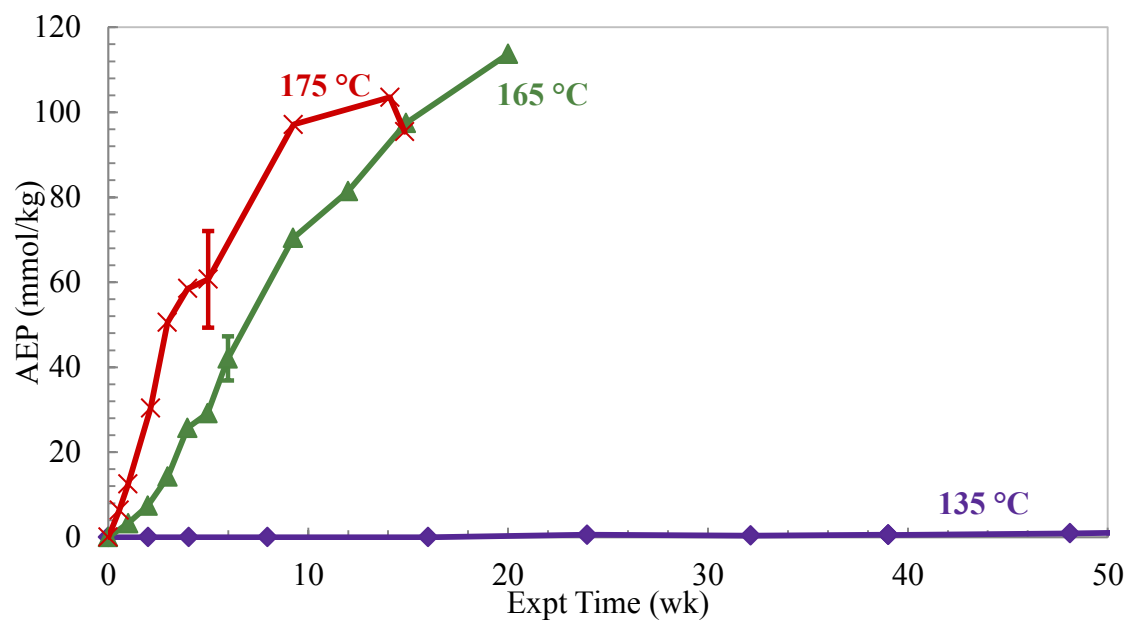


Figure 5.15: Comparison of AEP generation for 8 m PZ ($\alpha=0.4$) degraded at 135 to 175 °C

5.3.1.3 Effect of temperature for unloaded 8 m PZ

Finally, unloaded 8 m PZ was examined for the effect of temperature on low rates of thermal degradation. Since very little degradation is expected for an unloaded solution, this comparison highlights the minimal effect of temperature in this case. Even though temperature is a strong catalyst, very little degradation occurs in the absence of CO₂. Therefore, it is interesting to observe that the collaborative catalytic effect of temperature and CO₂ causes the high levels of degradation seen in loaded solutions. The PZ loss for unloaded 8 m PZ is compared for degradation occurring at 150 to 175 °C in Figure 5.16. The generation of formate, total formate, and EDA in the same experiments is compared in Figure 5.17, Figure 5.18, and Figure 5.19, respectively.

The PZ loss in this case is difficult to determine with accuracy, as demonstrated by the scatter seen in Figure 5.16. Only a slight increase of PZ loss was observed with an increase in temperature because of the low overall degradation rates of unloaded PZ. The generation of degradation products behaves similarly to the loaded experiments, although at a lower magnitude in concentration. There are appreciable trends in the formate and total formate data, signifying that the detection and quantification of degradation products is more appropriate than interpreting cation IC data in low degradation environments. The generation of EDA also shows similar behavior as the loaded experiments as the two higher temperature experiments have maximums in concentration between 35 and 40 mmole EDA per kg.

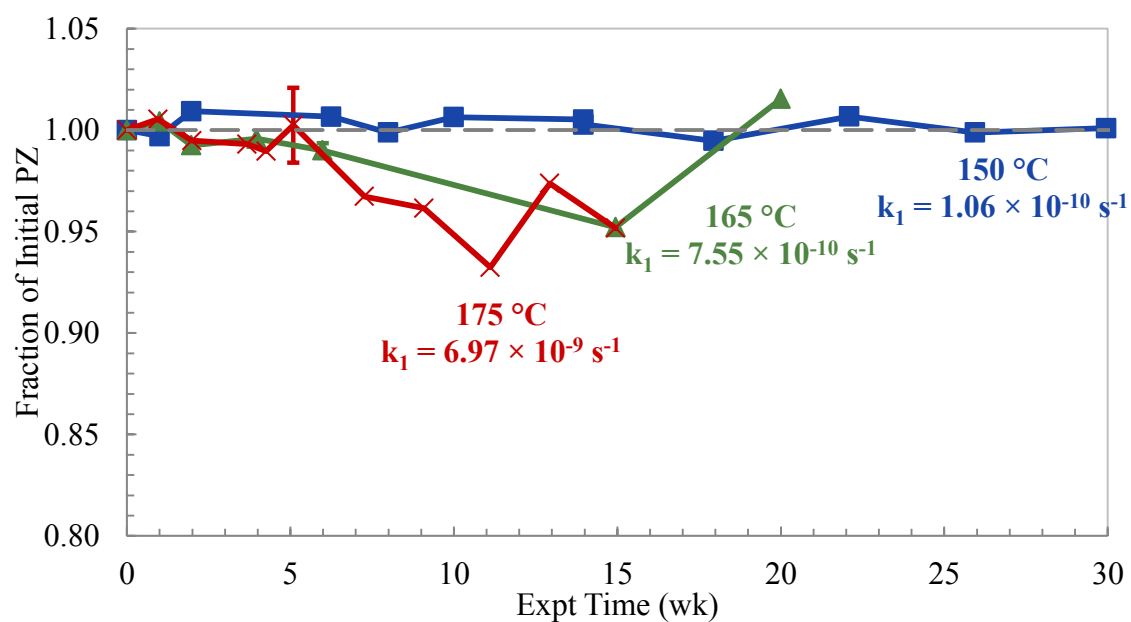


Figure 5.16: Comparison of PZ loss for 8 m PZ ($\alpha=0$) degraded at 150 to 175 °C

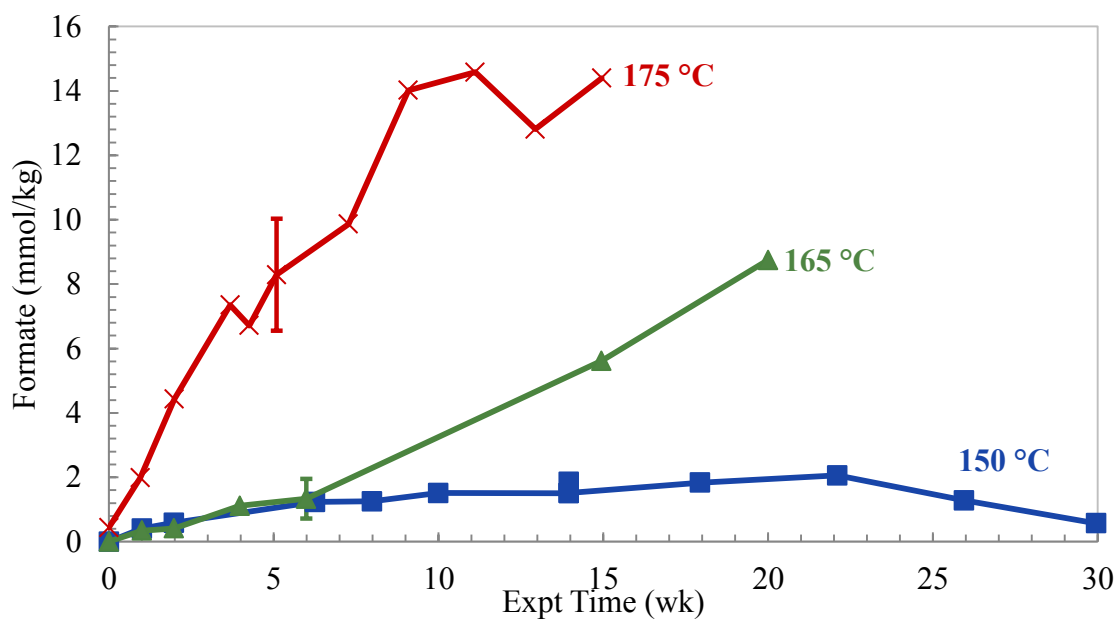


Figure 5.17: Comparison of formate generation for 8 m PZ ($\alpha=0$) degraded at 150 to 175 °C

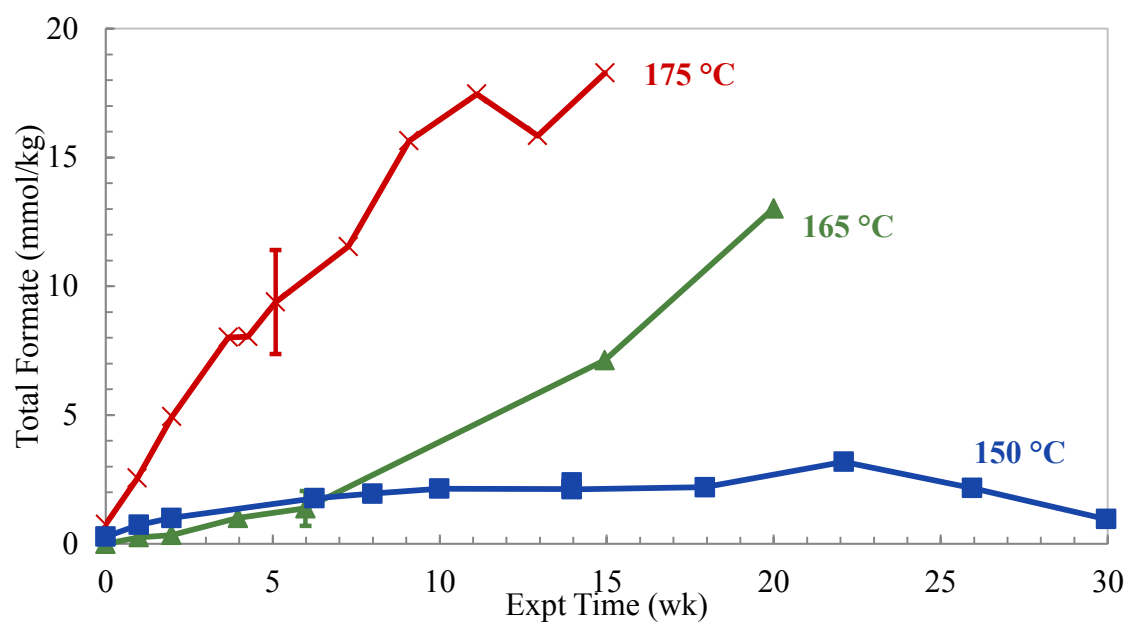


Figure 5.18: Comparison of total formate generation for 8 m PZ ($\alpha=0$) degraded at 150 and 175 °C

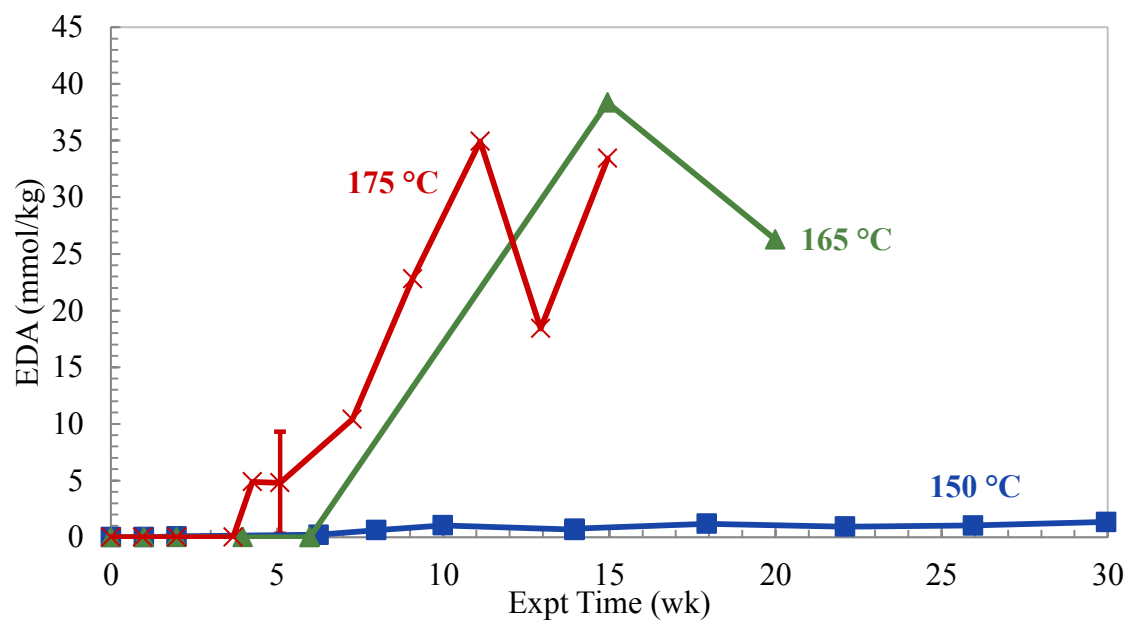


Figure 5.19: Comparison of EDA generation for 8 m PZ ($\alpha=0$) degraded at 150 and 175 °C

5.3.2 Effect of PZ concentration

The effect of PZ concentration on PZ thermal degradation was examined by degrading solutions at constant temperature and CO₂ loading. A summary of the experiments performed to examine this variable is given in Table 5.8. In total, four series of experiments were performed that highlighted the effect of PZ concentration. As with temperature comparisons in the previous section, only two will be discussed in detail to eliminate unnecessary repetition of concepts (bolded text in table). All data is available in Appendix D to reproduce any desired comparison.

Table 5.8: Experiment series to investigate the effect of PZ concentration

Solution Constants			Values Tested			
150 °C, $\alpha=0.3$	-	8 m PZ	10 m PZ	15 m PZ	-	20 m PZ
150 °C, $\alpha=0.4$	-	8 m PZ	10 m PZ	-	-	-
165 °C, $\alpha=0.3$	4 m PZ	8 m PZ	-	-	12 m PZ	-
175 °C, $\alpha=0.3$	4 m PZ	8 m PZ	-	-	12 m PZ	20 m PZ

The effect of amine concentration on thermal degradation has been quantified for MEA (Davis, 2009) over a range of 3.5 to 11 m. Davis found that the loss rate was only slightly more than first order in MEA concentration, with only slight differences observed between 3.5, 7, and 11 m MEA. Other studies of the thermal degradation of amines did not vary amine concentration so the expectation for PZ was difficult to predict without experimentation (Lepaumier et al., 2010; Lepaumier et al., 2009a; Lepaumier et al., 2009b; Reza and Trejo, 2006).

5.3.2.1 Effect of PZ concentration for a lean loading (0.3 mol/mol alkalinity) at 175 °C

The effect of PZ concentration was first assessed in lean loaded solutions as 4 to 20 m PZ with 0.3 mole CO₂ per mole alkalinity was degraded at temperatures from 175 °C. The loss of PZ in each experiment as a fraction of the initial PZ is compared in

Figure 5.20. The generation of formate, total formate, and EDA are compared for the same experiments in Figure 5.21, Figure 5.22, and Figure 5.23, respectively.

There is not a significant difference in the PZ loss for 4, 8, and 12 m PZ when plotted as a fraction of the initial PZ concentration. This indicates that thermal degradation of PZ over this temperature range behaves as nearly first order in PZ concentration. There is a slight increase of the loss rate between the 8 and 12 m experiments, but as an approximation, the system is close to first order. The data for the 20 m PZ experiment, on the other hand, does not share the behavior of the lower concentration systems. The initial rate is faster in this experiment, indicating that loss may be of higher reaction order in PZ concentration than the 4 to 12 m data. This high concentration solution is 63% PZ (CO_2 -free) or 53% PZ with a loading of 0.3 mole CO_2 per mole alkalinity. With this concentration of PZ, the concentration of water is becoming less significant and the activity of water may be vastly different in comparison with the 4 to 12 m PZ solutions. The speciation has also not been tested at this high level and may differ slightly due to the high PZ concentration.

The generation of all three degradation products exhibits unique behavior. For formate, less is produced in the 12 and 20 m PZ experiments than the 8 m case. This is not expected as degradation roughly increases, especially between 12 and 20 m PZ. Total formate, on the other hand, increases with increasing PZ concentration. Although 4, 8, and 12, have similar rates of thermal degradation when viewed as a fraction of the initial PZ concentration, the magnitude of PZ concentration degraded increases as the starting concentration increases. This increase translates to a higher concentration of total formate produced after degradation. The EDA concentration profiles all indicate that EDA is an intermediate degradation product, while the maximum concentration achieved is a function of the PZ starting concentration. The maximum concentration achieved

before EDA reacts to other products increases from 36 mmole per kg in the 4 m PZ experiment to over 100 mmole per kg in the 20 m PZ experiment. The time point of the maximum also occurred at nearly the same time for all four PZ concentrations. This is unlike the behavior seen in the temperature series experiments. In that case, the maximum of EDA concentration occurred later in experiments with less degradation (lower temperature). With the effect of PZ concentration, the maximum in EDA concentration occurs after 7 to 10 weeks in all four cases.

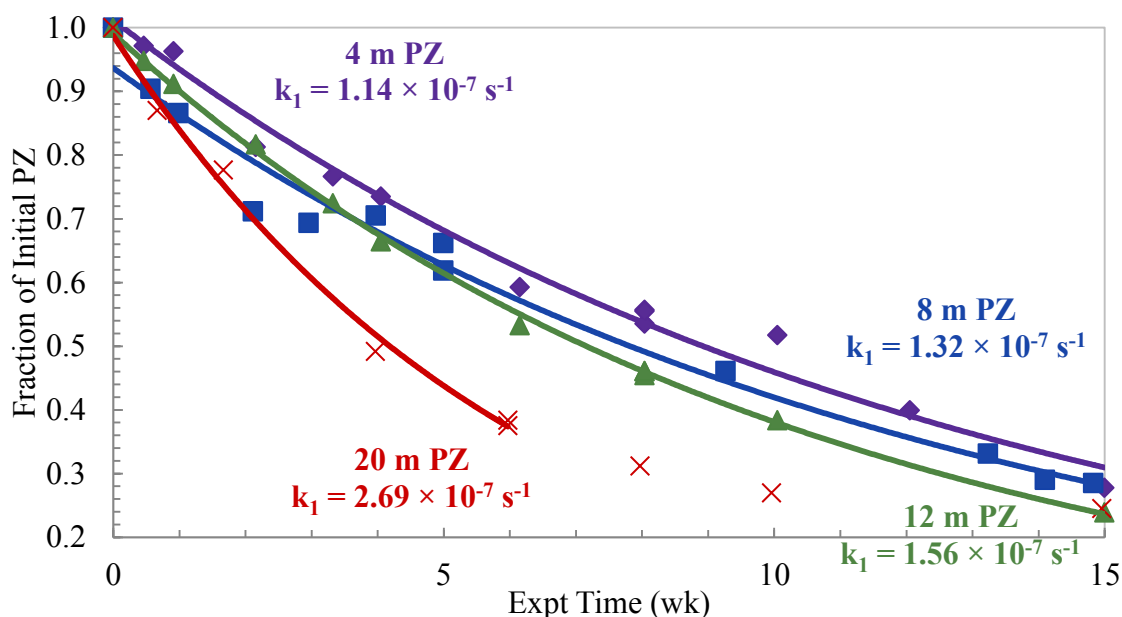


Figure 5.20: Comparison of PZ loss for lean ($\alpha=0.3$) solutions degraded at 175 °C from 4 to 20 m PZ

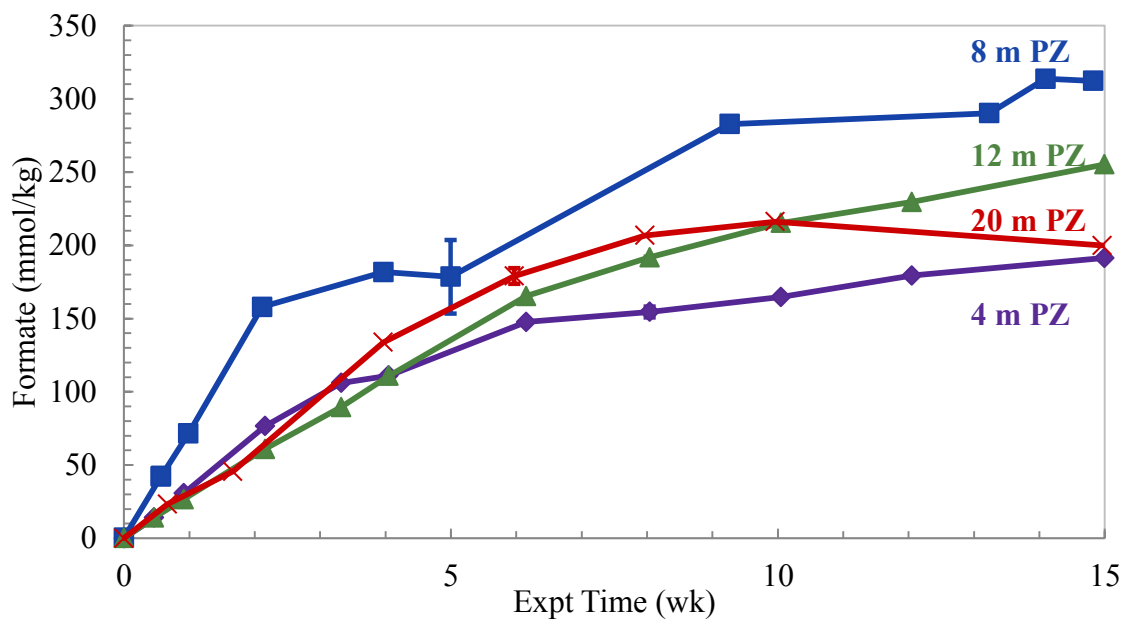


Figure 5.21: Comparison of formate generation for lean ($\alpha=0.3$) solutions degraded at 175 °C from 4 to 20 m PZ

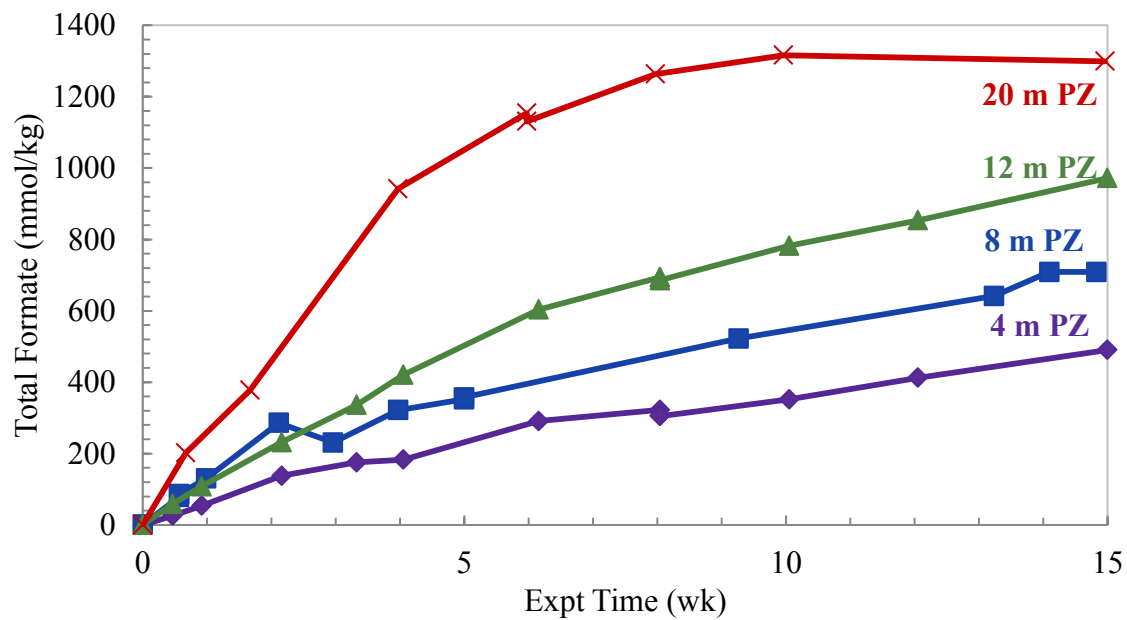


Figure 5.22: Comparison of total formate generation for lean ($\alpha=0.3$) solutions degraded at 175 °C from 4 to 20 m PZ

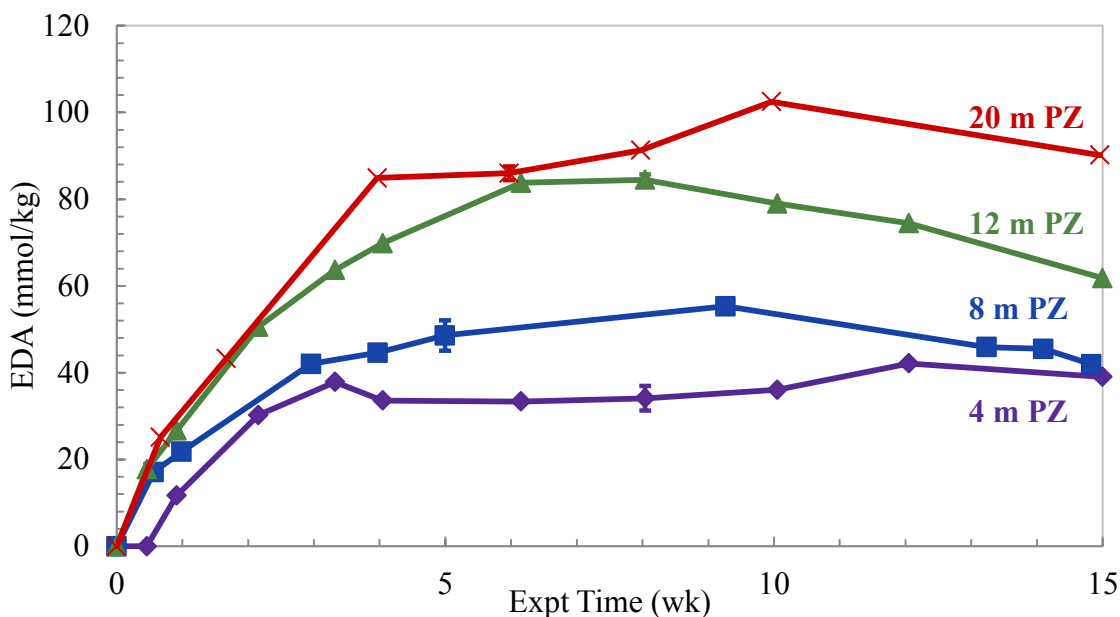


Figure 5.23: Comparison of EDA generation for lean ($\alpha=0.3$) solutions degraded at 175 °C from 4 to 20 m PZ

5.3.2.2 Evaluation of error for 1st-order approximation

The data in Figure 5.20 demonstrate a small effect of PZ concentration on the loss rate of PZ between 4 to 12 m PZ. In order to determine if the effect is significant, the same t-test analysis described earlier in the chapter was performed for this set of data (section 5.2.1). The t-test was performed in the same way with the same null hypothesis described in Equation 5.7 through 5.12. The linear regressions are represented as exponential regressions in Figure 5.20. The results of the test are shown in Table 5.9 for a comparison of each of the data sets with each other.

The data for 8 m PZ was found to be statistically similar to both the 4 and 12 m PZ data sets within a confidence of 95%. The comparison of the regressed slopes for the 4 and 12 m PZ data, however, were found to disprove the null hypothesis and are statistically different with 95% confidence. This result is expected given the data discussed in the previous section. There is not a strong effect of PZ concentration in

thermal degradation of PZ in comparison to the effect of CO₂ concentration or temperature, and the behavior is slightly more than first order. The first order analysis described in section 5.2 will be used throughout this project as a basis of comparison although some amines such as concentrated PZ, may be represented more accurately with a model with slightly more than first order behavior in amine.

Table 5.9: Results for statistical comparison of parallelism of PZ loss slope for TE4, TE12, and TE18 (8 m PZ, 0.3 mole CO₂ per mole alkalinity, 175 °C)

Data set 1	4 m PZ (TE32)	8 m PZ (TE12)	4 m PZ (TE32)
Data set 2	8 m PZ (TE12)	12 m PZ (TE33)	12 m PZ (TE33)
DOF	21	21	22
α	0.05	0.05	0.05
$t_{n1+n2-4, 1-\alpha/2}$	$t_{21,0.975}$	$t_{21,0.975}$	$t_{22,0.975}$
t value	2.080	2.080	2.074
$S^2_{P,Y/X}$	0.00299	0.0285	0.00185
$S_{m_1-m_2}$	0.0045	0.015	0.00373
T	0.29	1.39	4.03
T	0.29	1.39	4.03
H ₀	True	True	False

5.3.2.3 Effect of PZ concentration for a lean loading (0.3 mol/mol alkalinity) at 165 °C

The effect of PZ concentration for lean loaded solutions was also examined at a lower temperature. Solutions of 4 to 12 m PZ with 0.3 mole CO₂ per mole alkalinity were degraded at 165 °C. The PZ loss is compared for these experiments in Figure 5.24. The generation of formate, total formate, and EDA is compared for the same experiments in Figure 5.25, Figure 5.26, and Figure 5.27, respectively. Unfortunately, the 4 m PZ experiment suffered from a high rate of thermal cylinder failure and there are only three data points up to 6 weeks available.

The loss of PZ does not demonstrate the same behavior as the previous comparison at 175 °C. The 8 m PZ data has significant scatter in the earliest parts of the

data where the trend changes after 3 weeks. It is not clear if the original trend, which is similar to the 12 m PZ data, or the second trend, which behaves as the 4 m PZ data does, is the most appropriate trend. The generation of formate is the same for all three concentrations while the generation of total formate is enhanced as the PZ concentration increases. The generation of EDA is also faster in the higher PZ concentration experiments and none of the experiments reach a noticeable maximum in this time period. It is likely that as with data at 135 and 150 °C, there is not enough degradation at this point to allow for the EDA generation to accumulate and begin reacting onto other products.

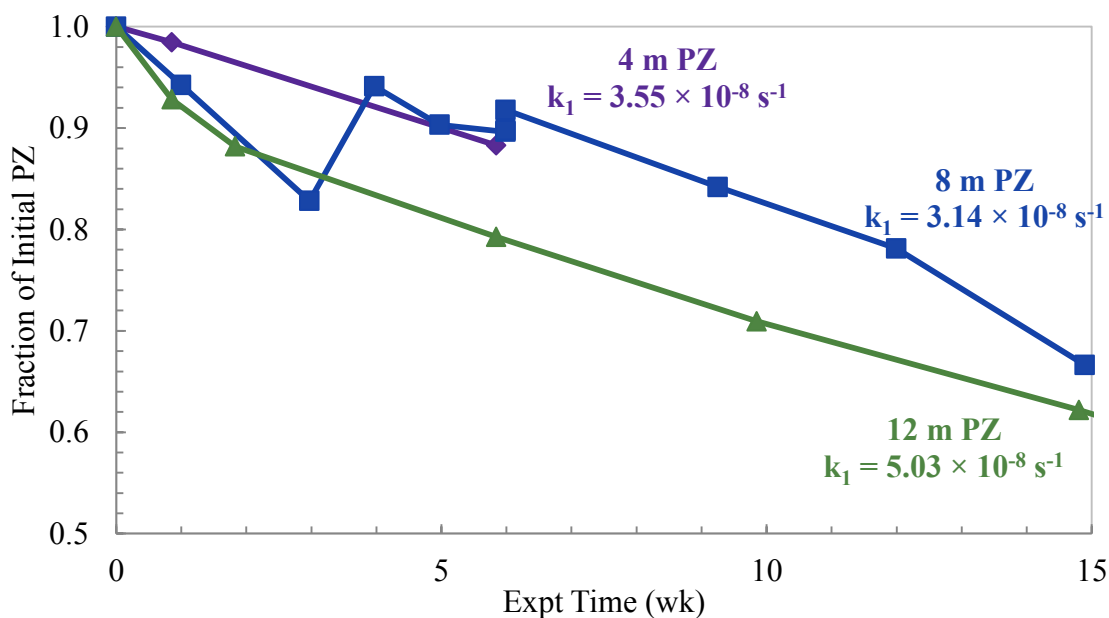


Figure 5.24: Comparison of PZ loss for lean ($\alpha=0.3$) solutions degraded at 165 °C containing 4 to 12 m PZ

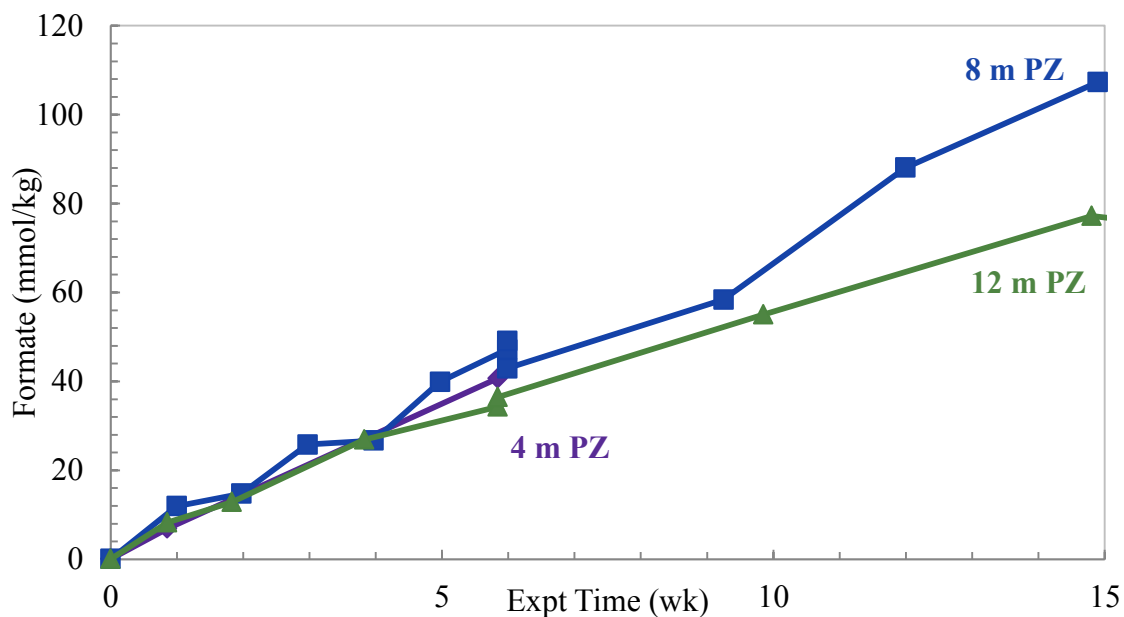


Figure 5.25: Comparison of formate generation for lean ($\alpha=0.3$) solutions degraded at 165 °C containing 4 to 12 m PZ

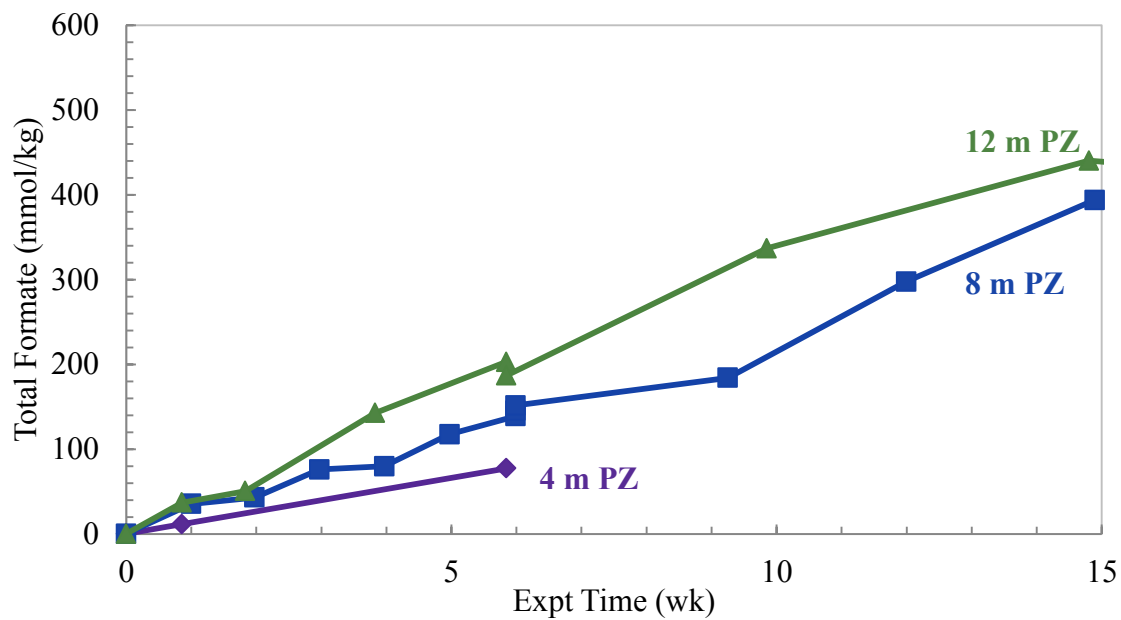


Figure 5.26: Comparison of total formate generation for lean ($\alpha=0.3$) solutions degraded at 165 °C containing 4 to 12 m PZ

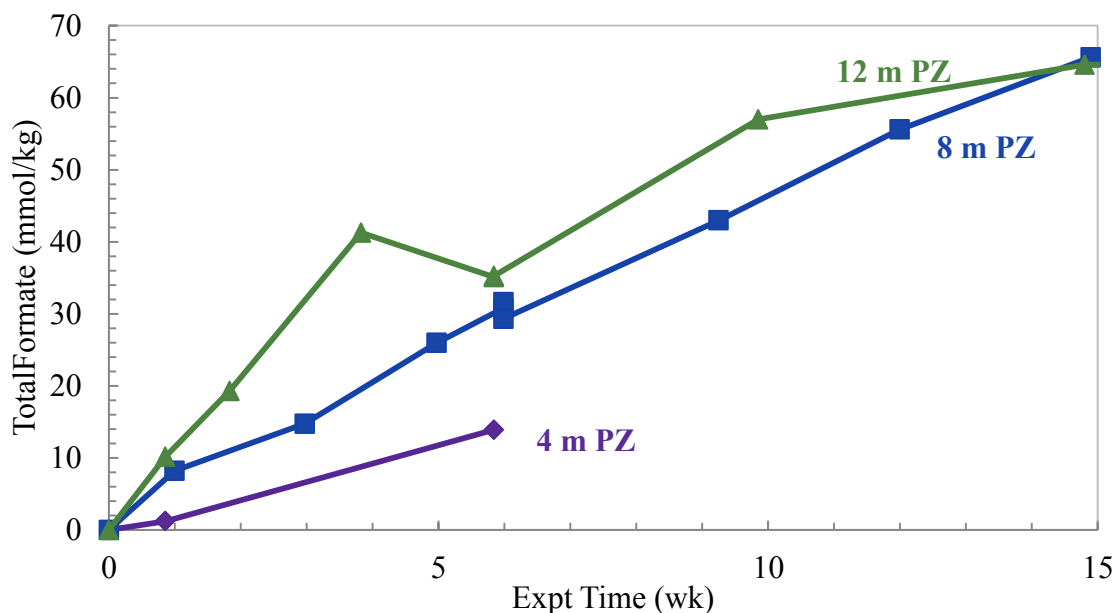


Figure 5.27: Comparison of EDA generation for lean ($\alpha=0.3$) solutions degraded at 165 °C containing 4 to 12 m PZ

5.3.3 Effect of CO₂ loading

The effect of CO₂ concentration on the PZ thermal degradation was examined by degrading solutions at constant temperature and PZ concentration. A summary of the experiments performed to examine this variable is provided in Table 5.10. In total, eight groups of experiments were performed that highlighted the effect of CO₂ concentration. As with the previous two sections, only three of the eight comparisons will be discussed in detail. All data is available in Appendix D to reproduce any comparison.

Previous authors have found CO₂ to be a strong catalyst for thermal degradation of amines (Davis, 2009; Lepaumier et al., 2009a). Davis determined that degradation of MEA was approximately first order in CO₂ concentration as he observed a doubling of MEA loss with an increase of CO₂ loading from 0.2 to 0.4 with 7 m MEA at 135 °C. Lepaumier found that all of the amines tested, including MEA, AMP, diethanolamine (DEA), methyldiethanolamine (MDEA), and N-(2-hydroxyethyl)ethylenediamine

(HEEDA), demonstrated a noted increase in the level of degradation in the presence of CO₂ compared to without CO₂ (Lepaumier et al., 2009a). The catalytic effect of CO₂ on each amine was slightly different, but all showed marked increases in degradation. For HEEDA, the presence of CO₂ increased the loss of HEEDA from 1% to nearly 100% with the same temperature and experiment length (Lepaumier et al., 2009a). The effect of CO₂ on PZ thermal degradation has not been studied previously, but it was hypothesized to follow the trends found with other amines and alkanolamines.

Table 5.10: Experiment series to investigate the effect of CO₂ Loading

Solution Constants	Values Tested (mole CO ₂ /mole alkalinity)					
8 m PZ, 135 °C	-	-	-	0.3	0.4	-
8 m PZ, 150 °C	-	-	-	0.3	0.4	-
8 m PZ, 165 °C	0	0.1	-	0.3	0.4	-
8 m PZ, 175 °C	0	0.1	0.2	0.3	0.4	0.47
10 m PZ, 135 °C	-	-	-	0.3	0.4	-
10 m PZ, 150 °C	-	-	-	0.3	0.4	-
10 m PZ, 175 °C	-	-	-	0.3	0.4	-
20 m PZ, 175 °C	-	0.1	-	0.3	-	-

5.3.3.1 Effect of CO₂ concentration for 8 m PZ at 175 °C

The widest range of CO₂ concentrations was examined with experiments performed on 8 m PZ at 175 °C. These experiments provide the best understanding of the effect of CO₂ concentration in thermal degradation of concentrated, aqueous PZ. The loss of PZ as a fraction of the initial PZ for experiments with initial CO₂ concentrations of 0, 0.1, 0.2, 0.3, 0.4, and 0.47 mole CO₂ per mole alkalinity are compared in Figure 5.28. The generation of formate, total formate, EDA, FPZ, and AEP for the same six experiments is compared in Figure 5.30, Figure 5.32, Figure 5.34, Figure 5.35, and Figure 5.36, respectively. Neither FPZ nor AEP were quantified in the unloaded experiment while AEP was not quantified for the 0.1 mole CO₂ per mole alkalinity.

Changes in CO₂ concentration have a complicated effect on PZ thermal degradation. In terms of PZ loss, the rate of PZ loss increases with increased CO₂ loading up to a loading of 0.3 moles CO₂ per mole alkalinity. Between 0.3 and 0.4 moles CO₂ per mole alkalinity, there is little difference in PZ loss. An increase to 0.47 moles CO₂ causes a decrease in degradation rate. Changes in CO₂ concentration, therefore, create a maximum in degradation rate between 0.3 and 0.4 moles CO₂ per mole alkalinity. The fraction of initial PZ degraded after 5 and 15 weeks at 175 °C is compared in Figure 5.29 over a range of 0 to 0.47 mole CO₂ per mole alkalinity to demonstrate this observation. The solution with 0.47 mole CO₂ per mole alkalinity has a noticeable change in rate with a lower initial rate that increases after 8 weeks of degradation. This change in rate is observable in Figure 5.29 as well as the shape of the curves at 5 and 15 weeks of degradation are different in regards to the very rich solution.

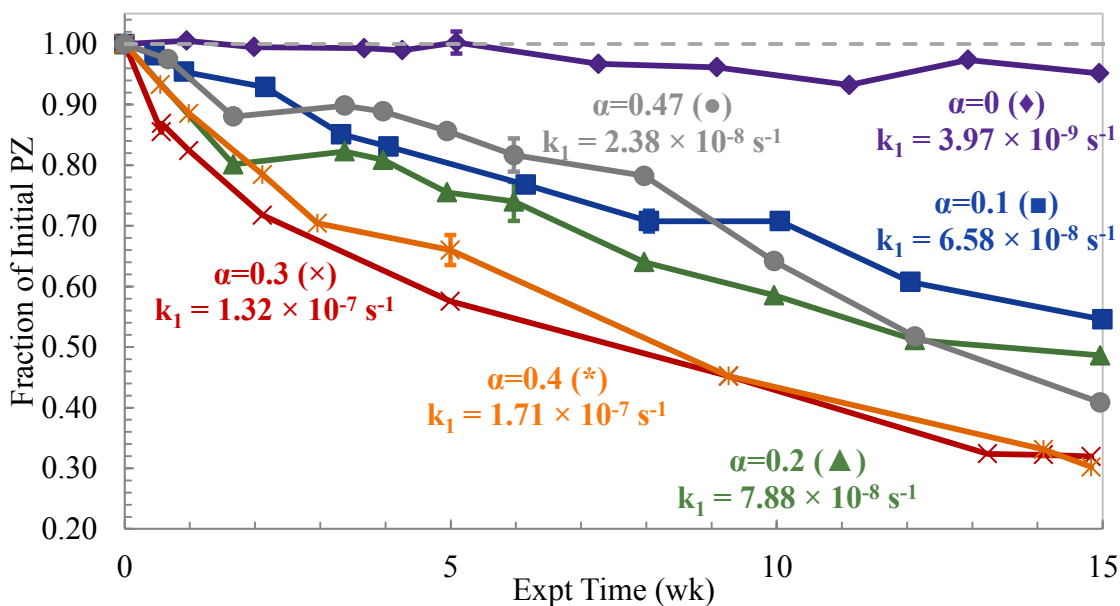


Figure 5.28: Comparison of PZ loss for 8 m PZ at 175 °C with 0 to 0.47 mole CO₂ per mole alkalinity

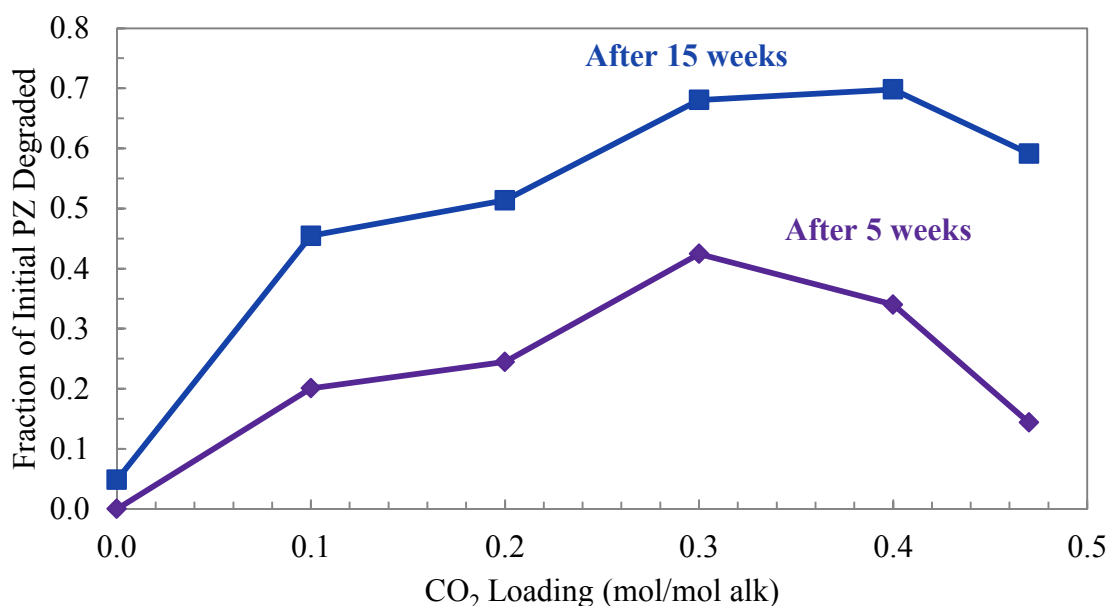


Figure 5.29: Fraction of PZ degraded after 5 and 15 weeks at 175 °C for 8 m PZ with 0 to 0.47 mole CO₂ per mole alkalinity

The generation of formate and total formate also demonstrate unique behavior with changes in CO₂ concentration. For formate, a maximum concentration is observed in the final concentration between the solutions with 0.3 and 0.4 mole CO₂ per mole alkalinity. The concentration of formate quantified after 5 and 15 weeks is compared in Figure 5.31 to demonstrate this. At both experimental times, the concentration of formate in the very rich loaded case (0.47 mole CO₂ per mole alkalinity) is lower than the rich loaded case. In the case of total formate, the concentration generated after 15 weeks of degradation increases steadily to a maximum at 0.4 mole CO₂ per mole alkalinity, then decreases in the very rich case. The concentration of total formate after 5 and 15 weeks is compared in Figure 5.33 to demonstrate this. The ratio of formate to formyl amides, therefore, does change slightly with differences in CO₂ concentration over this range. The FPZ quantified directly also has complicated behavior as 0.2 to 0.4 mole per mole

alkalinity produce similar final concentrations of FPZ while the very rich experiment produced the highest levels of FPZ.

The EDA data suggests, as with previous experiments, that EDA is an intermediate that is generated at varying initial rates, and then reacted away to form additional products. The initial rates of production can offer some clues to the effect of CO_2 . The data before 5 weeks of degradation suggest that the 0.3 and 0.4 mole CO_2 per mole alkalinity experiments have the fastest EDA generation rates while the other experiments are all lower. This suggests a maximum generation rate between 0.3 and 0.4 moles CO_2 per mole alkalinity, a similar behavior as was observed with formate and total formate. Since formate and formyl amides are final products, rather than intermediates, their behavior is more readily observable. AEP was produced at similar initial rates over a range of CO_2 loadings and final concentrations that show complex behavior at very lean and very rich loadings.

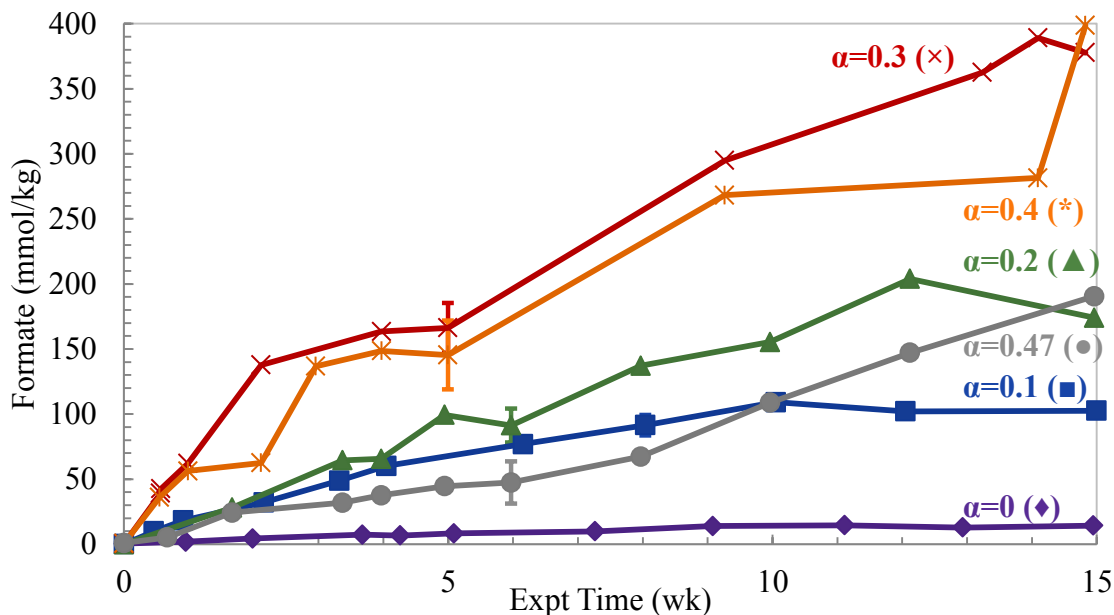


Figure 5.30: Comparison of formate generation for 8 m PZ at 175 °C with 0 to 0.47 mole CO_2 per mole alkalinity

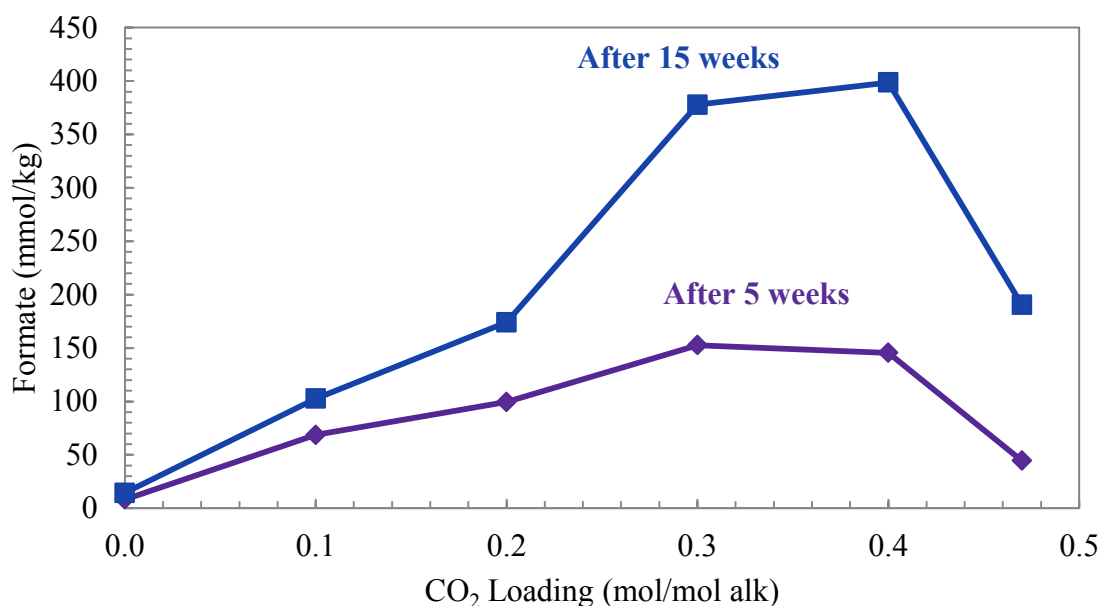


Figure 5.31: Generation of formate after 5 and 15 weeks at 175 °C for 8 m PZ with 0 to 0.47 mole CO₂ per mole alkalinity

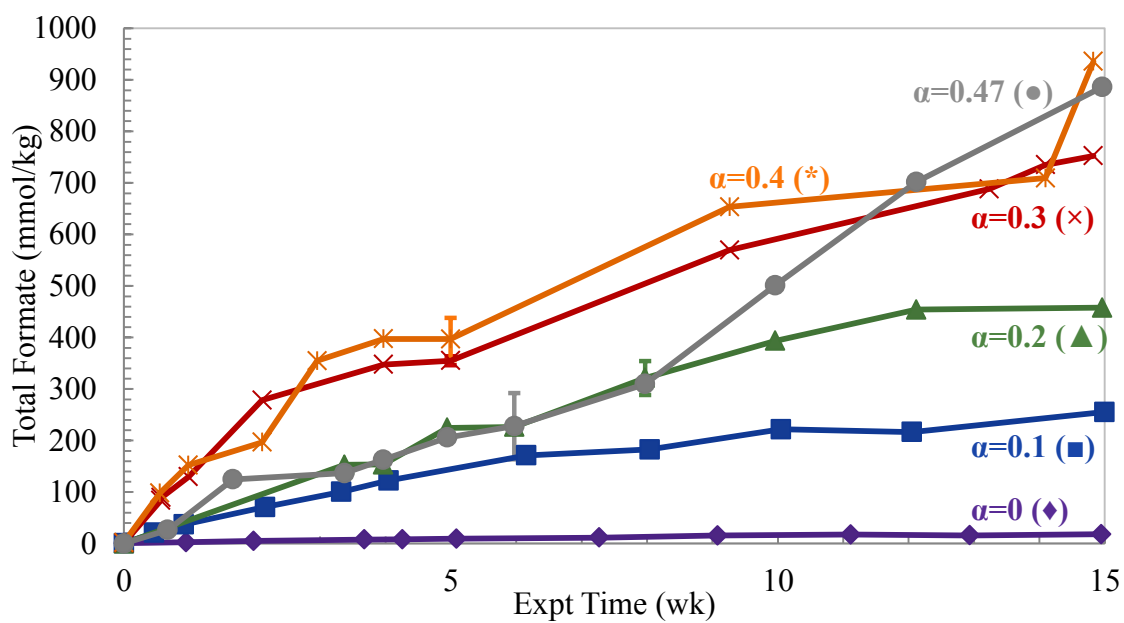


Figure 5.32: Comparison of total formate generation for 8 m PZ at 175 °C with 0 to 0.47 mole CO₂ per mole alkalinity

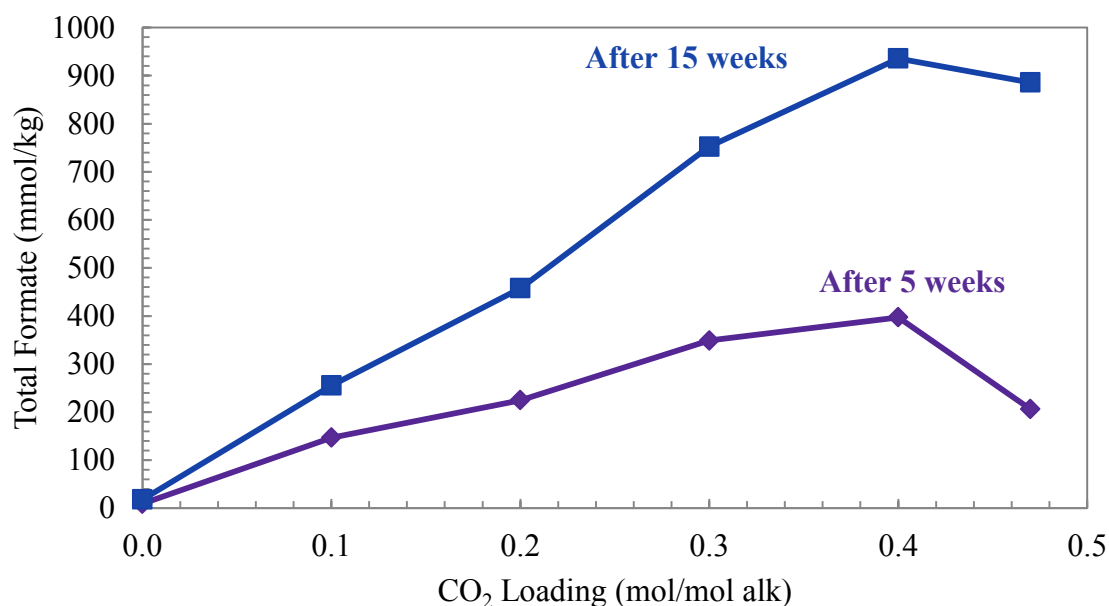


Figure 5.33: Generation of total formate after 5 and 15 weeks at 175 °C for 8 m PZ with 0 to 0.47 mole CO₂ per mole alkalinity

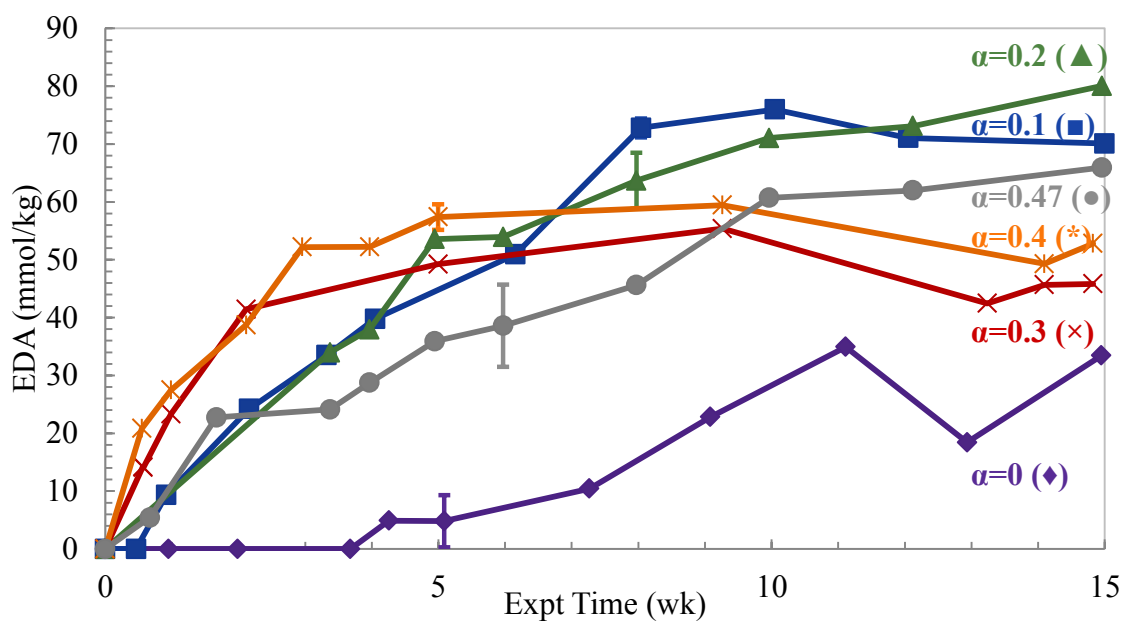


Figure 5.34: Comparison of EDA generation for 8 m PZ at 175 °C with 0 to 0.47 mole CO₂ per mole alkalinity

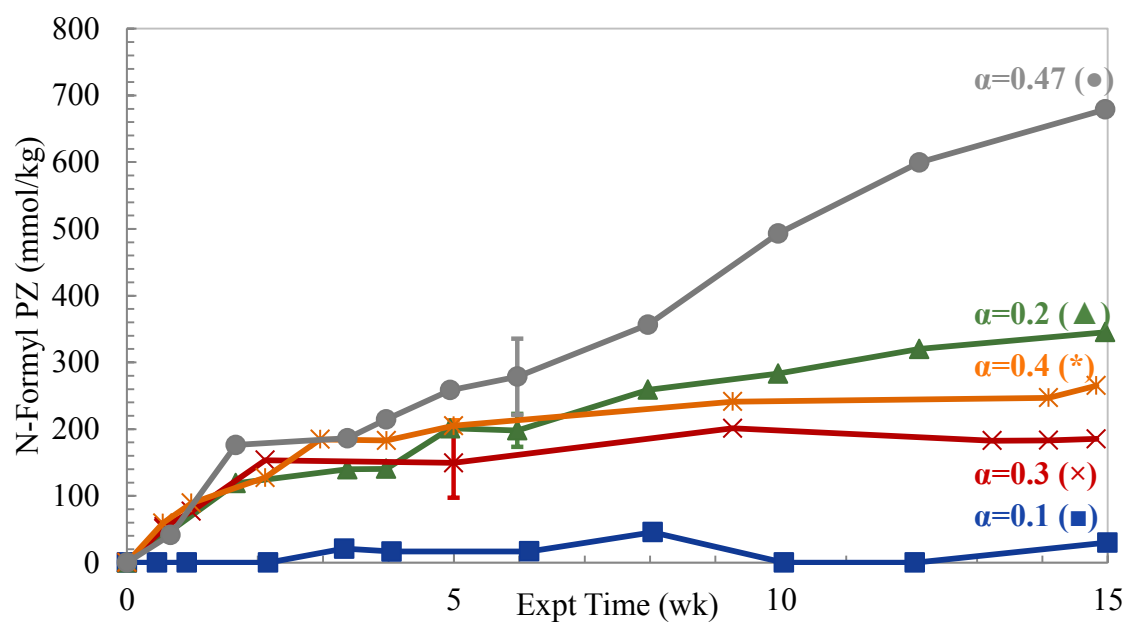


Figure 5.35: Comparison of FPZ generation for 8 m PZ at 175 °C with 0 to 0.47 mole CO₂ per mole alkalinity

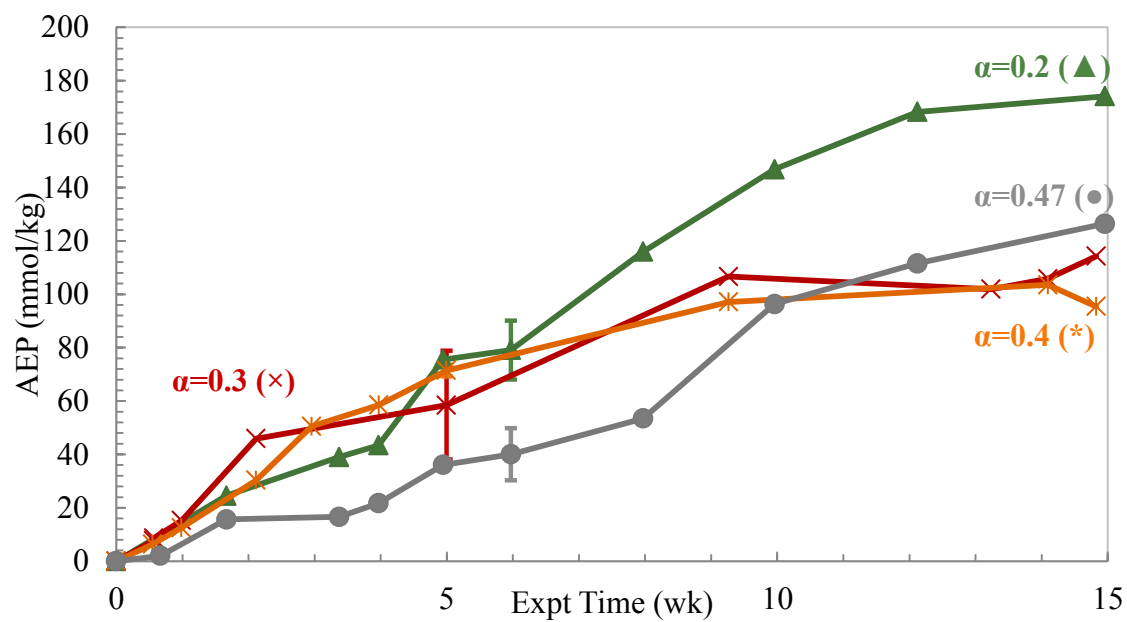


Figure 5.36: Comparison of AEP generation for 8 m PZ at 175 °C with 0 to 0.47 mole CO₂ per mole alkalinity

As the initial CO_2 concentration increases from 0 to 0.47 mole CO_2 per mole alkalinity, the rate of PZ loss and generation rates of degradation product experience a maximum rate at an intermediate CO_2 concentration. This behavior suggests a strong effect of speciation on the thermal degradation rate. The speciation predicted for 8 m PZ was discussed in section 2.1. The speciation expected for 8 m PZ at 175 °C is shown in Figure 5.37. The speciation does not show one species whose concentration matches the trend of the degradation rate, as may be expected. It is likely then, that the degradation effect is a balance of more than one active species. The concentration of PZCOO^- reaches a maximum between 0.2 and 0.3 mole CO_2 per mole alkalinity while the concentration of H^+PZ is continually increasing, although slowly after 0.3 mole CO_2 per mole alkalinity. As loading increases, PZCOO^- is protonated to form H^+PZCOO^- which is also likely involved with degradation as an active species. The exact cause of the degradation behavior is not known although H^+PZ , H^+PZCOO^- , and PZCOO^- are all expected to be involved in the initial mechanisms for degradation. It is possible that one species, such as H^+PZ , dominates the mechanism at low loadings and then the dominant mechanisms change as the concentration of other molecules increases in solution. For example, at low loadings, H^+PZ may dominant while at loadings greater than 0.3 mole CO_2 per mole alkalinity the unprotonated molecules become more influential on the degradation mechanisms. The effect H^+PZ , in particular, is discussed in more detail in section 6.3.

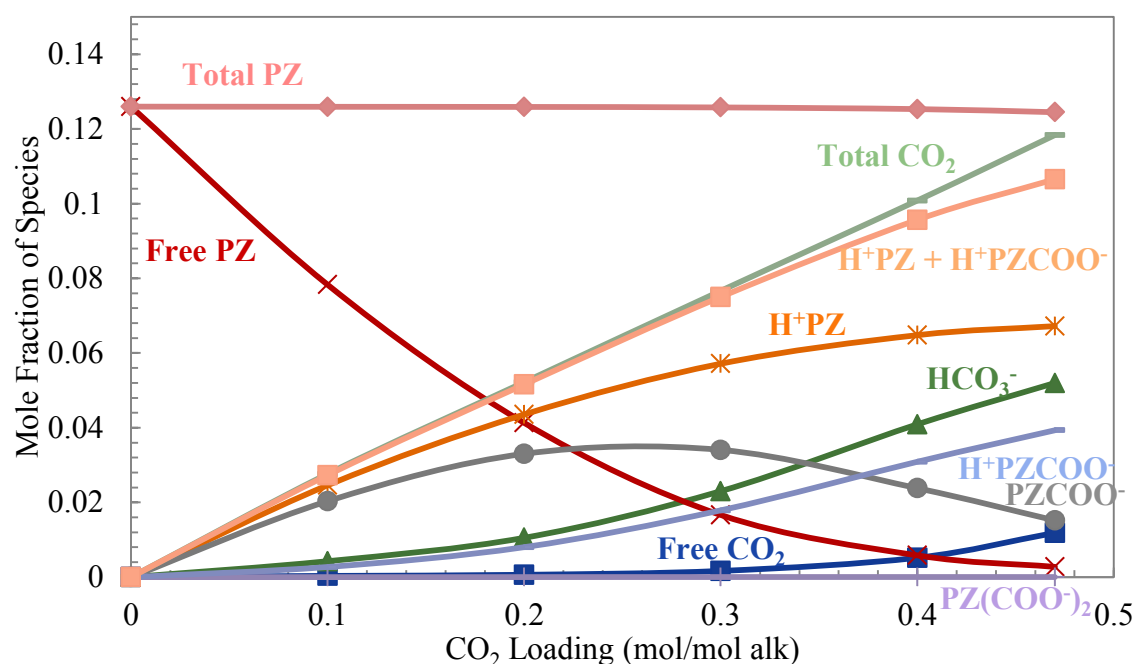


Figure 5.37: Predicted speciation of 8 m PZ at 175 °C (Frailie et al., 2011)

5.3.3.2 Effect of CO₂ concentration for 8 m PZ at 165 °C

The effect of CO₂ concentration on thermal degradation of 8 m PZ was investigated at 165 °C from 0 to 0.4 mole CO₂ per mole alkalinity. The PZ loss is compared in Figure 5.38. The generation of formate, total formate, and EDA are compared in Figure 5.39, Figure 5.40, Figure 5.41, Figure 5.42, and Figure 5.43, respectively. The rate of PZ loss increased with CO₂ loading between 0 and 0.4 mole CO₂ per mole alkalinity without a maximum being observed. The generation of formate, total formate, EDA, FPZ, and AEP all demonstrate increases in initial rate with increased loading, without a maximum being observed. At longer degradation times, the concentration differences in formate, total formate, FPZ, and AEP between the highest two loadings diminish. For EDA, maximum concentrations of 35 to 65 mmole per kg were observed and all CO₂ concentrations reached a maximum after 15 hours of degradation, mimicking the behavior observed with changes in PZ concentration.

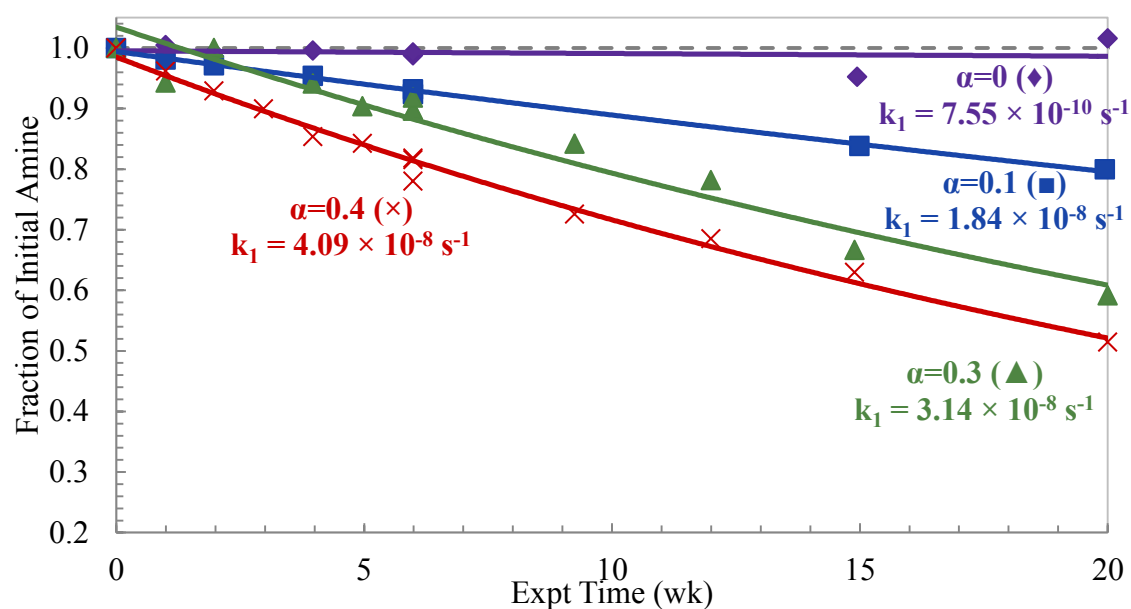


Figure 5.38: Comparison of PZ loss for 8 m PZ at 165 °C with 0 to 0.4 mole CO₂ per mole alkalinity

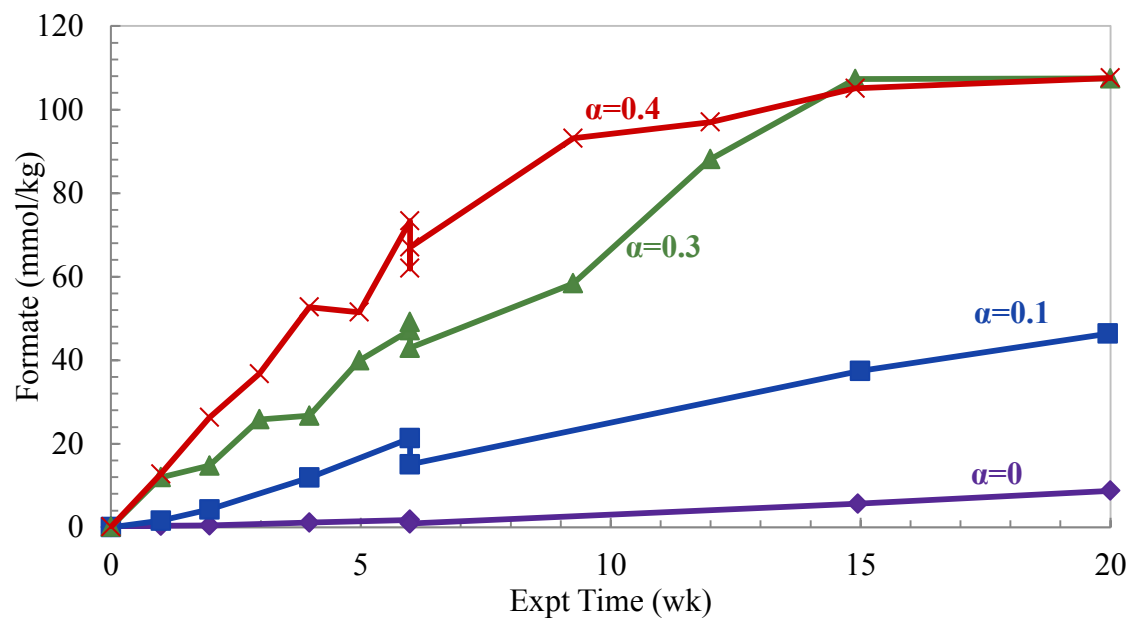


Figure 5.39: Comparison of formate generation for 8 m PZ at 165 °C with 0.3 and 0.4 mole CO₂ per mole alkalinity

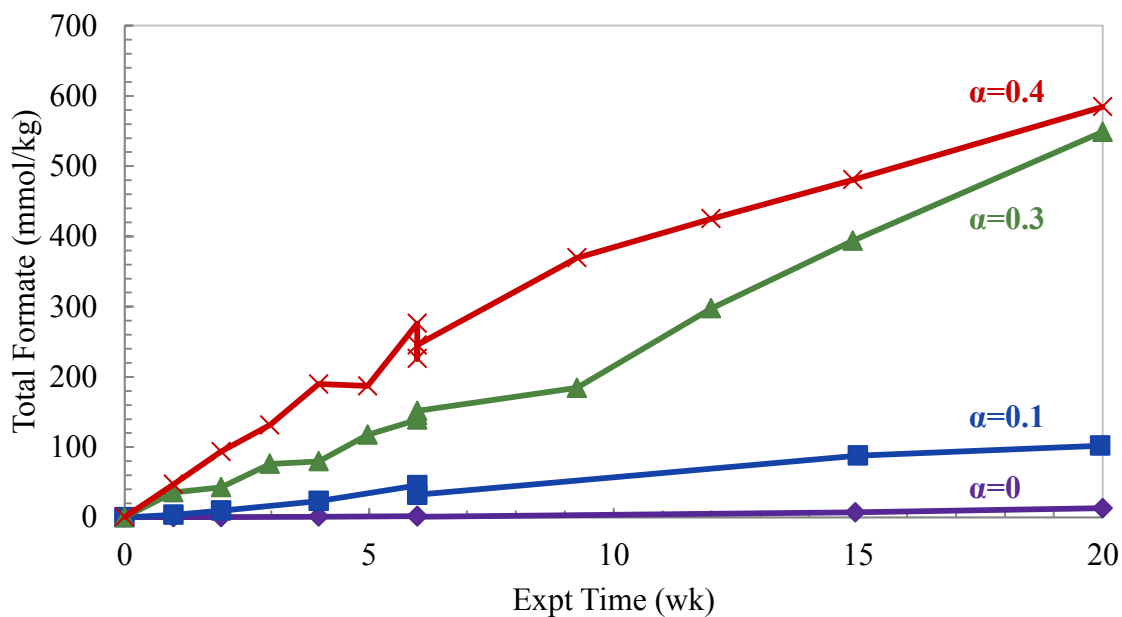


Figure 5.40: Comparison of total formate generation for 8 m PZ at 165 °C with 0.3 and 0.4 mole CO₂ per mole alkalinity

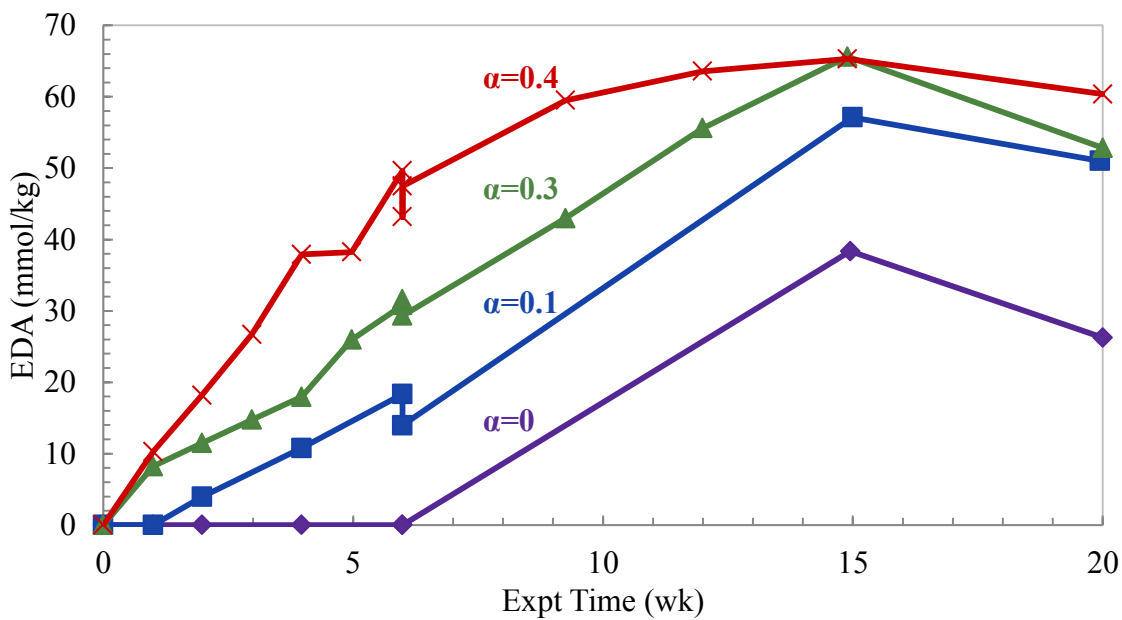


Figure 5.41: Comparison of EDA generation for 8 m PZ at 165 °C with 0.3 and 0.4 mole CO₂ per mole alkalinity

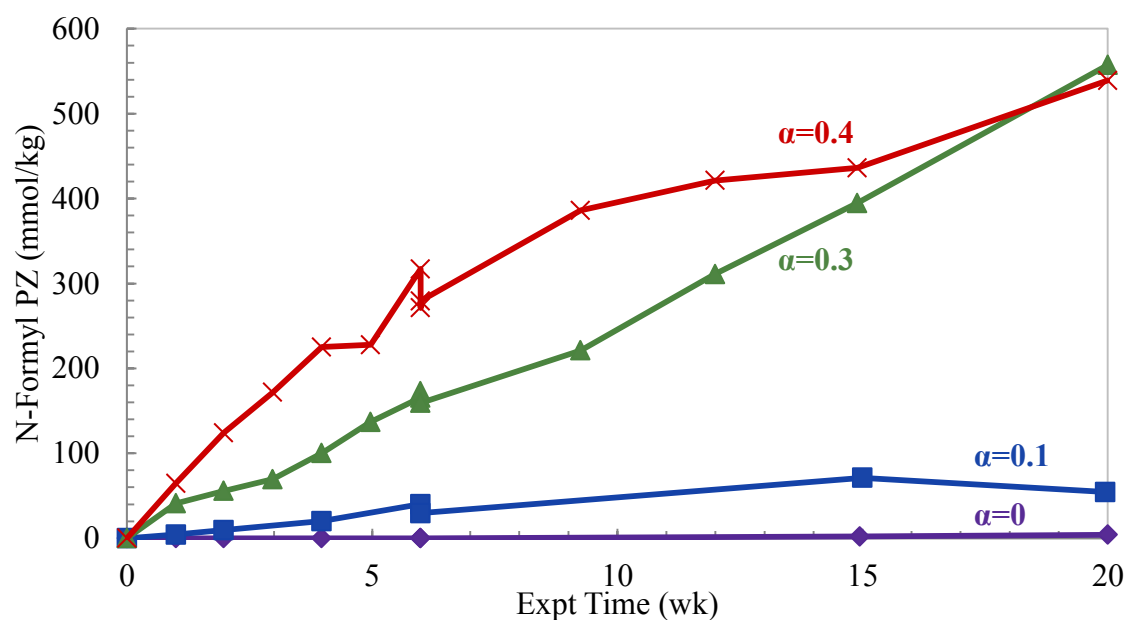


Figure 5.42: Comparison of FPZ generation for 8 m PZ at 165 °C with 0.3 and 0.4 mole CO₂ per mole alkalinity

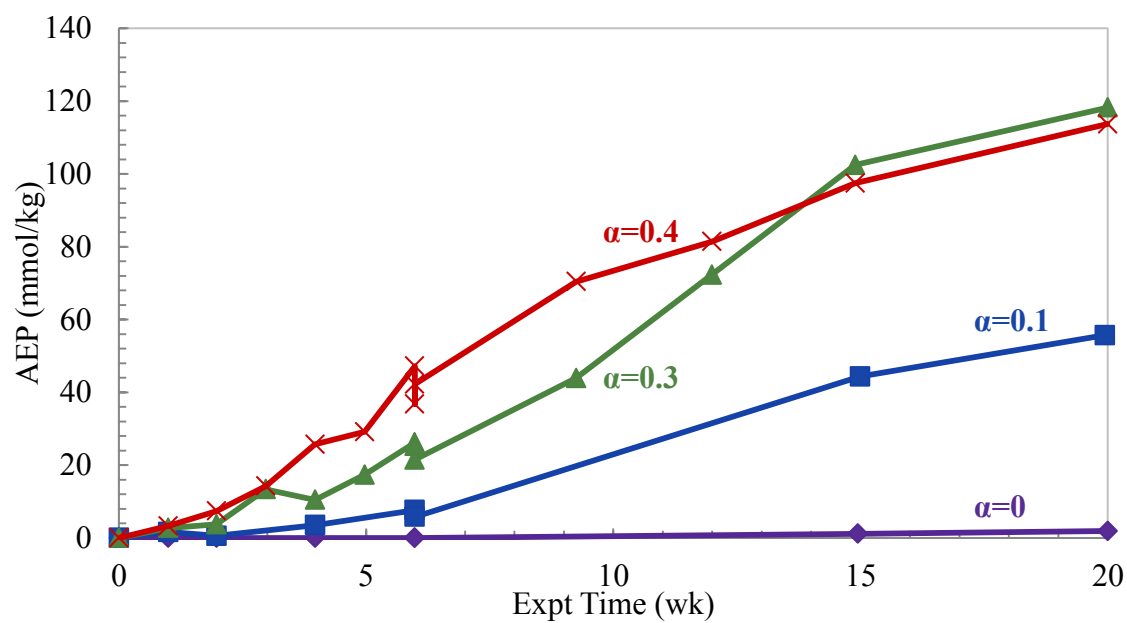


Figure 5.43: Comparison of AEP generation for 8 m PZ at 165 °C with 0.3 and 0.4 mole CO₂ per mole alkalinity

5.3.3.3 Effect of CO₂ concentration for 20 m PZ at 175 °C

The thermal degradation of 20 m PZ was measured for CO₂ loadings of 0.1 and 0.3 moles CO₂ per mole alkalinity at 175 °C. These two CO₂ concentrations were chosen because they were of interest to reclaiming activities where thermal reclaiming would concentrate the PZ concentration with the same approximately quantity of CO₂, decreasing the CO₂ loading by definition. The loss of PZ observed for these two experiments is compared in Figure 5.44. The generation of formate, total formate, and EDA are compared for the same experiments in Figure 5.45, Figure 5.46, and Figure 5.47, respectively.

As predicted, the thermal degradation of PZ and production of degradation products were significantly enhanced with increased CO₂ loading. PZ loss was doubled for an increase from 0.1 to 0.3 mole CO₂ per mole alkalinity after 15 weeks at 175 °C. Concentrations of formate and total formate more than doubled for the same increase in CO₂ concentration. FPZ and AEP generation demonstrated trends similar to that of formate and total formate, although not shown here. EDA production in these high PZ concentration experiments was not starkly different as both CO₂ loadings produced 100 to 120 mmole per kg EDA after 15 weeks. The EDA did not demonstrate an intermediate behavior, as the concentration did not decrease as in other PZ experiments, but the experiment may not have continued long enough to see this behavior.

5.3.4 Effect of additives

The effect of various additives on the thermal degradation of PZ was explored through high temperature experiments. A summary of the additive experiments is presented in Table 5.11. Thermal degradation in a real system will take place in the presence of metals, degradation products, and any solvent additives. These tests were planned to determine the effect that the presence of these molecules would have on PZ

degradation rates. The concentrations of each additive used were based on assumptions for either what would be used in industrial settings or the level expected from corrosion. For example, Inhibitor A was used at 100 mM because this is the anticipated concentration needed to deter oxidation in the absorber side of the system (Goff and Rochelle, 2006; Sexton and Rochelle, 2009a). The addition of 5 mM Cu^{2+} was used to simulate the use of a copper based corrosion inhibitor (Pearce, 1984; Reed, 1945). The addition of either 1 mM Fe^{2+} or 0.1 mM Fe^{2+} , 0.1 Ni^{2+} , and 0.6 mM Cr^{3+} was used to simulate the expected concentrations if there was corrosion in either a carbon steel or stainless steel stripper, respectively. Finally, an experiment was performed in the presence of the expected concentrations of three common degradation products in highly degraded PZ.

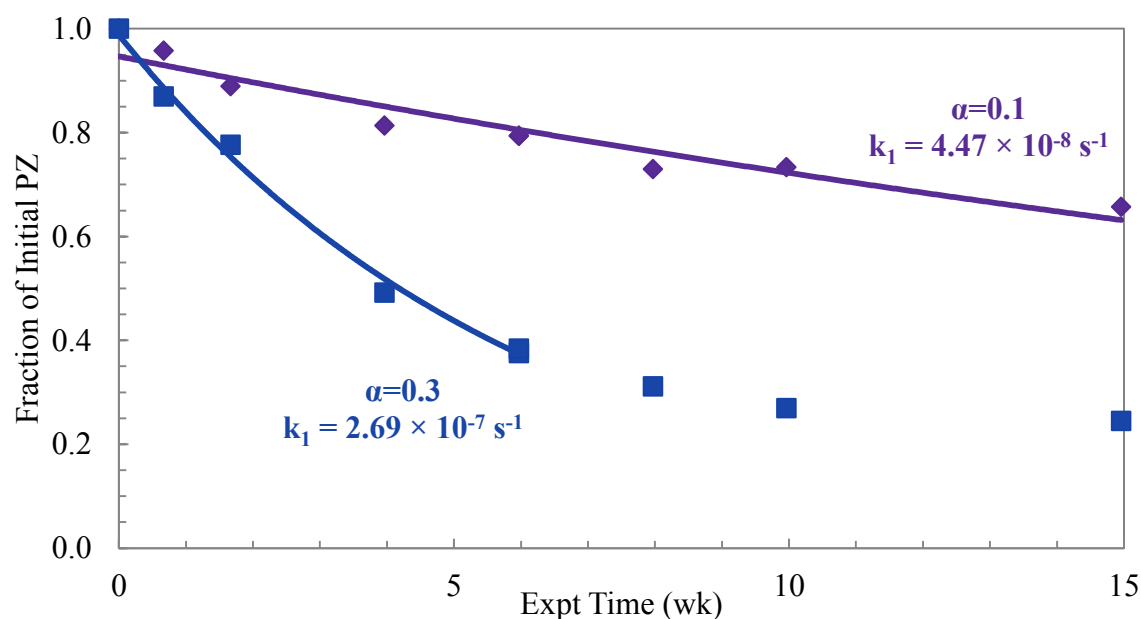


Figure 5.44: Comparison of PZ loss for 20 m PZ at 175 °C with 0.1 and 0.3 mole CO_2 per mole alkalinity

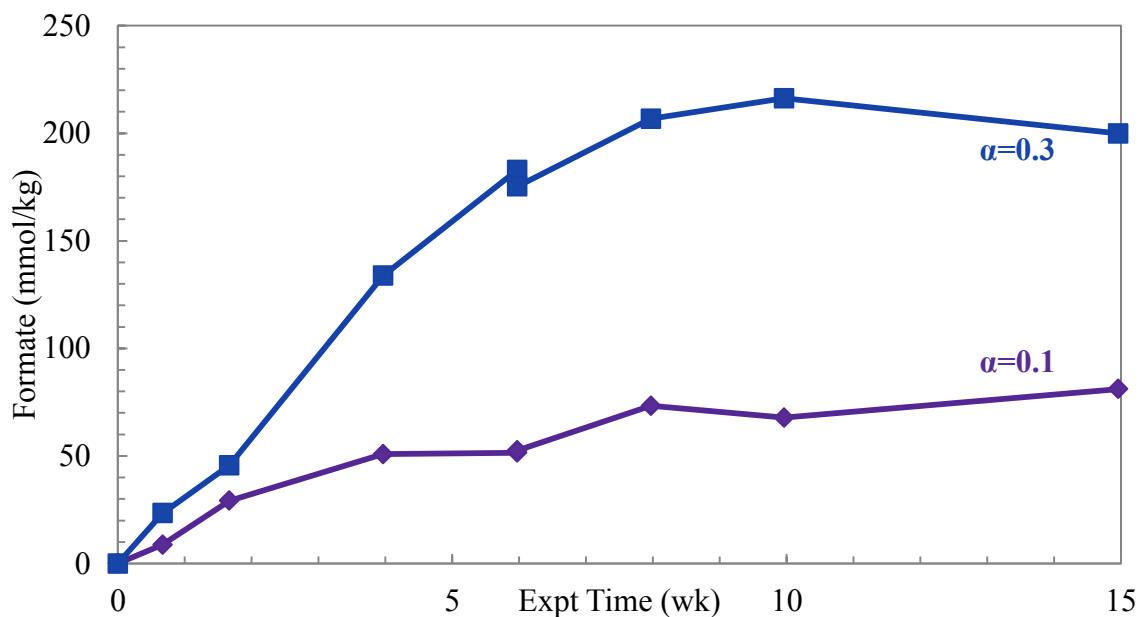


Figure 5.45: Comparison of formate generation for 20 m PZ at 175 °C with 0.1 and 0.3 mole CO₂ per mole alkalinity

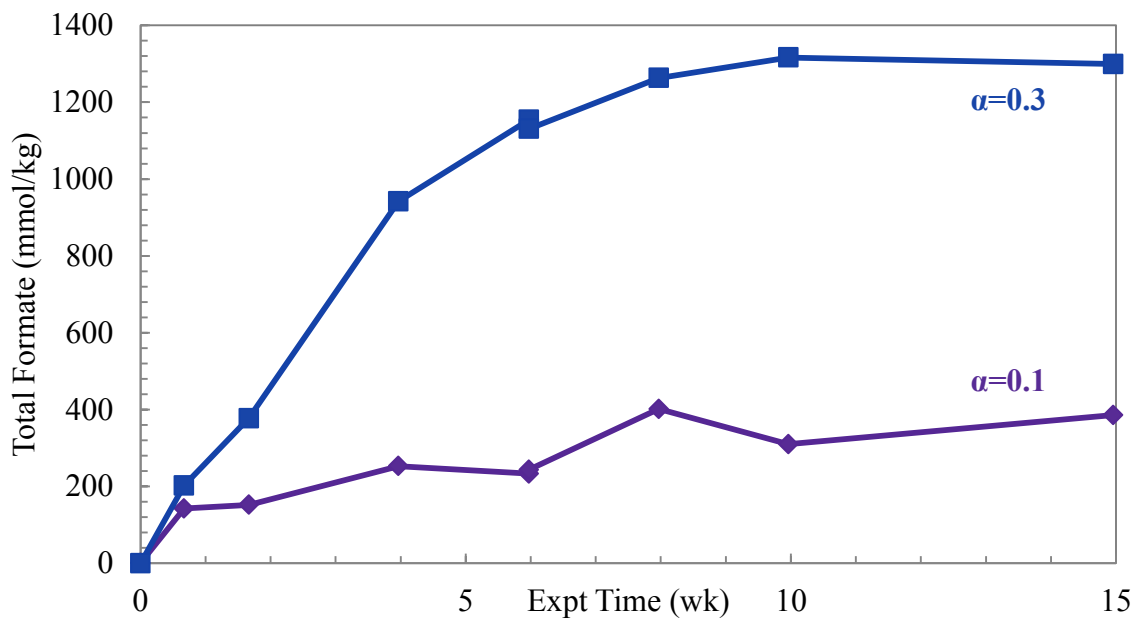


Figure 5.46: Comparison of total formate generation for 20 m PZ at 175 °C with 0.1 and 0.3 mole CO₂ per mole alkalinity

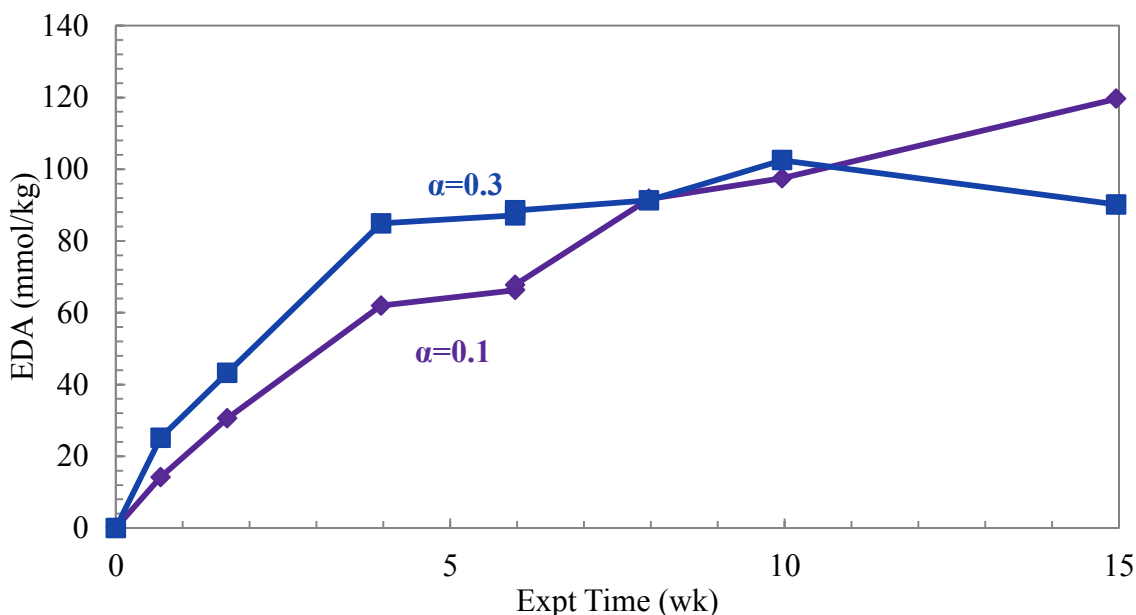


Figure 5.47: Comparison of EDA generation for 20 m PZ at 175 °C with 0.1 and 0.3 mole CO₂ per mole alkalinity

Table 5.11: Summary of PZ Thermal Degradation Experiments with Additives

Temp (°C)	PZ (m)	CO ₂ Loading (mol/mol alk)	Additive (mM)	Expt.
175	8	0.3	100 Inhibitor A	TE56
	8	0.3	5 Cu ²⁺ , 1 Fe ²⁺	TE5
	8	0.3	5 Cu ²⁺ , 1 Fe ²⁺ , 100 A	TE6
	8	0.3	0.1 Fe ²⁺ , 0.1 Ni ²⁺ , 0.6 Cr ³⁺	TE8
	8	0.3	1000 Formate, 100 Oxalate, 150 EDA	TE7

5.3.4.1 Addition of 100 mM Inhibitor A

Inhibitor A is an oxidation inhibitor used to minimize the effect of metal-catalyzed degradation. In chapter 9, Inhibitor A is shown to be useful at mitigating Cu²⁺-catalyzed oxidation of concentrated PZ solutions. PZ systems are proposed to include Inhibitor A as a standard additive to decrease degradation, so the effect of this additive on thermal degradation was assessed. The thermal degradation of 8 m PZ in the presence of 100 mM Inhibitor A was investigated at 175 °C. The loss of PZ is compared between the

uninhibited and inhibited experiments in Figure 5.48. The uninhibited experiment is a set of data from three separate repeated experiments exploring thermal degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 175 °C. The addition of Inhibitor A appears to decrease the loss of PZ over the course of the 15 week experiment. The error in the cation IC analysis for PZ has some scatter, but the addition of Inhibitor A decreases PZ loss by 20% as only 54% of the initial PZ is lost after 15 weeks compared to 68% in the uninhibited experiments.

The generation of total formate and EDA are shown for the same two data sets in Figure 5.49 and Figure 5.50, respectively. The generation of total formate appears to be diminished, especially in the initial portion of the experiment, while the EDA concentration is slightly higher than the uninhibited experiment. These observations follow with an overall decrease in the degradation rate of the system. With less PZ degradation, less total formate is converted. The EDA on the other hand, appears to increase in concentration rather than decrease, which is counterintuitive. This occurs because of the reaction of EDA with CO₂ to create 2-imidizolidone (2-Imid). This equilibrium is discussed in detail in section 6.4 of this thesis. With less degradation, the reaction of EDA with CO₂ occurs more slowly and EDA, therefore, builds up and appears to increase the concentration of EDA in solution compared with the baseline experiment.

The generation of total formate may occur through a free radical mechanism whose details are not yet known. Inhibitor A is thought to be a free radical or peroxide scavenger and may, therefore, inhibit formate generation during thermal degradation of PZ. With lower formate concentrations, there will be lower concentrations of FPZ and less PZ loss associated with forming FPZ. Additional oxidation products that may be produced through the free radical mechanism have not been identified.

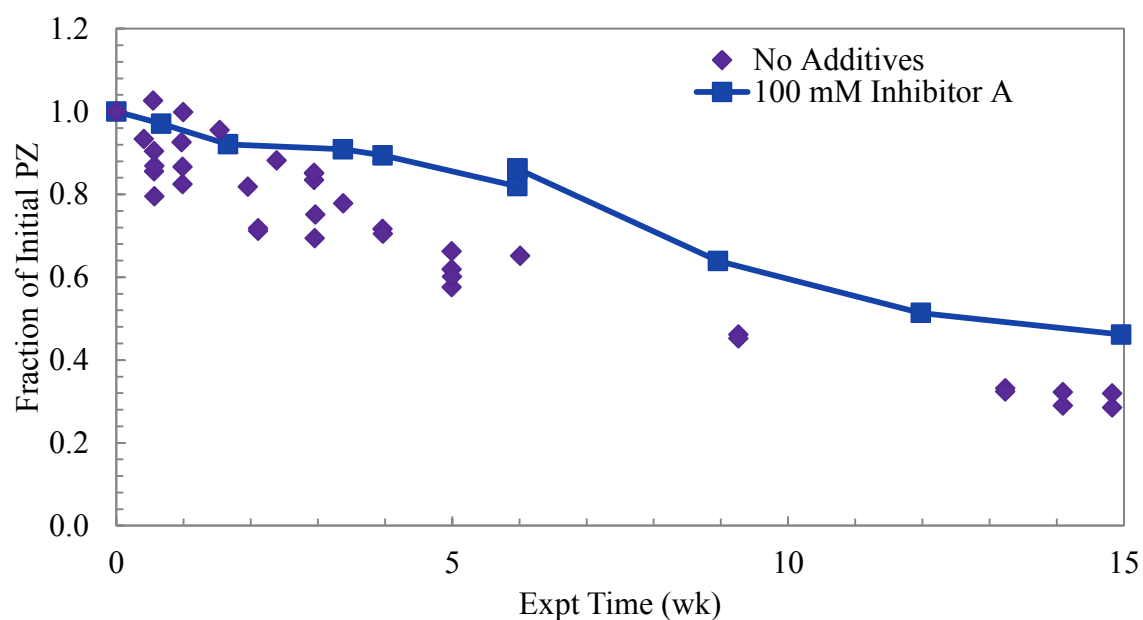


Figure 5.48: Effect of 100 mM Inhibitor A on degradation of 8 m PZ degradation with 0.3 mole CO₂ per mole alkalinity at 175 °C

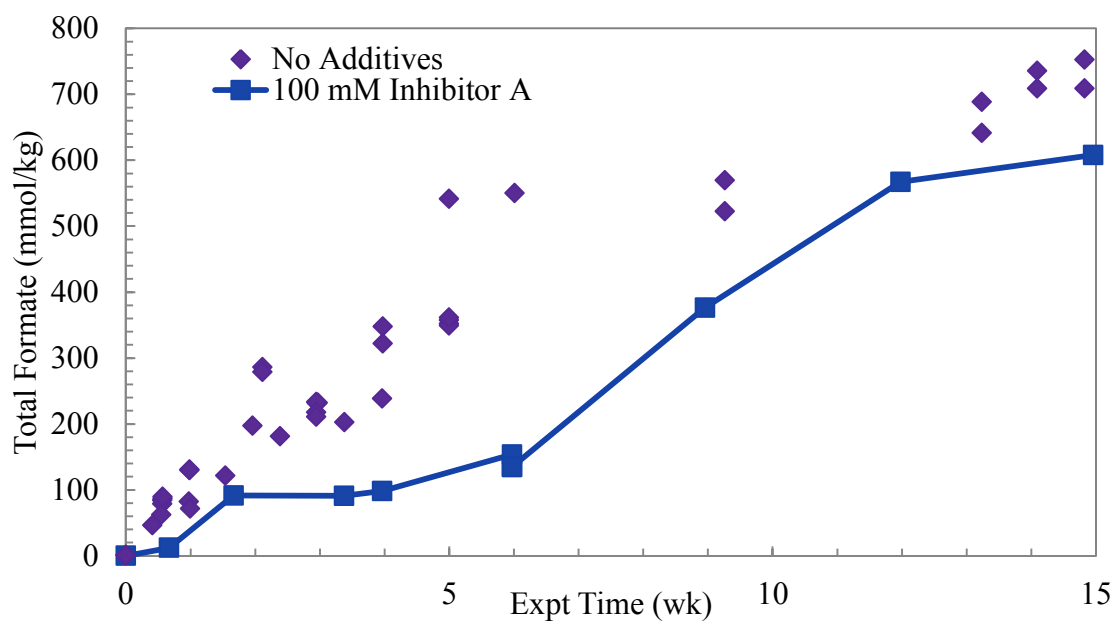


Figure 5.49: Effect of 100 mM Inhibitor A on generation of total formate during degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 175 °C

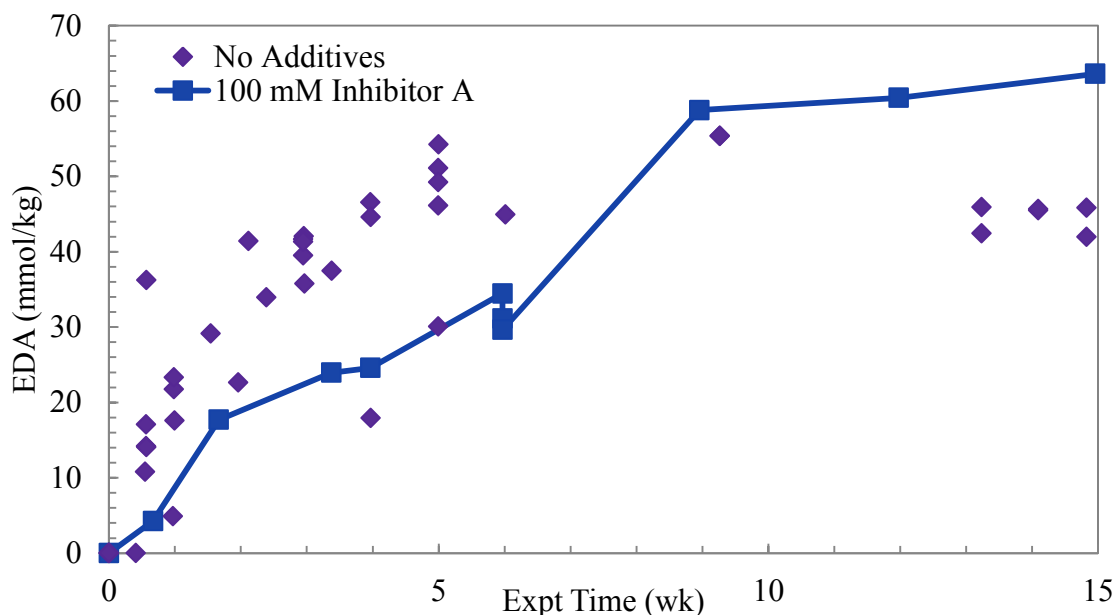


Figure 5.50: Effect of 100 mM Inhibitor A on generation of EDA during degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 175 °C

The addition of Inhibitor A to a concentrated PZ solution used for CO₂ capture will not negatively affect the thermal degradation characteristics of the system. Inhibitor A caused a decrease of 20% in PZ loss in this experiment. Although different temperatures and concentrations were not tested, it does not appear that there will be an adverse effect on thermal degradation due to the presence of Inhibitor A. If any, it could cause a decrease in thermal degradation losses, which is an added advantage of the inhibitor.

5.3.4.2 Addition of 5 mM Cu²⁺ and 1 mM Fe²⁺

To simulate a PZ solvent that is used in a carbon steel system with a Cu²⁺-based corrosion inhibitor and a small amount of corrosion, 8 m PZ with 0.3 moles CO₂ per mole alkalinity was degraded at 175 °C in the presence of 5 mM Cu²⁺ and 1 mM Fe²⁺. The loss of PZ for this experiment is compared with a collated set of baseline data for the

thermal degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 175 °C in Figure 5.51. The generation of total formate and EDA for these experiments is compared in Figure 5.52 and Figure 5.53. Additional curves are present in this figure that will be discussed in subsequent sections.

The addition of Cu²⁺ and Fe²⁺ did not significantly affect the loss rate of PZ or the generation of total formate and EDA. The data falls in line with the baseline data without the addition of metals. It is not expected that the addition of a Cu²⁺-based corrosion inhibitor or the accumulation of Fe²⁺ due to corrosion will accelerate thermal degradation of concentrated PZ solutions.

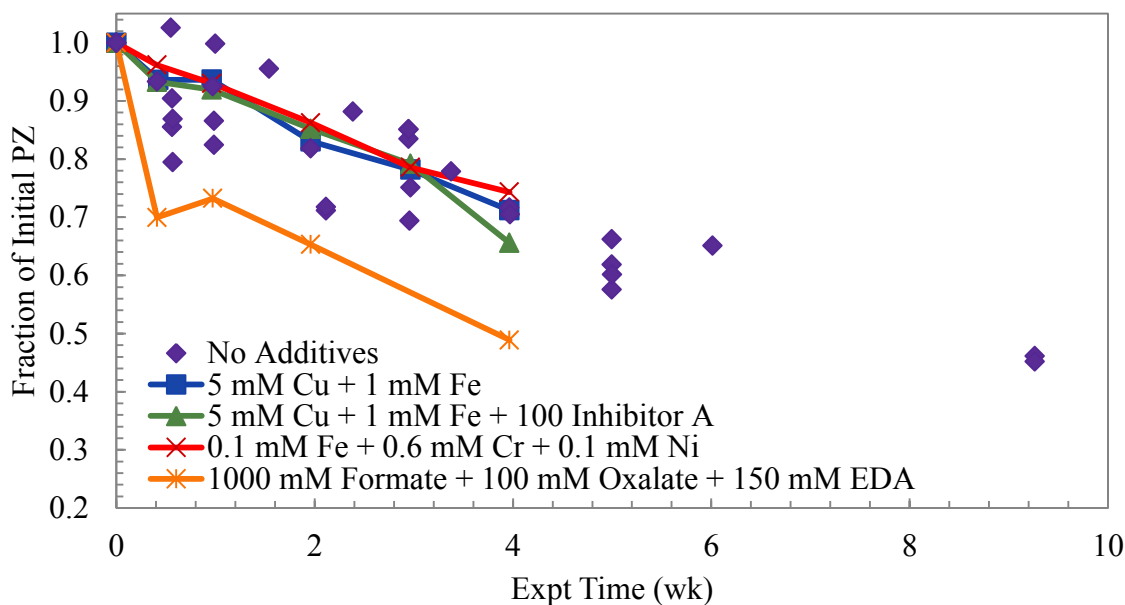


Figure 5.51: Effect of additives on the degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 175 °C

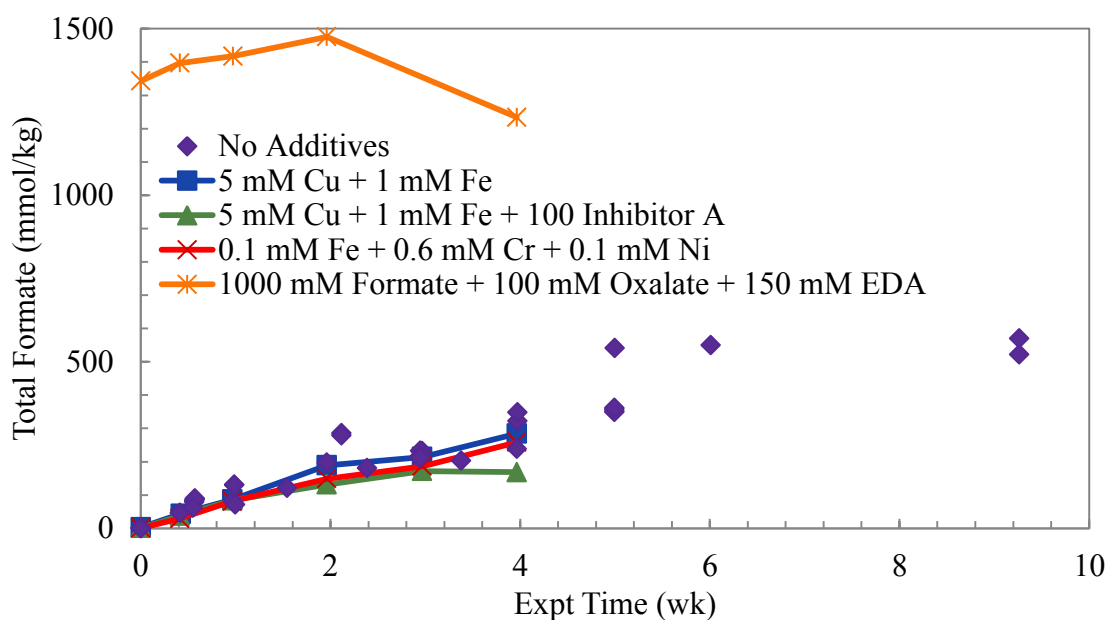


Figure 5.52: Effect of additives on the generation of total formate during degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 175 °C

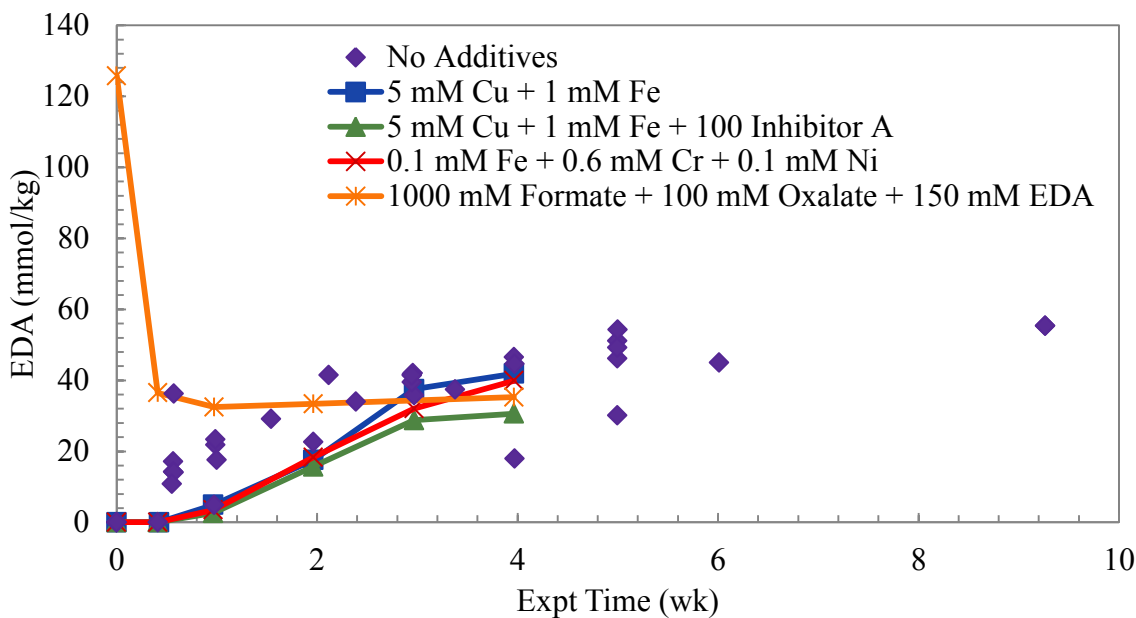


Figure 5.53: Effect of additives on the generation of EDA during degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 175 °C

5.3.4.3 Addition of 5 mM Cu²⁺, 1 mM Fe²⁺, and 100 mM Inhibitor A

The effect of Inhibitor A on thermal degradation was confirmed through a second experiment that also simulated Fe²⁺ corrosion and the addition of a Cu²⁺-based corrosion inhibitor. A solution of 8 m PZ with 0.3 mole CO₂ per mole alkalinity, 5 mM Cu²⁺, 1 mM Fe²⁺, and 100 mM Inhibitor A was degraded at 175 °C for 15 weeks. The loss of PZ, generation of total formate, and EDA production are compared with a baseline, unspiked set of data in Figure 5.51, Figure 5.52, and Figure 5.53, respectively. The solution behavior was found to be in agreement with the data in the previous two subsections as metals and Inhibitor A were not found to accelerate or inhibit thermal degradation. The rate of loss of PZ and generation of degradation products in the spiked experiment closely matched that of the unspiked condition.

5.2.4.4 Addition of 0.1 mM Fe²⁺, 0.1 mM Ni²⁺, and 0.6 mM Cr³⁺

Industrial CO₂ capture systems are expected to be made from stainless steel rather than carbon steel to minimize the long term corrosive effects of amines and CO₂. The effect of metals due to stainless steel corrosion was tested by degrading 8 m PZ with 0.3 moles CO₂ per mole alkalinity at 175 °C with 0.1 mM Fe²⁺, 0.6 mM Cr³⁺, and 0.1 mM Ni²⁺. The loss of PZ, generation of total formate, and EDA production are compared with a baseline, unspiked set of data in Figure 5.51, Figure 5.52, and Figure 5.53, respectively. As observed in the two previous metal spiked experiments, there was no effect from stainless steel metals on the rate of PZ loss or generation of degradation products during degradation at 175 °C.

5.3.4.5 Addition of 1000 mM Formate, 100 mM Oxalate, and 150 mM EDA

Finally, the effect of degradation products on the rate of thermal degradation was measured through the addition of formate, oxalate, and EDA, the dominant degradation

products. An 8 m PZ solution with 0.3 moles CO₂ per mole alkalinity was degraded at 175 °C in the presence of 1000 mM formate, 100 mM oxalate, and 150 mM EDA. This solution was meant to represent a highly degraded PZ solution to assess the catalytic effect of the most dominant degradation products. The loss of PZ, generation of total formate, and generation of EDA are compared with a baseline, unspiked set of data in Figure 5.51, Figure 5.52, and Figure 5.53, respectively. The equilibrium between formate and total formate is shown in Figure 5.54.

The presence of degradation products enhanced the initial loss rate for PZ. After one week, 27% of the initial PZ was degraded compared to 0-18% in the unspiked data. The rate was enhanced in the first week, but then demonstrated the same rate as seen in the unspiked experiments for the last three weeks of the experiment. The presence of formate in the initial sample created a rapid equilibrium with formyl amides, most likely N-formyl PZ (Figure 5.54). At this temperature, formate can quickly react with either PZ or EDA to form the corresponding formyl amide. This reaction with PZ could explain the high rate of loss of PZ (1200 mmole PZ per kg) after one week. EDA also rapidly reacts and reaches an equilibrium concentration of 30 to 35 mmole per kg within one week that is the same as the concentrations found in unspiked experiments. EDA is known to react quickly in solution with CO₂ to form 2-Imidazolidone (2-Imid) which is discussed in detail in section 6.5.

At the start of the experiment, the 100 mmole per kg of oxalate quickly reacted to form oxalyl amides detected in the initial sample. After the initial sample, both free oxalate and oxalyl amides reacted to an unknown product and all subsequent oxalate and oxalyl amide concentrations were less than 1 mmole per kg. It is suspected that the primary oxalyl amide was N-oxalyl piperazine and this species reacted to form N-formyl PZ or formate. Mislyuk and colleagues found that when heated, N-oxalyl PZ and N,N'-

dioxalyl PZ form N-formyl PZ and N,N'-diformyl PZ through the breaking of a C-C bond (Mislyuk et al., 1985). Górski and Kraśnicka determined that the thermal decomposition of sodium formate produced oxalate species in the presence of CO and CO₂ (Górski and Kraśnicka, 1987a). The same authors also determined that the thermal decomposition of solid, alkali oxalate compounds produced a dissociation of oxalate into CO₂ and CO₂⁻² ion as a short lived intermediate (Górski and Kraśnicka, 1987b). A more recent study by Crossley confirmed that aqueous oxalate species thermally decompose to formate species and CO₂ at temperatures from 160-230 °C (Crossley, 1991). The decomposition of oxalate is not known under the specific conditions of this experiment, but the noticeable increase in total formate after the initial sample indicates that some or all of the oxalate ended up as formate or formyl amides. Oxalate has not been a major degradation product in any thermal degradation experiment for concentrated PZ and any production of oxalate likely ends up as formate or CO₂ species under the high temperature conditions of PZ thermal degradation.

Overall, the addition of formate, EDA and oxalate primarily affected the speciation of degradation products and their respective amides or imidazolidones, and were not found to enhance PZ thermal degradation overall.

5.3.5 Effect of the metal contamination

Previous work in literature has explored the catalytic effect of metals contamination on thermal degradation (Eide-Haugmo et al., 2011). In this work, glass cuvettes were used to line thermal degradation cylinders to prevent the contact of amine solution with the walls of the cylinders during the degradation tests. The author's hypothesis was that decreasing metals contamination would limit catalyst in solution and could potentially inhibit thermal degradation in a variety of amines. Their results

showed the same level of degradation for all amines tested except one, N-methylmonoethanolamine (MMEA) (Eide-Haugmo et al., 2011). Based on these results, concentrated PZ solutions were tested for thermal degradation with glass-lined degradation cylinders. The hypothesis was that preventing metals contamination of the amine will not change PZ stability and thermal degradation will proceed as expected at the given conditions.

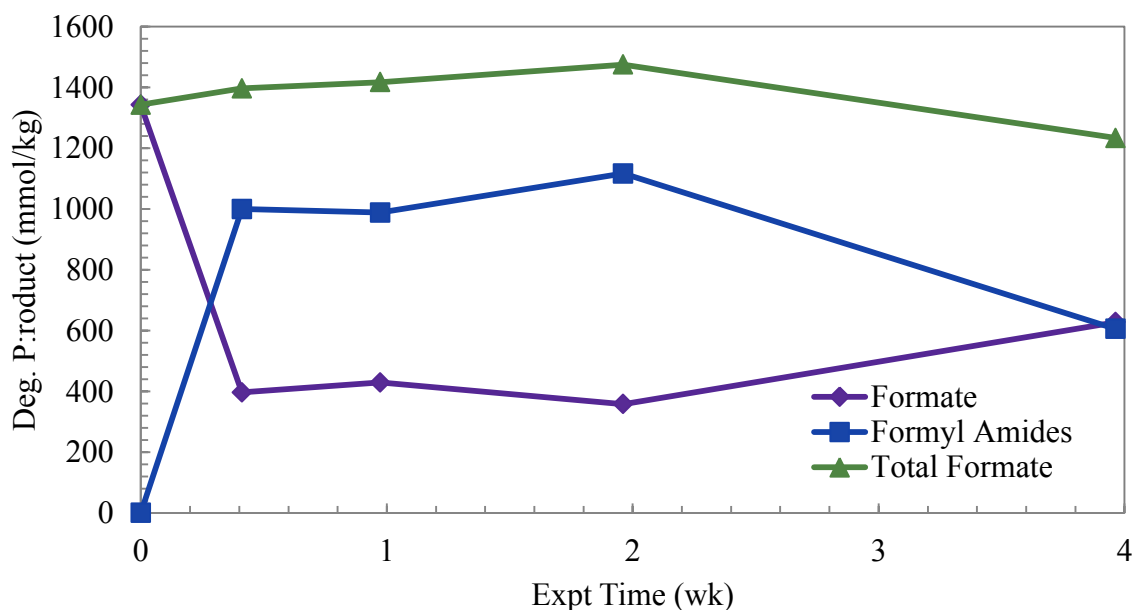


Figure 5.54: Equilibrium of formate and formyl amides in degradation of 8 m PZ at 175 °C with 1000 mM formate, 100 mM oxalate, and 150 mM EDA

With this new experimental protocol, 8 m PZ with a loading of 0.3 moles CO₂ per mole alkalinity was degraded at 175 °C for 15 weeks. The loss of PZ and generation of total formate and EDA are compared with a baseline case of thermal degradation in Figure 5.55, Figure 5.56, and Figure 5.57, respectively. As with the previous sub-section, the comparison is made with the collated thermal degradation data obtained from three experiments for 8 m PZ with 0.3 moles CO₂ per mole alkalinity degraded at 175 °C.

The concentration profiles for both PZ and degradation products indicate that the lack of metals had a nearly negligible effect on thermal degradation. The PZ loss was minimally affected, with only 1% less PZ loss observed in the glass experiment. As for degradation products, generation of total formate was decreased by 24% while EDA generation was the same as the unlined case. These measurements indicate that the mechanism responsible for the generation of formate and total formate may be sensitive to the presence of metals or may be metal catalyzed. That mechanism is discussed in greater detail in section 6.4.

The observations of Eide-Haugmo appear to be confirmed with concentrated PZ (Eide-Haugmo et al., 2011). It is important to note, however, the differences between the experimental protocols for this experiment. The cuvettes used in this experiment did not reach the top of the thermal cylinder when placed inside. That is to say, the cuvettes were too short for the standard thermal cylinders and the top of the cuvette was approximately 2 cm from the top of the cylinder. Therefore, less solution fit in the cuvette than a traditional experiment (7 mL vs. 10 mL). The extra headspace in the cylinder could have contributed to the differences seen in the figures. The CO₂ concentration in the solution would have been slightly different as the high temperature would drive CO₂ into the headspace.

Analysis of metals concentration using ICP-OES showed that there was no detectable Fe²⁺, Ni²⁺, or Cr³⁺, except for one sample. The concentrations of Fe²⁺, Ni²⁺, and Cr³⁺ in the glass-lined experiments (TE22) are compared with two experiments with the same solution of PZ degraded in stainless steel thermal cylinders (TE12 and TE18) in Figure 5.58. The lack of metals confirms that the solutions were maintained separate from the stainless steel side walls of the solution during the glass-lined experiment.

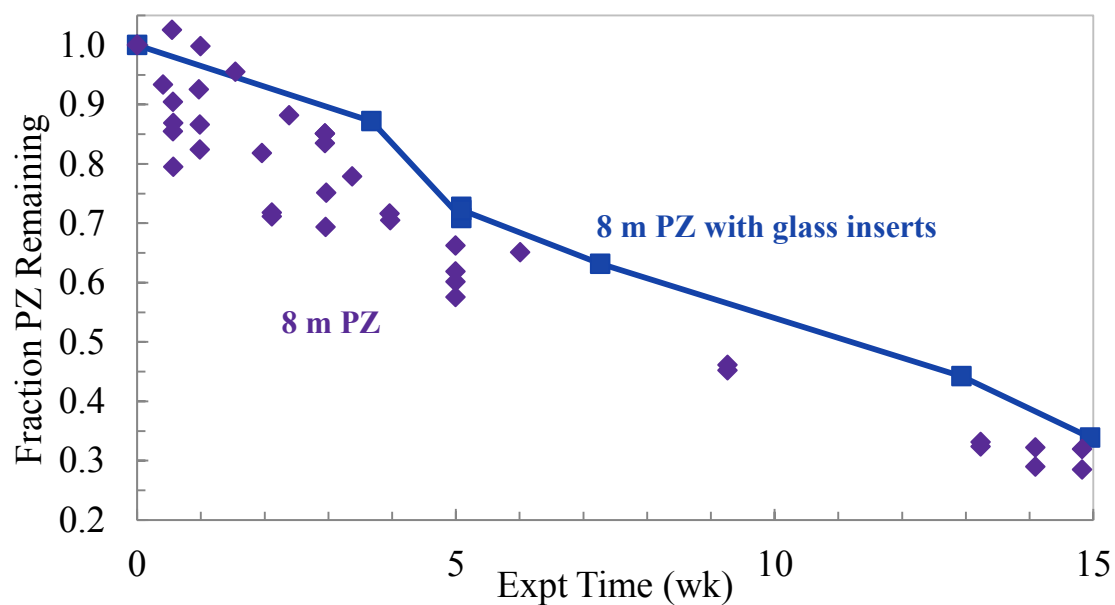


Figure 5.55: Effect of glass inserts on the degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 175 °C

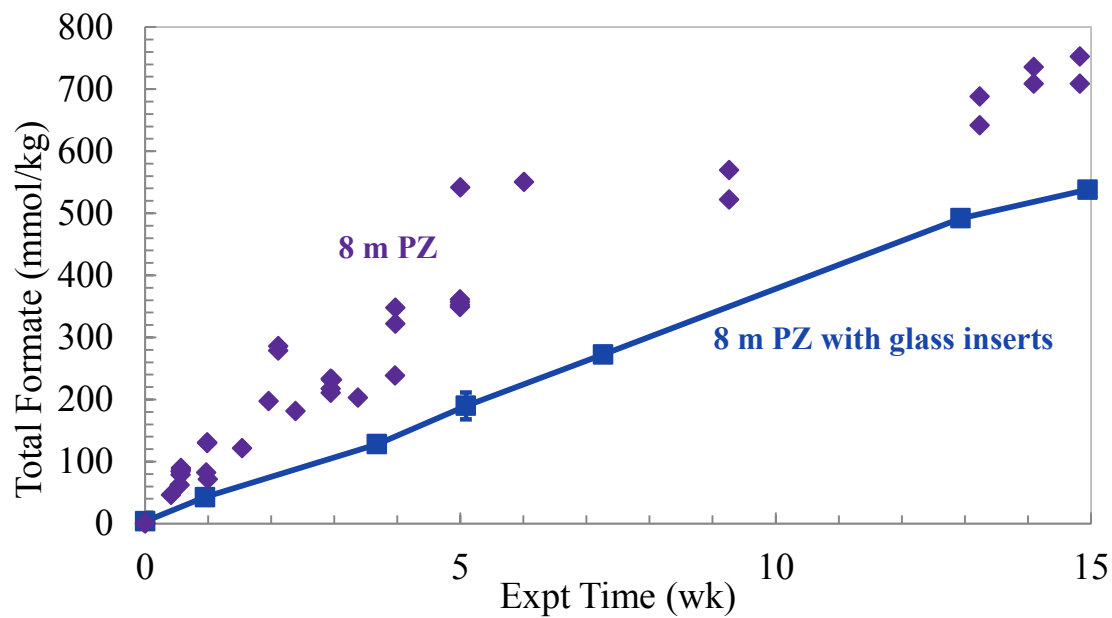


Figure 5.56: Effect of glass inserts on the generation of total formate during degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 175 °C

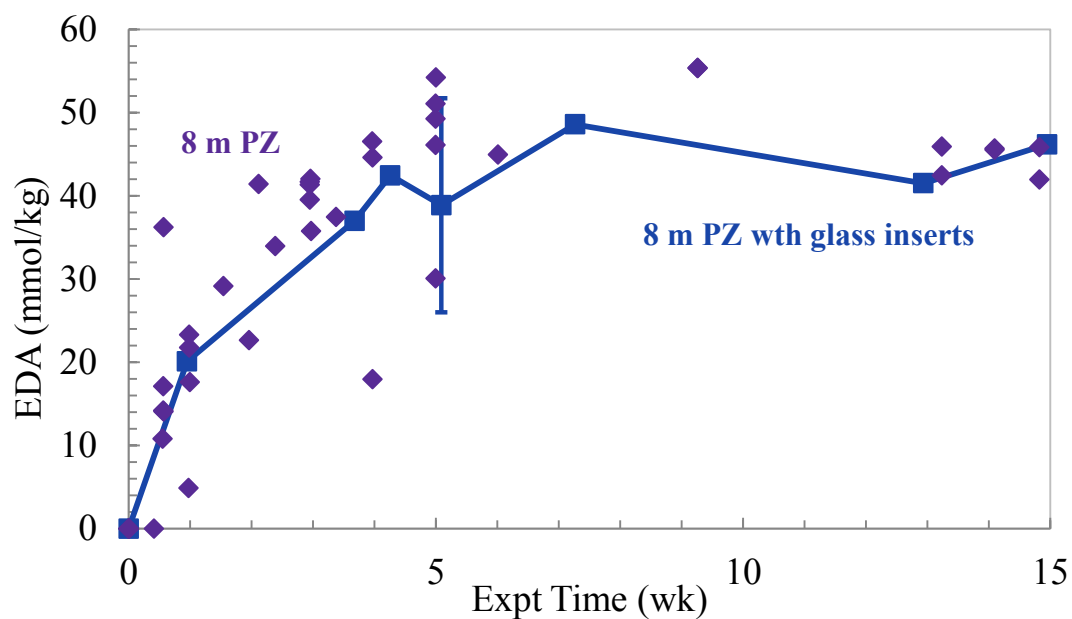


Figure 5.57: Effect of glass inserts on the generation of EDA during degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 175 °C

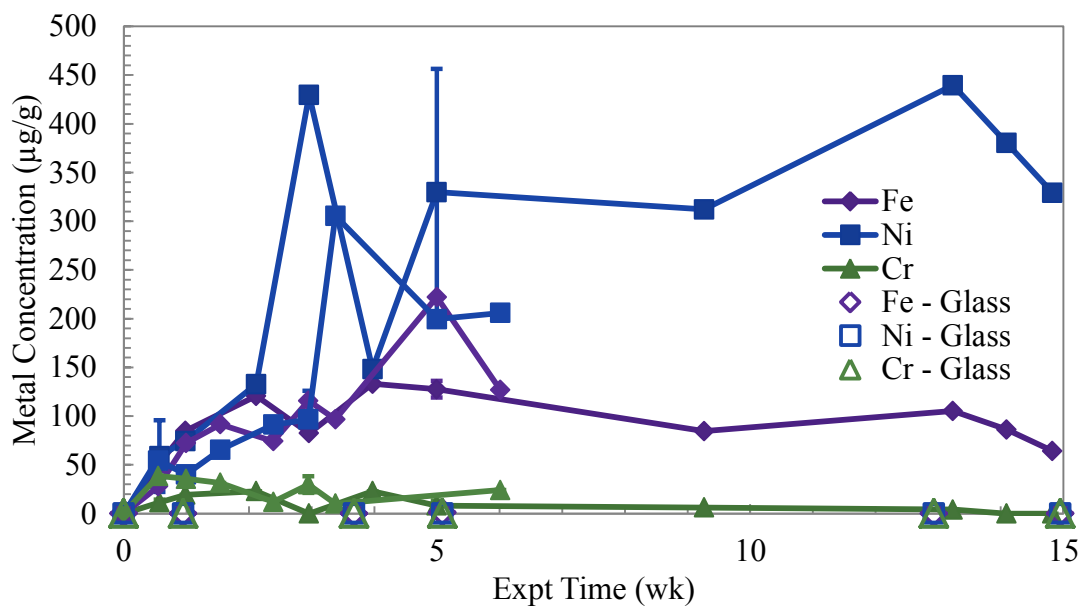


Figure 5.58: Fe²⁺, Cr³⁺, and Ni²⁺ concentrations for 8 m PZ with 0.3 mole CO₂ per mole alkalinity degraded at 175 °C with (open points, all sitting on x-axis) and without glass inserts (filled points).

5.3.4.1 Corrosion of stainless steel thermal cylinders

In all of the PZ thermal degradation experiments described in this chapter, no measures were taken to prevent the leaching of metals into solution, except for the experiment described in the last section. The loaded PZ solutions analyzed were exposed to the stainless steel surface for the duration of the experiment, ranging from 10 to 72 weeks, and corrosion occurred. A majority of the experimental samples were tested for metals concentration at the conclusion of the experiment using the ICP-OES as described in section 3.1.10. The corrosion tendency of PZ solutions can be assessed by analyzing the metals concentrations resulting from long-term, high temperature exposure to stainless steel.

One caveat of this analysis is the fact that the thermal cylinders were reused repetitively throughout the course of this project. Some cylinders were also used previously by other researchers and the individual histories of the cylinders were not known at the start of each experiment. When a new set of cylinders was made, it was possible to assess the fresh corrosion rate. Since the histories of the cylinders were not known with any accuracy, an estimation of the actual corrosion rate was not attempted. Instead, the tendency to corrode was assessed by comparing raw metals concentrations in solution. Also, since experimental samples are individual cylinders, there is more scatter in the metals concentration data than any other liquid phase analysis.

The concentrations of Fe^{2+} , Ni^{2+} , and Cr^{3+} during the degradation of 8 m PZ with 0.3 mole CO_2 per mole alkalinity at 150 °C are shown in Figure 5.59. This general trend in metals concentration was found for a variety of conditions where the magnitude of concentrations was similar between the three metals and all usually reached some sort of equilibrium concentration quickly where there was not more metal leached into the solution. The Fe^{2+} , Ni^{2+} , and Cr^{3+} concentrations are compared for experiments at 135 to

175 °C in Figure 5.60, Figure 5.61, and Figure 5.62, respectively. As expected, the overall trend is that more corrosion is occurring at higher temperatures, evidenced by the increasing concentrations of metals in solution as experimental temperature increases.

The relative corrosion rate of various amines can be inferred by comparing the metals concentrations in degraded solutions. The concentration of Fe^{2+} , Ni^{2+} , and Cr^{3+} is compared for 8 m PZ with 0.3 mole CO_2 per mole alkalinity and 7 m MEA with 0.4 mole CO_2 per mole alkalinity degraded at 135 °C in Figure 5.63. MEA solutions have a higher tendency to corrode stainless steel, as shown by the high levels of metals found in degraded MEA solutions. There was 275, 15, and 32 times more Fe^{2+} , Ni^{2+} , and Cr^{3+} , respectively, found in degraded, loaded MEA than PZ. This enhanced corrosion activity may also be influenced by the fact that the MEA solutions are much more degraded at 135 °C than PZ which is thermally resistant. The limited corrosion tendency of PZ is also demonstrated when compared to the accumulation of metals in degrading EDA and 3-(methylamino)propylamine (MAPA). In Figure 5.64 the concentration of Fe^{2+} is compared for 8 m PZ with 0.3 mole CO_2 per mole alkalinity, 7 m MEA with 0.4 mole CO_2 per mole alkalinity, 8 m EDA with 0.4 mole CO_2 per mole alkalinity, and 9 m MAPA with 0.4 mole CO_2 per mole alkalinity all degraded at 135 °C (Rochelle, 2010b; Vevelstad, 2010; Zhou et al., 2010). PZ has the lowest concentration of Fe^{2+} in solution followed by MAPA, MEA, and then EDA in order of increasing tendency to corrode.

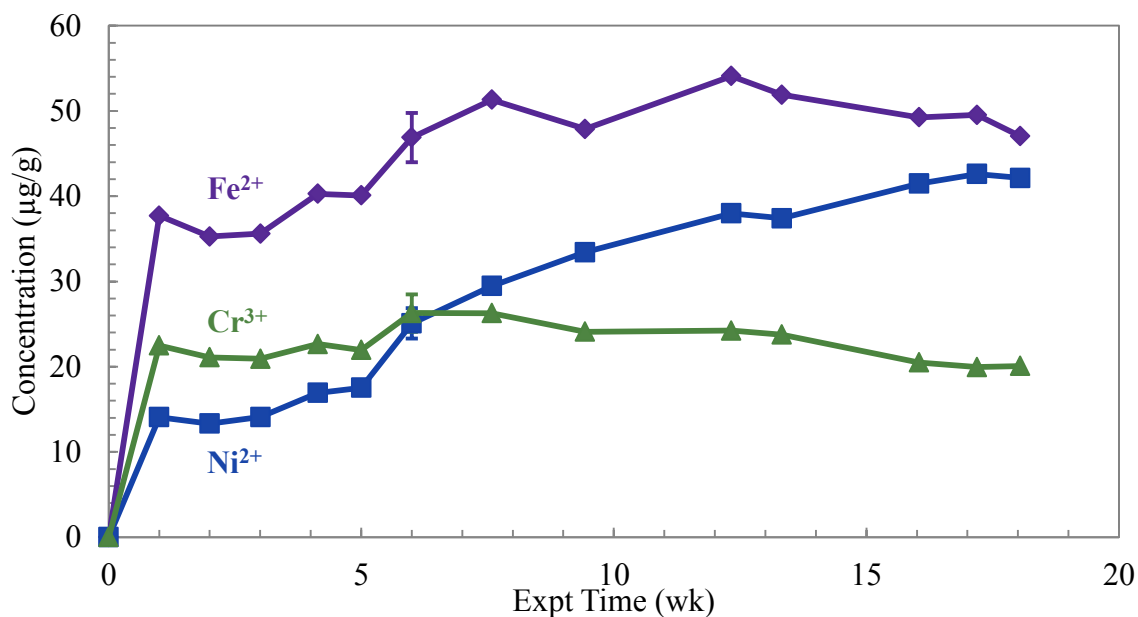


Figure 5.59: Leaching of Fe²⁺, Ni²⁺, and Cr³⁺ during the thermal degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 150 °C

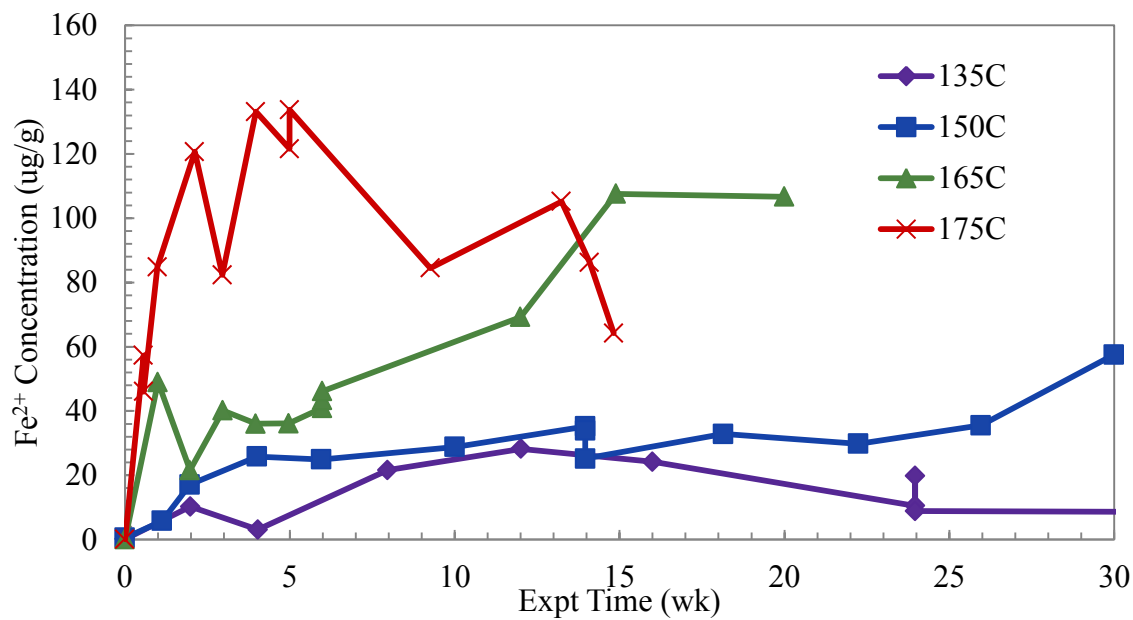


Figure 5.60: Fe²⁺ concentration for thermal degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity degraded at 135 to 175 °C

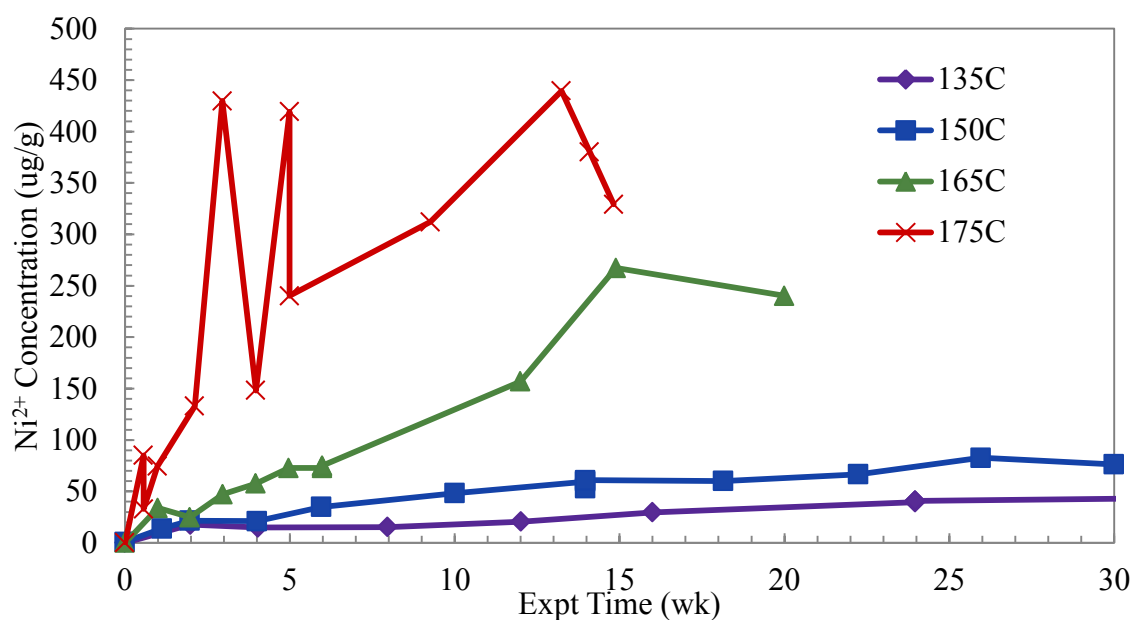


Figure 5.61: Ni³⁺ concentration for thermal degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity degraded at 135 to 175 °C

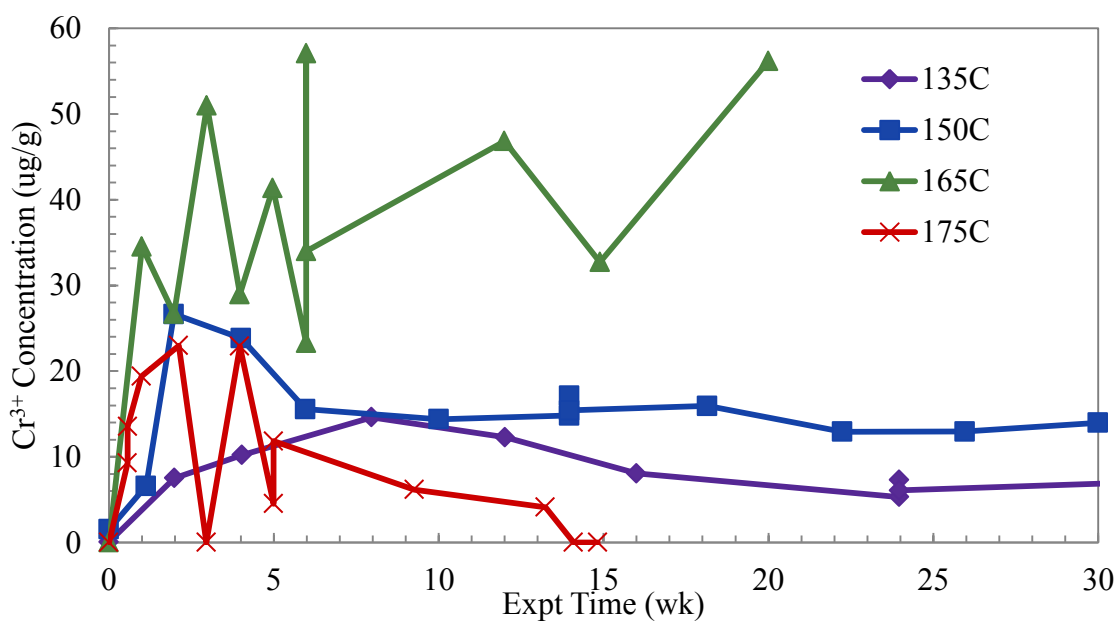


Figure 5.62: Cr³⁺ concentration for thermal degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity degraded at 135 to 175 °C

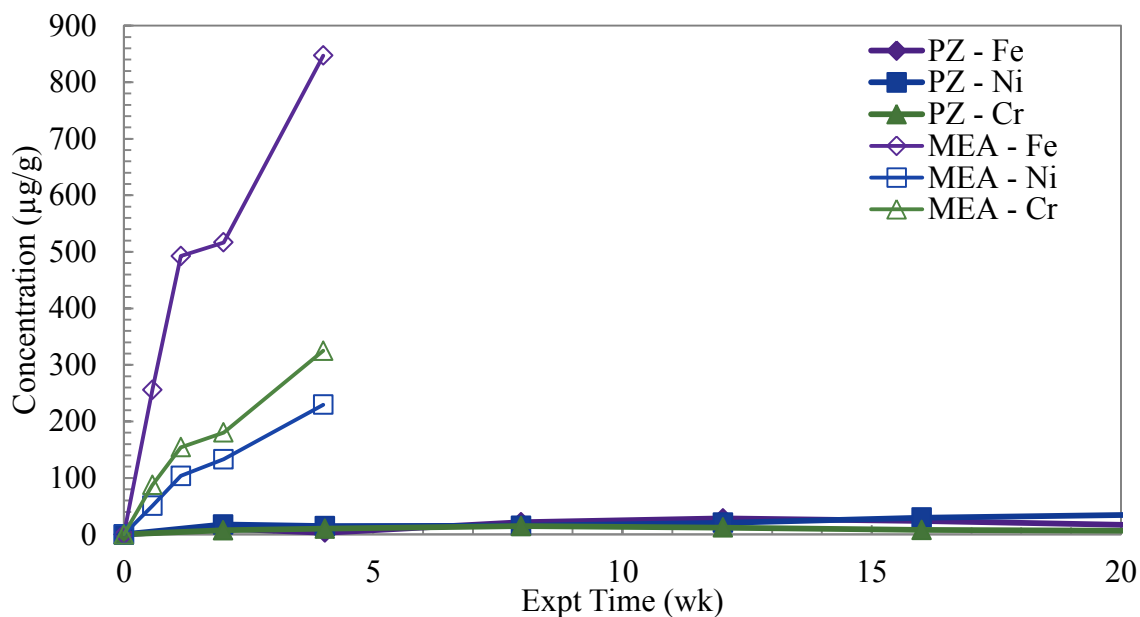


Figure 5.63: Comparison metals content for 8 m PZ with 0.3 mole CO₂ per mole alkalinity (filled points) and 7 m MEA with 0.4 mole CO₂ alkalinity (open points) degraded at 135 °C

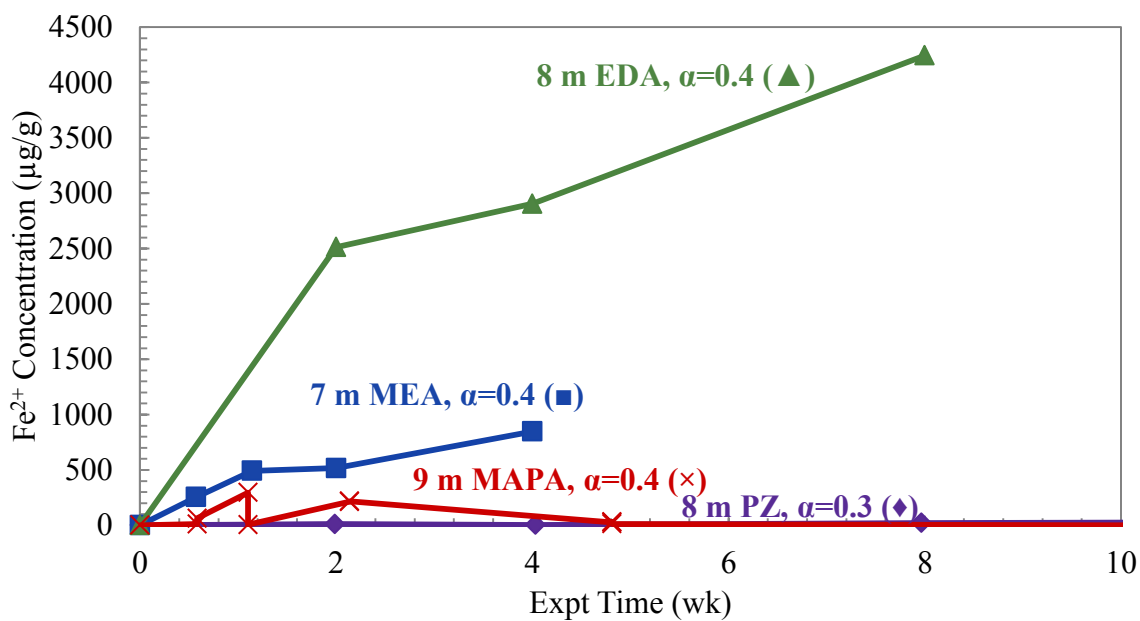


Figure 5.64: Comparison of Fe²⁺ concentration in thermally degraded solutions of PZ, MEA, EDA (Zhou et al., 2010), and MAPA (Vevelstad, 2010)

5.4 SUMMARY OF FIRST-ORDER RATE CONSTANTS FOR PZ EXPERIMENTS

The calculated k_1 values for a variety of experiments can now be compared in order to understand the global behavior of concentrated PZ during thermal degradation. The k_1 inherently changes with temperature, as demonstrated in the previous section, so the effect of CO_2 concentration and PZ concentration will be evaluated. The k_1 values for 8 m PZ over a range of CO_2 loading and temperatures are shown in Figure 5.65. For conditions with data at multiple temperatures, the linear behavior confirms Arrhenius temperature dependence for a range of loadings. For the unloaded case, the trend is impacted by the fact that at there is limited degradation occurring at 150 °C. This trend is observed throughout this project where the error in the lowest temperature measured is higher due to the confidence at which the cation IC can measure small changes of less than 5% in amine concentration.

The Arrhenius equation can be derived using a linear regression through data plotted for the logarithm of k_1 against inverse temperature. This is a linear regression through the data in Figure 5.65, for example. The Arrhenius equation for the k_1 value of 8 m PZ with 0.3 or 0.4 mole CO_2 per mole alkalinity are shown in Equations 5.13 and 5.14. For Equation 5.8, the data obtained at 135 °C were omitted from regression.

$$k_1 = 2.78 \times 10^{14} \cdot \exp\left(\frac{183.5 \text{ kJ}}{\text{mole}} \cdot \frac{1}{RT}\right) \quad (5.13)$$

$$k_1 = 3.19 \times 10^{15} \cdot \exp\left(\frac{191.4 \text{ kJ}}{\text{mole}} \cdot \frac{1}{RT}\right) \quad (5.14)$$

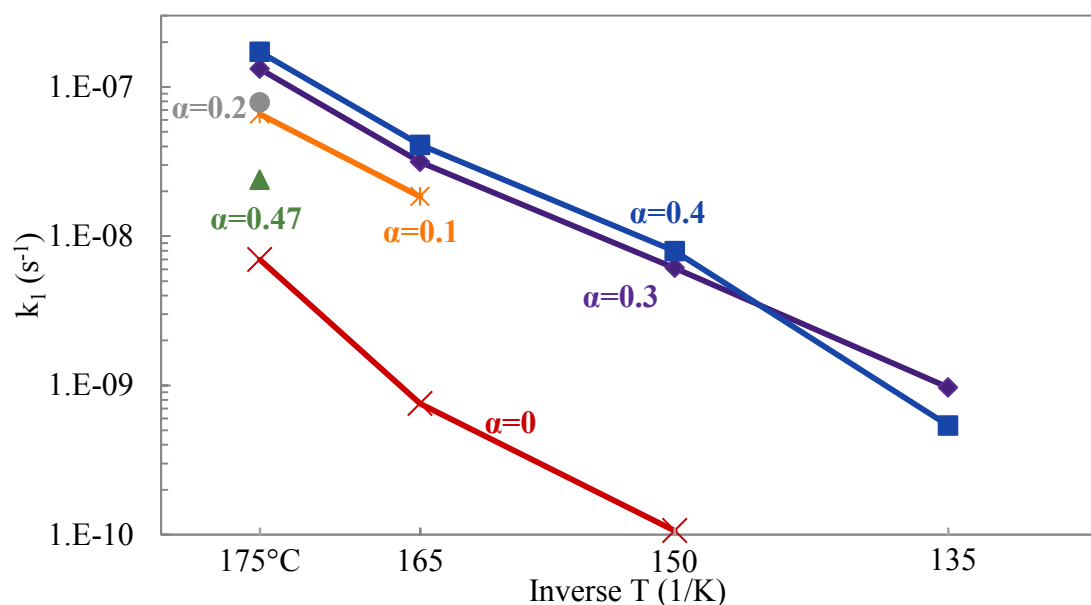


Figure 5.65: Values of k_1 for 8 m PZ with 0 to 0.47 mole CO_2 per mole alkalinity

The k_1 values for 4 to 20 m PZ at either 0.1 or 0.3 moles CO_2 per mole alkalinity are compared in Figure 5.66. For 20 m PZ with 0.3 mole CO_2 per mole alkalinity, the regression for k_1 was done over the first 6 weeks of the experiment, rather than the entire 15 weeks of data due to non-first order behavior. This value is therefore an apparent first order rate constant because more complex mechanisms are likely involved in this particular solution. As PZ concentration increases from 4 to 20 m for solutions with 0.3 mole per mole alkalinity, the k_1 value increases only a small amount. This matches data from section 5.2.2 where PZ loss was found to be only a slight function of amine concentration. The lean loaded 20 m PZ had a lower k_1 value than 8 m PZ. The speciation of 20 m PZ and activity of water are expected to be quite different in these two solutions, perhaps leading to a suppressed degradation rate in the concentrated solution. The data for 10 m PZ demonstrates enhanced error in the data at 135 °C where the degradation rate was difficult to measure accurately.

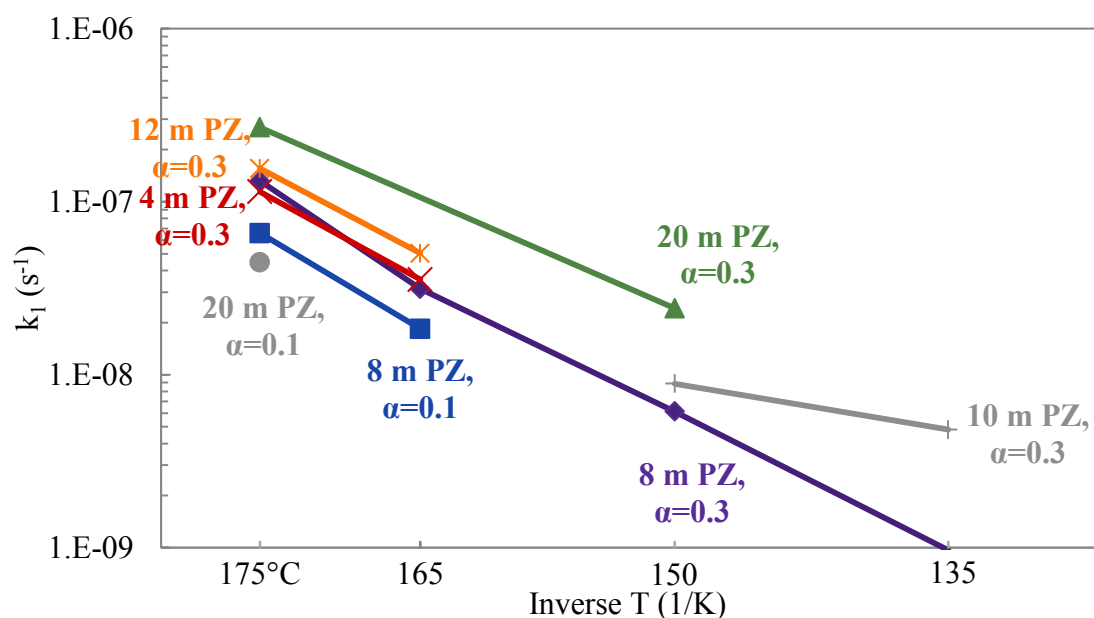


Figure 5.66: Values of k_1 for 4 to 20 m PZ with 0.1 or 0.3 mole CO_2 per mole alkalinity

The k_1 values for all experiments exploring the thermal degradation of PZ are summarized in Table 5.1. The k_1 values are presented in a simplified form ($\times 10^9$) to allow more direct comparison of values. Two experiments, TE1A and TE3B, are not included in this summary table due to difficulty in accurately quantifying a k_1 value. In the case of TE1A, 10 m PZ with 0.4 moles CO_2 per mole alkalinity was degraded at 135 °C but its degradation rate was found to be higher than a complimentary experiment at 150 °C. In the case of TE3B, 15 m PZ with 0.3 moles CO_2 per mole alkalinity was degraded but its degradation rate was found to be positive, giving a negative k_1 , due to a quantified increase of PZ concentration during the experiment. Both of these experiments were done early in the project and the calculated k_1 values were determined to contain a large amount of error given the difficulty of measuring degradation rates accurately on the cation IC at low temperature.

In chapter 7, the k_1 values discussed here will be compared with that of substituted PZs, PZ structural analogs, and other CO₂ capture amines to put the PZ data in perspective. The greatest strength of concentrated PZ solvents is its thermal resistance. The stability of this solvent to high temperature allows for energy advantages that will decrease costs and extend solvent lifetimes. The comparisons in chapter 7 to other CO₂ capture amines will highlight this advantage.

5.5 CONCLUSIONS

At 150 °C, 8 m PZ with 0.3 mole CO₂ per mole alkalinity thermally degrades with a first order rate constant of $6.12 \times 10^{-9} \text{ s}^{-1}$, or approximately 500 mmole PZ lost per kg solution after 30 weeks. PZ thermal degradation is approximately first order in PZ and can be described effectively with a first rate constant, k_1 , with Arrhenius temperature behavior. For 8 m PZ with the expected lean loading of 0.3 mole CO per mole alkalinity, the fraction of PZ remaining (F_{PZ}) is provided by the following set of equations that include a temperature dependence of k_1 .

$$F_{\text{PZ}} = F_{\text{PZ},0} \cdot \exp(-k_1 \cdot t) \quad (5.4)$$

$$k_1 = 2.78 \times 10^{14} \cdot \exp\left(\frac{183.5 \text{ kJ}}{\text{mole}} \cdot \frac{1}{RT}\right) \quad (5.13)$$

The activation energy of the system was determined to be 183.5 kJ per mole. At the rich loading condition, 8 m PZ with 0.4 mole CO₂ per mole alkalinity experiences slightly faster PZ loss according the following equation.

$$k_1 = 3.19 \times 10^{15} \cdot \exp\left(\frac{191.4 \text{ kJ}}{\text{mole}} \cdot \frac{1}{RT}\right) \quad (5.14)$$

The activation of the rich loaded condition was determined to be 191.1 kJ per mole. Both activation energies are higher than hypothesized based on the results of Davis which found the activation energy for six MEA degradation reactions to range from 131 to 144 kJ per mole (Davis, 2009). The activation energies suggest that temperature has a stronger effect on concentrated, aqueous PZ than MEA.

At 175 °C, PZ degradation occurred at a maximum rate between 0.3 and 0.4 mole CO₂ per mole alkalinity. The degradation increased as a linear function of CO₂ loading from 0 to 0.3 mole CO₂ per mole alkalinity, and then decreased from 0.4 to 0.47 mole CO₂ per mole alkalinity. This behavior suggests that solution speciation, dictated by CO₂ loading, strongly affects thermal degradation. Model predictions of speciation at 175 °C do not indicate one species is solely responsible for this behavior, but it is rather a combination of H⁺PZ, PZCOO⁻, and H⁺PZCOO⁻ concentrations.

On the whole, PZ loss during thermal degradation is first order in PZ loss, as is the basis of the k_1 analysis. A slight effect of increasing PZ concentration was observed that increases the k_1 value approximately 30% between 4 and 12 m PZ solutions at the same conditions (0.3 mole CO₂ per mole alkalinity, 175 °C). Highly concentrated PZ solutions do not match this behavior and degradation kinetics of more than first order was observed in 20 m PZ with 0.3 mole CO₂ per mole alkalinity. The equilibrium between the concentrations of formate and formyl amides is affected by increased PZ concentration as more amides are produced in the presence of higher concentration PZ.

The addition of 100 mM of Inhibitor A decreased PZ loss by 20%. Total formate and EDA generation also indicated less degradation in the inhibited case. It is possible that Inhibitor A, a free radical scavenger, inhibits formation of formate. The addition of 5 mM Cu²⁺, 0.4 mM Fe²⁺, 0.1 mM Cr³⁺, or 0.05 mM Ni²⁺ did not affect overall PZ loss rates or the generation of degradation products. Solutions degraded in the

absence of metals were found to have slightly repressed rates of generation of formate and formyl amides. It is likely that the mechanisms responsible for these species, potentially free radical mechanisms, are catalyzed by metals and impeded by Inhibitor A.

Concentrated PZ has decreased tendency to corrode stainless steel metals in comparison to MEA, EDA, and MAPA based on the concentration of leached metals during thermal degradation.

Chapter 6 – Thermal Degradation Products and Insights into Thermal Degradation Pathways

The degradation characteristics of concentrated PZ were discussed in Chapter 5 in terms of PZ loss and the generation of three tracer products. In this chapter, the remaining degradation products produced during those experiments will be discussed in detail including the variety of products detected and quantified, other suspected but not confirmed products, and potential reaction pathways to explain the more abundant molecules. Experiments targeted at identifying particular products or mechanisms are discussed along with experiments designed to measure basic PZ thermal degradation.

6.1 PROPOSED THERMAL DEGRADATION PATHWAYS

Thermal degradation of PZ produces a wide variety of molecules as degradation products. The chemical mechanisms involved in producing each known product are not

yet clear, but an overall set of pathways was developed that involves typical reactions and can describe the generation of the major products. This proposed set of pathways is meant for illustrative purposes and is not known at this time to be correct with complete confidence. The purpose is to suggest the types of reactions believed to be occurring and offer examples of how particular degradation products may be formed. Further research into specific reaction pathways may disprove any portion of the mechanism.

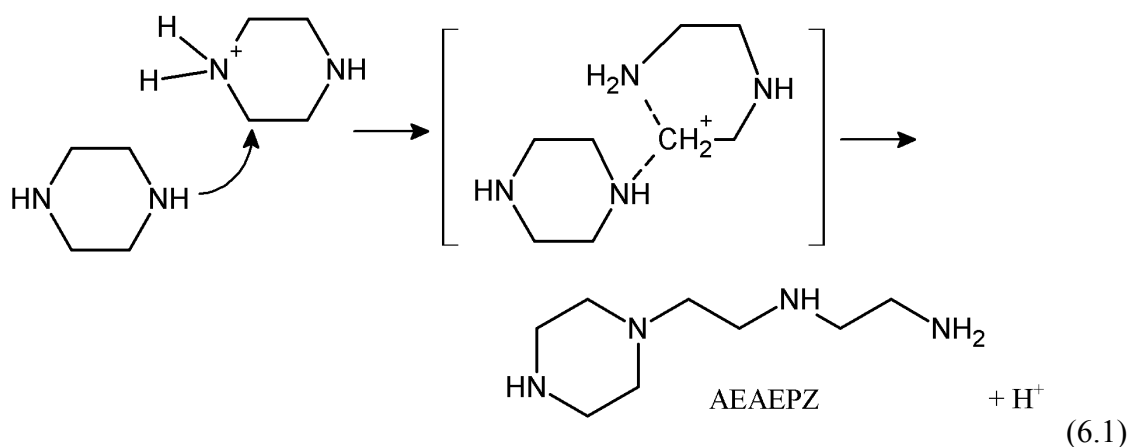
The thermal degradation of concentrated PZ can be described as proceeding with four types of reactions: secondary S_N2 type substitution reactions, elimination reactions, urea generation, and formate generation from CO_2 -containing molecules. The S_N2 label indicates a reaction that is nucleophilic, bimolecular (2 molecules) substitution (McMurry, 2000). Nucleophilic substitutions, as described by S_N2 reactions, are believed to be the most prominent type of degradation reaction due to the strong nucleophilic nature of PZ and its substituted products. In the S_N2 reactions of PZ, the α -carbon to an amino function or protonated amino function is subject to attack that can occur at either secondary or tertiary amines. The pathway for formate generation is the least clear mechanism of those discussed and the general attributes of the mechanism will be discussed, rather than specific reactions.

It should be noted that the influence of speciation on all of the reactions discussed is currently unknown. The reactions described below that include attacking reactive sites or functional groups being attacked should be considered as just the active site discussed, while the rest of the molecule may be in a difference form. For example, in Equation 6.1 where PZ is shown attacking the α -carbon to a protonated PZ, it is just the amino group of the attacking PZ and the protonated amino group that are of interest to the reaction. The reaction may actually proceed with free amino group on either $PZCOO^-$ or H^+PZ while the attacked protonated amino function could be on H^+PZ , H^+PZH^+ , or H^+PZCOO^- ,

because all exist in a CO₂-loaded solution. Reactions likely occur with any combination of the molecules present, with the rate of reaction being dependent on the individual reacting species. Overall, a particular pair may dominate, such as PZ and H⁺PZ, but all of the species are likely involved in quick reaction and equilibrium steps. All of the following reactions are proposed and the effect of speciation is a large consideration when discussing the degradation of loaded, concentrated PZ.

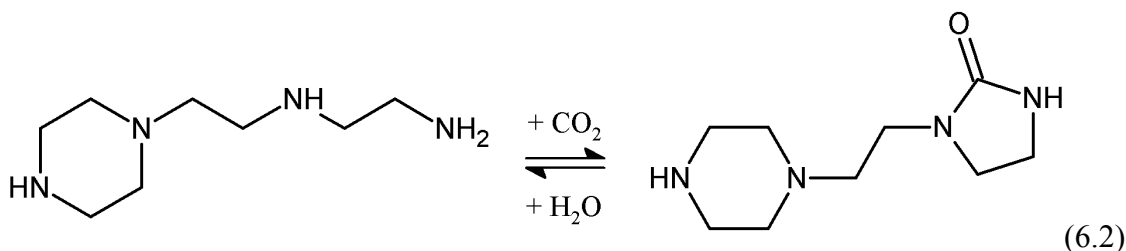
6.1.1 Secondary S_N2 type substitution reactions

S_N2 substitution reactions of PZ and its related molecules probably account for a large portion of the degradation products. The first step in high temperature degradation of PZ is most likely the attack of H⁺PZ at the α-carbon by another PZ molecule that proceeds through an intermediate complex. The product is 1-[2-[(2-aminoethyl) amino]ethyl] PZ (AEAEPZ), as shown in equation 6.1. The exact form of the intermediate complex is not known and this is a suggested form. Further S_N2 reactions will not include any hypothesized intermediate complexes.



In the presence of CO₂, AEAEPZ should react with CO₂ in solution to produce its internal urea. It is believed that both of these molecules are present in solution and exist

in equilibrium based on the observation of other cyclic ureas in solution (see section 6.5). This equilibrium is shown in Equation 6.2.

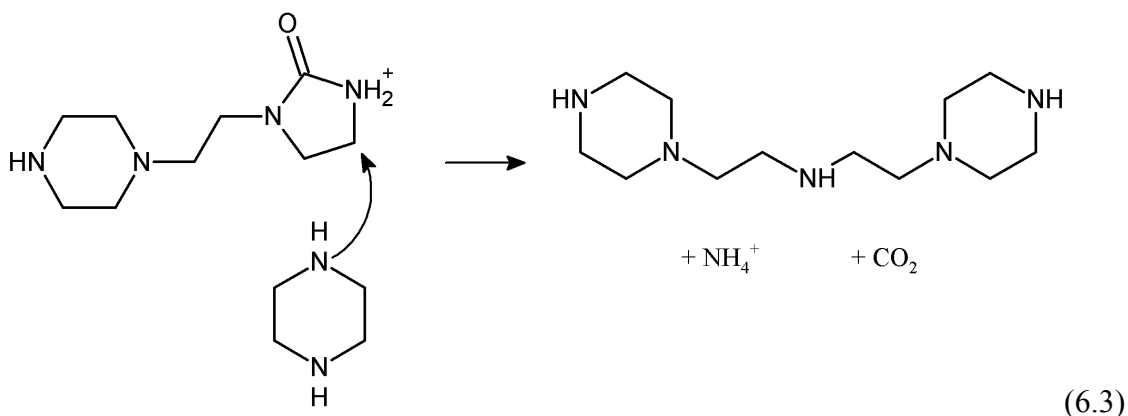


CO₂ will also populate the solution with the carbamates formed by reversible reaction with primary and secondary amine functions. The carbamates rapidly equilibrate so that the respective free amine is still available for S_N2 reactions and free CO₂ is available for urea formation.

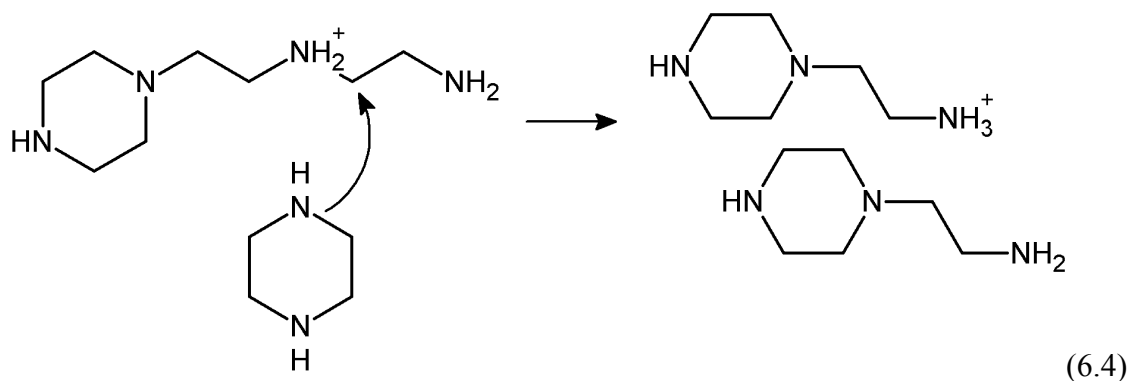
Once AEAEPZ and its urea are formed, a variety of other S_N2 type reactions can occur to produce degradation products. The reaction mixture can be complicated very quickly when all of the potential nucleophiles and attack sites are considered. First, only PZ will be considered as the attacking nucleophile, but analogous reactions could potentially be occurring by other nucleophiles in solution such as amine degradation products (e.g. ethylenediamine (EDA)). Until a significant amount of PZ has been lost to degradation, it is the most likely nucleophile due to its abundance in solution.

At the elevated temperature of thermal degradation, the urea of AEAEPZ will be in equilibrium with AEAEPZ itself. S_N2 reactions involving both AEAEPZ and the urea of AEAEPZ are suspected to proceed in a similar fashion. One example of S_N2 reaction of the urea of AEAEPZ will be provided (Equation 6.3) while the remaining examples will be shown using AEAEPZ. All of the potential reactions are not laid out here, but could be predicted to produce the same molecules plus a CO₂ molecule.

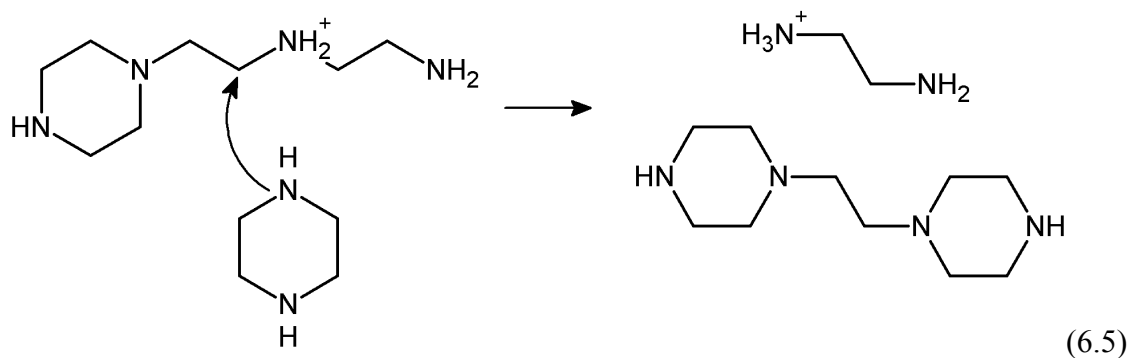
PZ can attack and cause an S_N2 substitution at multiple points on the AEAEPZ molecule, assuming the amino function can be protonated. If the terminal amino function is protonated on the urea of AEAEPZ, an ammonia (NH₄⁺), CO₂, and quintamine molecule are produced (Equation 6.3). This is an example of the reaction occurring on with urea of AEAEPZ while the remaining reactions occur with AEAEPZ. For the following examples of S_N2 reactions, the residual proton is shown on the original nitrogen to clarify the structures produced and maintain a charge balance, rather than to suggest a specific detailed mechanism



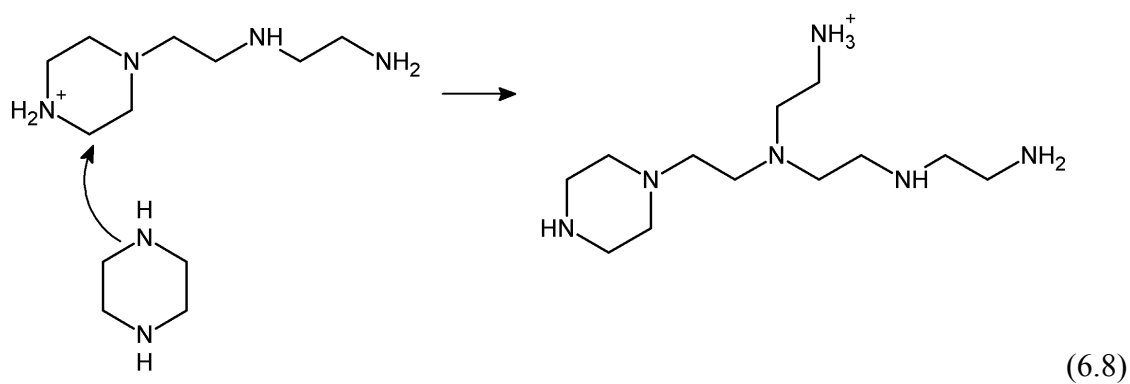
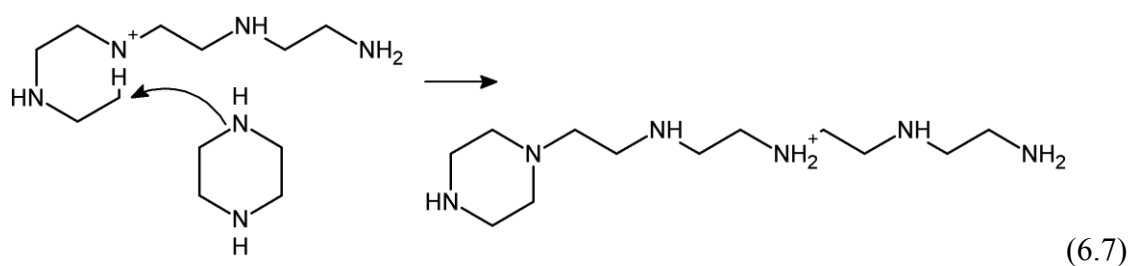
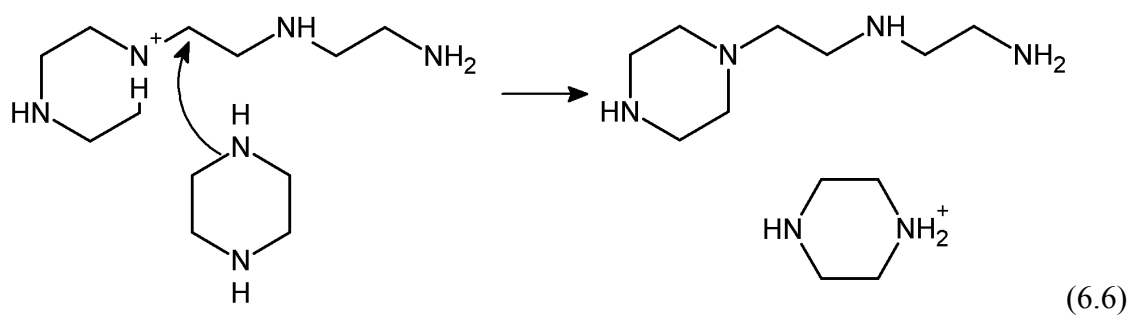
If the internal secondary amino function is protonated, or exists as the cyclic urea, either of its α -carbons can be attacked to produced different molecules. First, if the carbon on the right is attacked, two N-(2-aminoethyl) piperazine (AEP) molecules are produced (Equation 6.4).



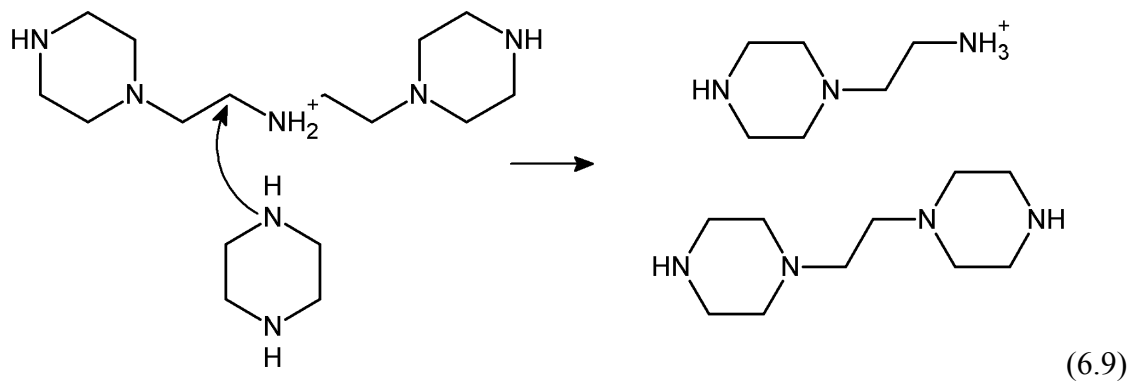
If the carbon on the left is attacked, an EDA and 1,1'-(1,2-ethanediyl)bis-PZ (PEP) are produced (Equation 6.5).



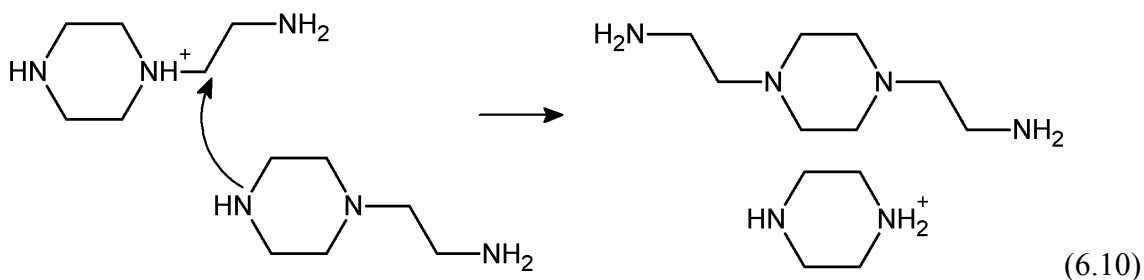
If either of the amino functions within the cyclic PZ structure are protonated, which is less likely, either the reactants are regenerated (Equation 6.6) or long chain PZ hexamines are produced (Equations 6.7 and 6.8). The long chain PZ hexamines are expected to be only minor products if they are produced. It could be further hypothesized that these types of long-chain monoamines could react further to create molecules such as diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), or other polymeric ethylenediamine molecules.



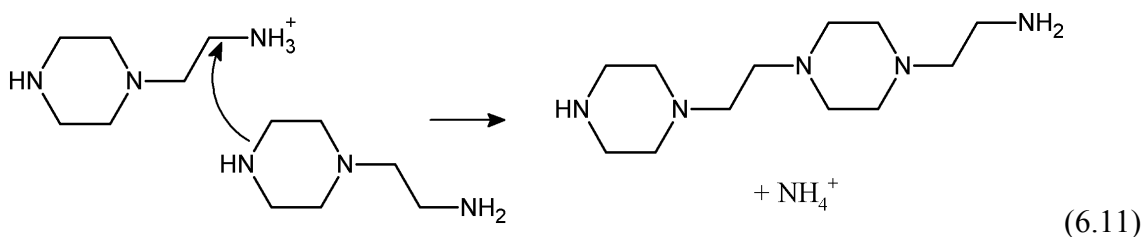
Further S_N2 reaction of the quadramine produced in Equation 6.3 could be proposed that produces AEP and PEP (Equation 6.9)



All of the above reactions consider PZ as the attacking nucleophile in S_N2 substitution reactions. EDA, AEP, N-(2-hydroxyethyl)piperazine (HEP), or any of the other degradation products could also act as a nucleophile. The tendency to attack depends on the pK_a of the attacking amino group and the concentration in solution. The following reactions are examples of the products that could be formed if AEP was the attacking nucleophile. First, if AEP attacked another AEP molecule, PZ and N,N'-di(2-aminoethyl) piperazine (DAEP) are produced (Equation 6.10). DAEP is expected to be only a minor product and could be generated with this type of reaction which is essentially an arm-switching reaction.



If PZ was the attacking molecule in the above reaction (Equation 6.10), the reactants would be generated again. If the terminal amino function on AEP was protonated instead, an ammonia and a polyAEP structure would be produced (Equation 6.11). This could be another route to generate the NH_4^+ quantified in solution.

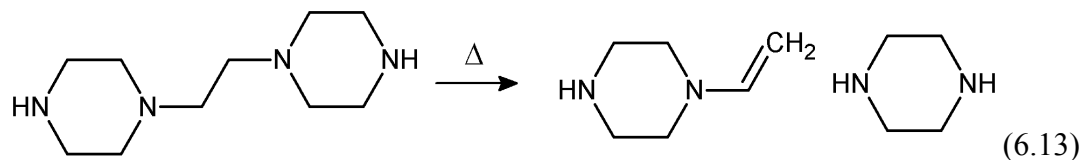
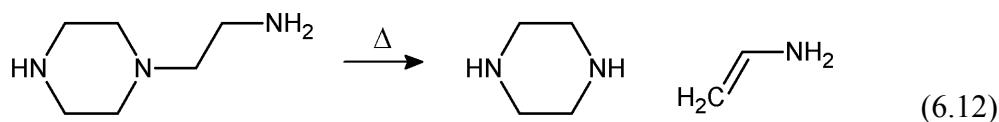


S_N2 type reactions in the presence of PZ can generate a variety of products as shown in the reactions above. Those shown are likely only a subset of the potential reactions and an extrapolation of the reactions here could be proposed that included every kind of attacking nucleophile and molecule being attacked. Included in the reactions shown are plausible routes to produce EDA, AEP, and NH_4^+ , quantified degradation products in thermally degraded PZ. Also, AEAEPZ, the urea of AEAEPZ, and PEP were produced, which are all important suspected intermediates.

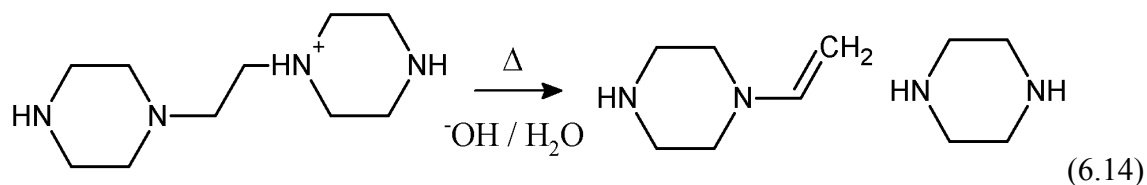
6.1.2 Elimination reactions

Another type of reaction that is believed to be occurring in thermally degraded PZ is elimination at a tertiary amine. In elimination reactions, two substituents are removed from a molecule, usually to produce an alkene, and rely on the presence of a good leaving group (McMurry, 2000). It is not known whether the one-step, second order E2 mechanism or two-step, first order E1 mechanism dominates in the case of high temperature PZ degradation. Since this is the case, a specific mechanism with the appropriate intermediate molecules will not be hypothesized, only the products. S_N2 reactions are usually favored over E2 eliminations except when basicity increases, at higher temperatures or when the nucleophile is poor, among other circumstances (McMurry, 2000). In the case of PZ thermal degradation, it is possible that both S_N2 and E2 eliminations are occurring simultaneously because of the high temperature and mix of nucleophiles and leaving groups.

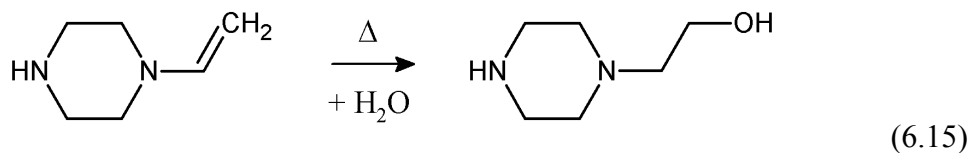
An elimination reaction of AEP, could produce PZ and ethenamine (CAS: 593-67-9; vinylamine) (Equation 6.12). In another example, an elimination reaction of PEP would produce 1-ethylenyl-piperazine and PZ (Equation 6.13).

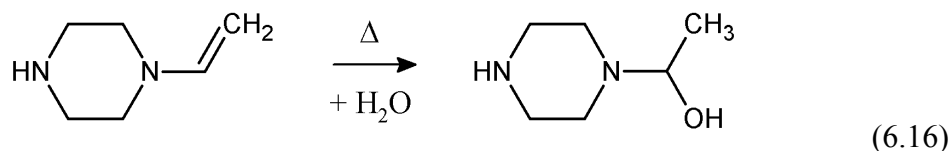


Hofmann elimination takes place at a quaternary amine function to form an alkyl and a tertiary amine. This could take place on PEP, for example if one of the interior amino functions was protonated (Equation 6.14).



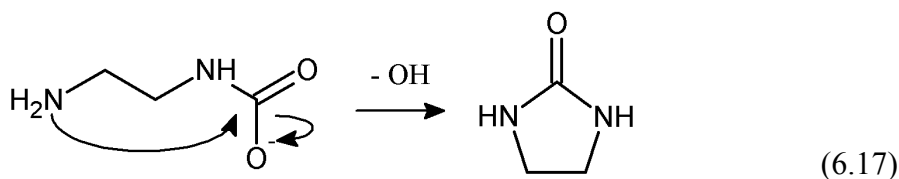
Once the alkene or olefin compound has been generated, the double bond could be hydrated. Hydrations usually occur in acidic conditions, but it could be reasoned that under these high temperature conditions, hydrations are possible. Anti-Markovnikov hydration of 1-ethylenyl-piperazine would produce N-(2-hydroxyethyl) piperazine (HEP) (Equation 6.15). Markovnikov hydration of 1-ethylenyl-piperazine would produce α -methyl-1-piperazinemethanol, (CAS: 65703-81-3), a hemiaminal form of N-ethyl piperazine (Equation 6.16).



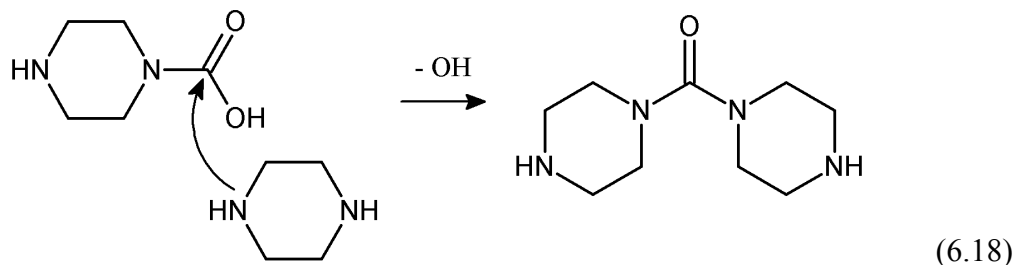


6.1.3 Urea generation

Ureas are a particular subset of amides that contain two amino functions connected by a carbonyl. Ureas can be readily formed in the presence of CO_2 and amines under alkaline conditions. For example, EDA in the presence of CO_2 can form EDACOO^- (EDA carbamate), and the terminal amino function can react to form the cyclic, internal urea of EDA, 2-Imidiazolidone (2-Imid) (Equation 6.17).



This reaction is known to take place readily under thermal degradation conditions as has been described previously and discussed in section 6.5 of this chapter (Zhou et al., 2010). Provided the rapid reaction of EDA to 2-Imid at high temperature, it appears the proximity of the terminal nitrogen in EDACOO^- accelerates reactions. It is not expected, for example, that the formation of the diPZ urea would proceed as rapidly from PZCOO^- in loaded solutions (Equation 6.18).



Ureas are believed to be important molecules for PZ thermal degradation because they are stable, contain a CO₂ molecule, and are rapidly generated at high temperatures. Since the ureas contain a CO₂ molecule, they could prove to be important in the reaction of CO₂ to form formate, which is not yet understood. Ureas are expected to be important in the overall study of thermal degradation of CO₂ capture amines due to the fact that reactive amino functions and CO₂ molecules are readily present in nearly all amine-based solvents under study for this application.

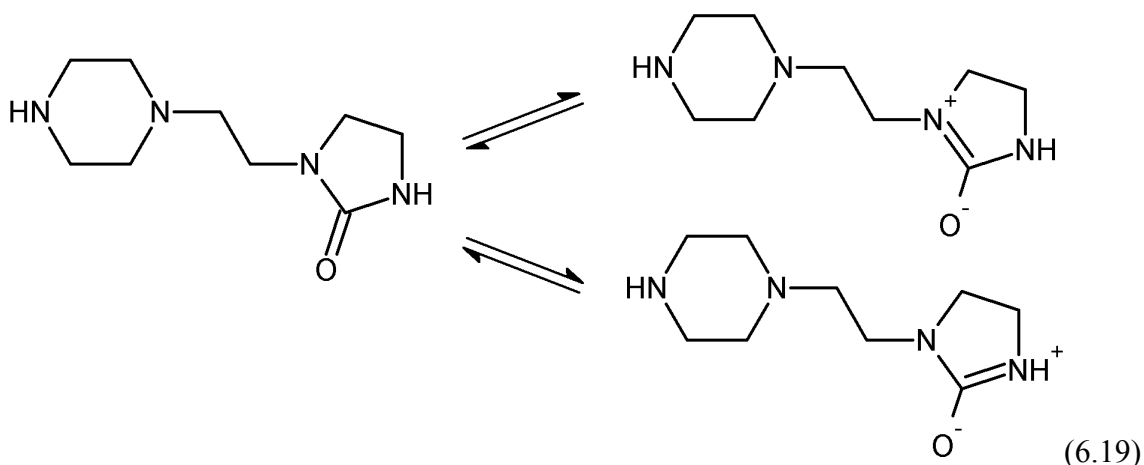
6.1.4 Formate generation from CO₂-containing molecules

As the discussion in section 6.4 will show, formate is generated from CO₂ or CO₂-containing molecules. The reduction of CO₂ to formate was not predicted and there are not any obvious pathways for this to occur. It is also not clear if the formate or a formyl amide is first produced. These molecules establish an equilibrium once they are present in solution and it was not clear in any experiment which was produced first. In terms of the actual generation mechanism, it is also not clear if free CO₂ or a CO₂-containing molecule such as PZCOO⁻ or H⁺PZCOO⁻ reacts to form the first formate or formyl amide molecule.

If formate is generated through the reduction of CO₂ to formate, it is expected that another molecule would be oxidized in the process as a companion redox reaction. At this point, there have not been any specific oxidation products identified in thermally degraded solutions, but a few possible species are discussed in this chapter.

Another possibility is the generation of formate or formyl amides from ureas. Ureas, as discussed in the preceding section, are generated during thermal degradation due to the presence of CO₂ molecules in solution. Ureas, as with other amides, have a delocalization of electrons between the nitrogens and the carbons and oxygens that create

resonance forms (Brown, 1994). For example, the resonance forms of the urea of AEAEPZ are shown in Equation 6.19.



Another concept for formate generation is through free radical mechanisms. Similar to those expected to be occurring in oxidation, free radicals of peroxides or other oxygen containing molecules could be generated due to pyrolysis at high temperature. When formate is produced, it exists at high temperature in equilibrium with formyl amides such as N-formylpiperazine (FPZ).

6.2 THE GENERATION OF THERMAL DEGRADATION PRODUCTS

A variety of molecules are generated when concentrated, loaded PZ is exposed to high temperature. Elevated temperature accelerates reactions that would otherwise be slow or undetectable at a decreased temperature. Experiments were performed with the intention of accelerating or maximizing thermal degradation in order to more easily quantify the reactions occurring. Because of this, the experimental conditions do not directly represent a real CO₂ capture system. In reference to the focus of this chapter, solutions were allowed to degrade significantly beyond what would be normally seen in an amine-based absorption-stripping system, producing large concentrations of

degradation products. Operations resulting in 30 to 70% PZ degradation would not be observed in industry as is typical of the experiments discussed here. The approach is to understand this high level of degradation and then apply that knowledge to the initial rates and causes of degradation in real systems. A summary of degradation products successfully identified and quantified as well as suspected new products are summarized in Table A.3 (Appendix A).

6.2.1 Representative thermal degradation product mix

A typical thermally degraded PZ sample includes amines, amides, carboxylate ions, imidazolidones, and ureas. This sample could also include aldehydes, oxazolidones, and polymeric compounds, although these have not been positively quantified in degraded PZ. As an example of what would be expected in a typical thermal degradation experiment for concentrated, loaded PZ, a representative experiment will be discussed in detail. For this example, the thermal degradation of 8 molal (m) PZ with 0.3 mole CO₂ per mole alkalinity degraded at 165 °C for 20 weeks (TE44) will be used. This experiment was performed toward the end of this project and was subjected to the most advanced analytical techniques developed. This temperature is also of specific interest to new PZ projects that call for stripper or two-stage flash operation around 150 °C.

In this experiment, 10 major degradation products were identified and quantified. In order to simplify the results, the concentration profiles are split among multiple figures. First, the loss of PZ and CO₂ during the 20 weeks of degradation is shown in Figure 6.1. Over the course of 20 weeks, 1730 mmole PZ per kg solution was degraded or 40.8% of the initial concentration. In that same time period, 888 mmole CO₂ per kg solution was lost or 32.3% of the initial concentration. The significance of the PZ and CO₂ losses will be discussed in the following sections.

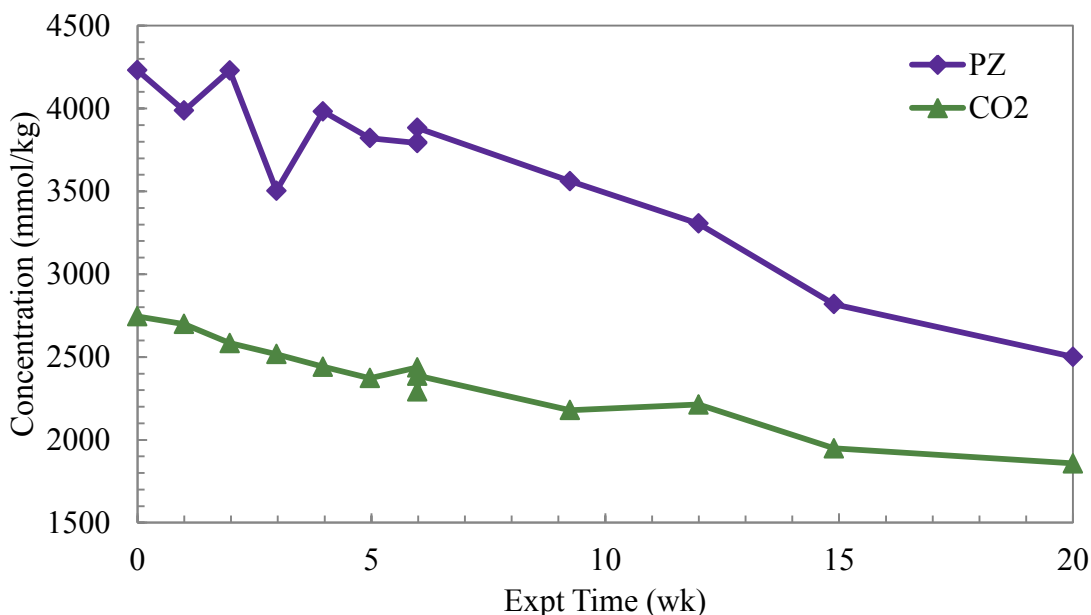


Figure 6.1: Loss of PZ and CO₂ during thermal degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 165 °C (TE44)

Carboxylate ions, also known as heat stable salts, are commonly produced in thermal degradation experiments and are quantified using anion IC. Anion IC can also quantify non-carboxylate degradation products such as nitrite or nitrate, as well as other ions that are not degradation products such as sulfate, chloride, or thiosulfate. Nitrite and nitrate were not found to be dominant degradation products in any thermal degradation experiment. Due to the importance of nitrite in nitrosamine formation, it is important to be clear on this point. An unidentified anion IC peak has been misidentified in the past as nitrite, as discussed in section 6.1.4. The carboxylate ions produced in TE44 are shown in Figure 6.2. The concentrations of the basic carboxylate ions (glycolate, acetate, formate, and oxalate) are shown in this figure along with their concentrations after NaOH treatment. This value, labeled “Total [Ion]” represents the concentration of the original ion and the concentration increase that may have resulted from the reversal of any amide

formation (see Section 3.1.6 for details). The difference between the two values would represent the concentration of amides of that carboxylate ion.

Formate was the dominant carboxylate ion produced in every PZ thermal degradation experiment and the differences in magnitude between formate and the other carboxylate ions shown in Figure 6.2 is representative of most experiments. The concentration range is magnified in Figure 6.3 to highlight the behavior of the non-formate carboxylate ions. It is important to note that all of the data series shown contain non-zero values.

Amine products, including substituted PZ molecules, account for a majority of both the carbon and nitrogen mass recovered after thermal degradation. The concentration profiles for the amines positively identified and quantified using cation IC are shown in Figure 6.4 and include NH_4^+ , EDA, FPZ, 1-methylpiperazine (1-MPZ), HEP, and AEP. A magnified view of the same figure is shown in Figure 6.5. NH_4^+ was found to have one of the largest concentrations in thermally degraded experiments. N-formyl PZ, although an amide, is included in this figure since N-Formyl PZ can be quantified directly with cation IC and is a substituted PZ. The previous graphs showed the total formyl amides quantified through alkaline treatment.

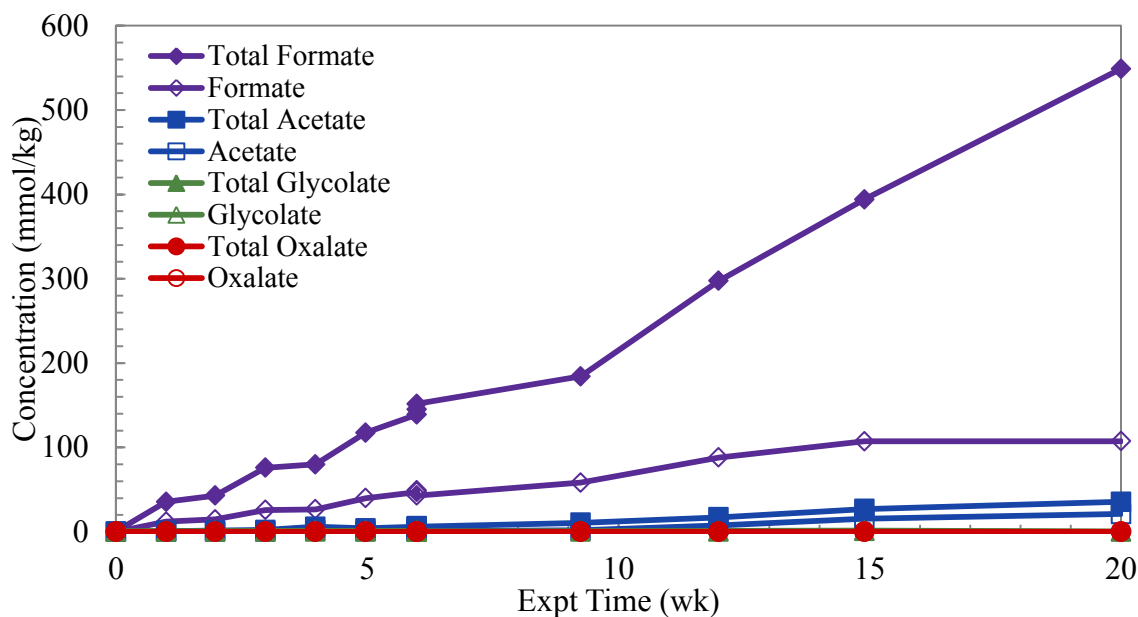


Figure 6.2: Production of carboxylate ions during thermal degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 165 °C (TE44) (legend matches order of curves)

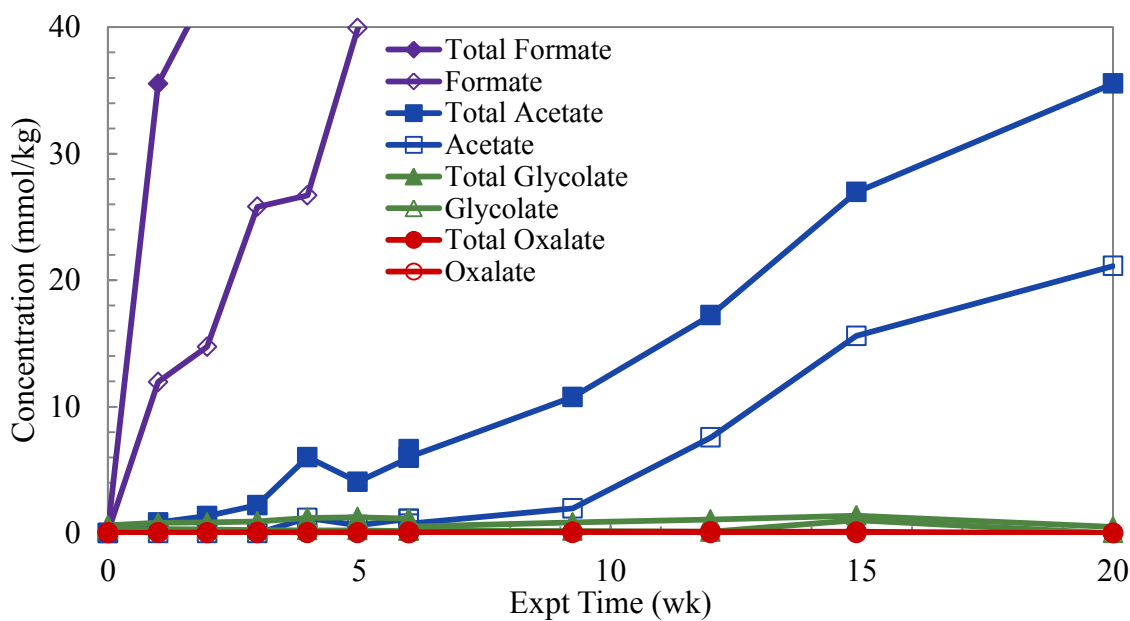


Figure 6.3: A magnified view of the production of carboxylate ions during thermal degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 165 °C (TE44) (legend matches order of curves)

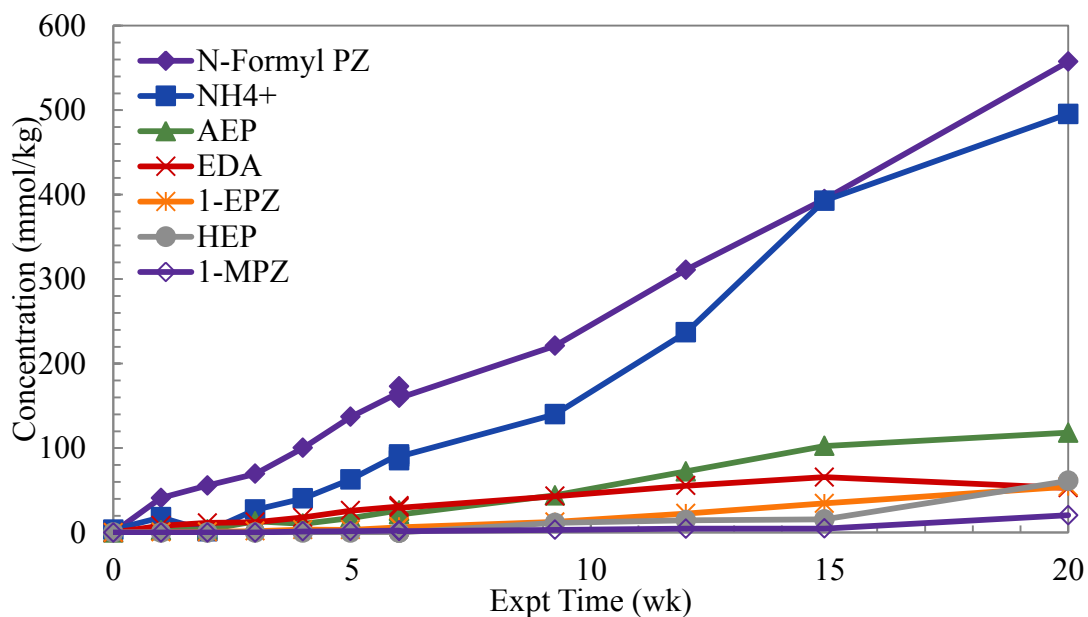


Figure 6.4: Production of amine degradation products during thermal degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 165 °C (TE44) (legend matches order of curves)

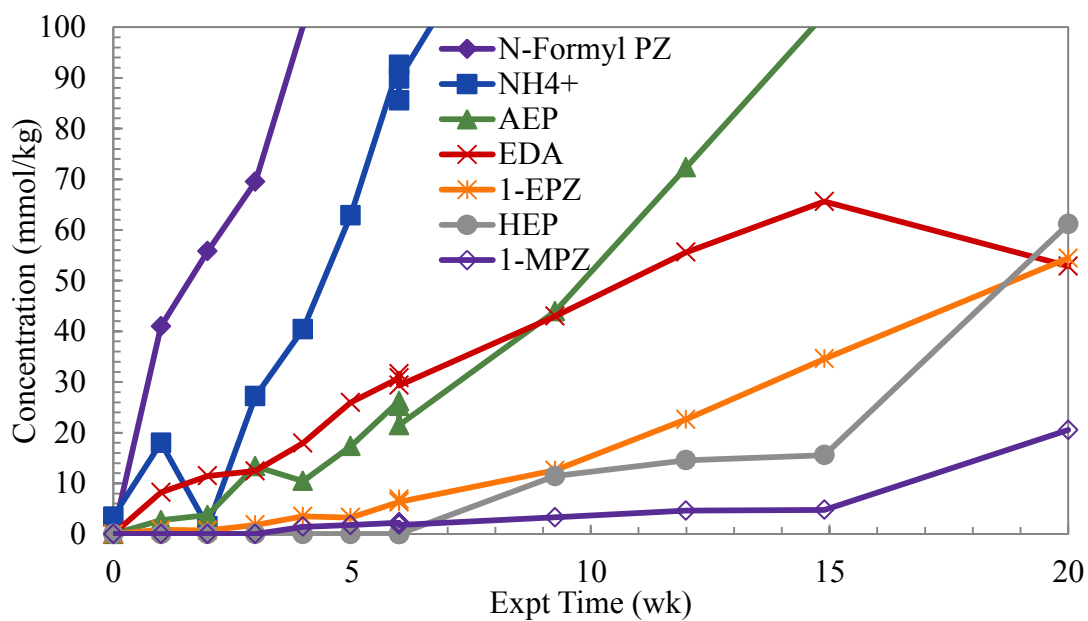


Figure 6.5: A magnified view of the production of amine degradation products during thermal degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 165 °C (TE44) (legend matches order of curves)

Only one compound was positively identified and quantified using HPLC. The generation of 2-Imid is compared with that of formate, NH_4^+ , FPZ and AEP in Figure 6.6 to put the 2-Imid concentration in perspective in the total degradation mix. Also, this plot demonstrates how formate, AEP, and 2-Imid were generated in concentrations very similar to each other.

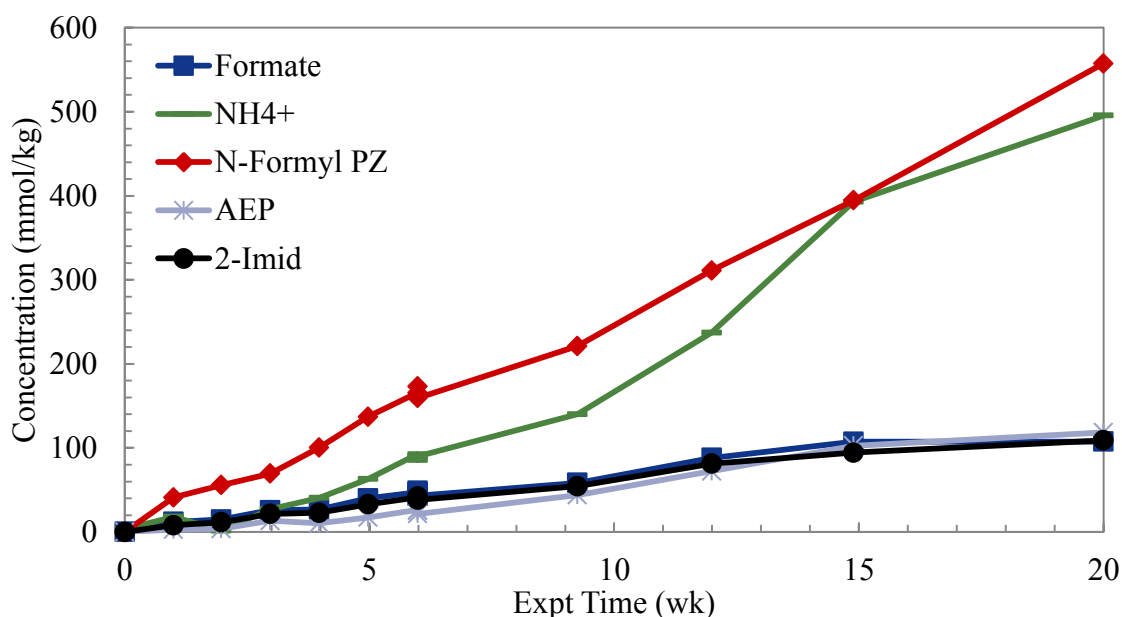


Figure 6.6: Production of 2-Imid during thermal degradation of 8 m PZ with 0.3 mole CO_2 per mole alkalinity at 165 °C (TE44)

6.2.2 Total Nitrogen (TN) and Total Organic Carbon (TOC) analysis

The samples from this experiment were analyzed for total organic carbon (TOC) and total nitrogen (TN). The fraction of both TOC and TN as a function of the initial concentration are shown in Figure 6.7. Over the 20 weeks of degradation, the TOC concentration remained steady while the TN concentration decreased by 13%. The error associated with both measurements is high, between 2 and 6.5%, as demonstrated by the error bars on each data point, but a downward trend in TN is observable. This loss of N

indicates the generation of volatile products during degradation beginning after approximately 10 weeks. This loss of volatile N may correlate with the delay in production of some of the minor liquid phase products such as 1-EPZ, 1-MPZ, HEP, and acetate. Since the TOC did not decrease during the experiment, it is expected that the loss of TN is in the form of volatile ammonia (NH_3), NO_x (NO and N_2O), or molecular nitrogen (N_2). These volatile species would have escaped from the liquid phase once the thermal cylinders were opened and the samples were stored for analysis. The presence of detectable NH_4^+ in solution supports the conclusion that volatile NH_3 was lost in the gas phase in some concentration. The absence of nitrite or nitrate in the liquid phase makes NO_x less probable

The loss of total alkalinity, PZ, and TN is compared for this experiment in Figure 6.8. The effect of PZ thermal degradation is clear as all three quantities decrease. As PZ is degraded, there is generation of amine products that maintain alkalinity, indicated by the higher concentration of alkalinity than PZ. The difference between total alkalinity and TN is likely the concentration of ureas, amides, and amino acids that would be detected as TN, but are not detected by acid titration as alkalinity. The presence of carboxylic acids may also underestimate alkalinity measurements using acid titration, although the concentration of free carboxylate ions is low compared to the concentration of carboxylate tied up as amides.

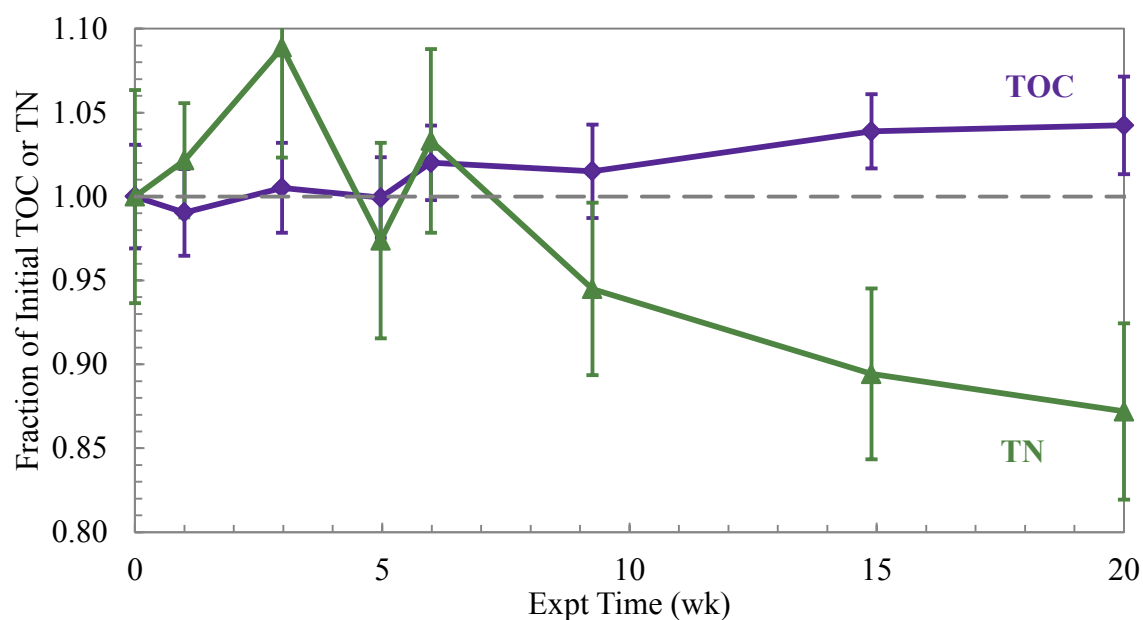


Figure 6.7: Fraction of initial TOC and TN during thermal degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 165 °C

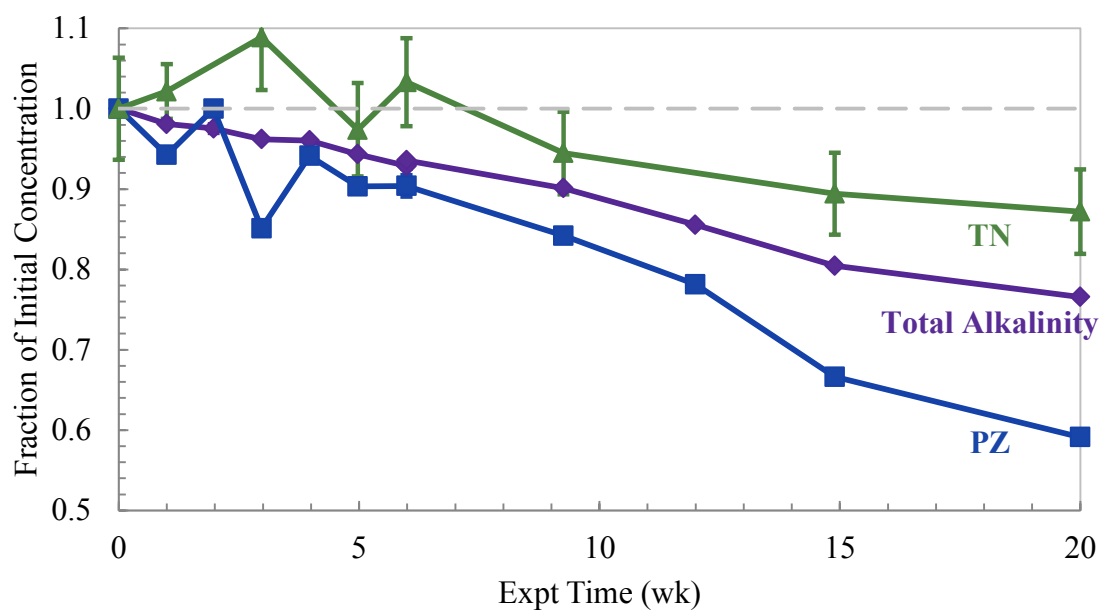


Figure 6.8: Comparison of the fraction of initial total alkalinity, PZ, and TN for thermal degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 165 °C (TE44)

6.2.3 Carbon and nitrogen mass balance

Using the concentrations of PZ, CO₂, and degradation products, the recovery of mass during this sample thermal degradation experiment can be analyzed as an example of a typical mass balance in concentrated PZ thermal degradation experiments. The nitrogen and carbon balance achieved in TE44, the sample experiment, is shown in Table 6.1. These balances were calculated for the final sample of TE44 after 20 weeks of degradation at 165 °C and do not include any unidentified peaks discussed in the next section. Two molecules, 1-MPZ, and HEP, saw distinct increase in concentration in the final sample (t = 20 weeks), so their concentrations may be overestimated in the mass balances. Formyl amides calculated from alkaline amide reversal were not included in the balances while N-Formyl PZ quantified using cation IC was included. Glycolate, glycolyl amides, oxalate, and oxalyl amides were not included in the balances due to their negligible concentrations. This table, as well as the following two tables that contain balances, show the raw concentration of each molecule in solution in the first column for reference. The degradation products are listed in decreasing N concentration and the order is maintained for all tables in this section.

After 20 weeks, 1730 mmole PZ per kg and 887 mmole CO₂ per kg were lost to thermal degradation pathways. The mass recovered after 20 weeks of degradation is fairly high with 74% of the nitrogen and 63% of the carbon recovered. N-Formyl PZ, NH₄⁺, AEP, and 2-Imid are the most prominent degradation products of thermally degraded PZ. These four molecules account for 63 and 49%, respectively of the N and C mass lost as PZ and CO₂ during degradation.

The apparent loss of TN over the course of the experiment should correspond to a volatile N product that does not contain C. Ammonia (NH₃) may be volatile enough to be lost to the atmosphere when the cylinders were opened. Other possible volatile N

products include nitrogen (N_2) and NO_x (NO , NO_2), none of which were quantified. NH_4^+ was quantified in liquid solution so volatile NH_3 is expected. TN analysis indicates a 13% loss of TN where the initial concentration was 8500 mmole N per kg. The difference in the N and C balance also indicates that there are C-containing liquid phase degradation products that have not been identified that do not contain N.

Table 6.1: Nitrogen and carbon mass balance closure for thermally degraded PZ at 165 °C for 20 weeks

	Conc. mmol/kg	Nitrogen Balance		Carbon Balance	
		N Conc. mmol/kg	Lost N %	C Conc. mmol/kg	Lost C %
PZ Lost in 20 weeks	1729	3458	-	6916	-
CO ₂ Lost in 20 weeks	888	-	-	888	-
TOTAL Lost		3458		7804	
DEGRADATION PRODUCTS:					
N-Formyl PZ	558	1115	32.2	2787	35.7
NH_4^+	496	496	14.3	0	-
AEP	118	355	10.3	710	9.1
2-Imid	109	218	6.3	327	4.2
HEP	61	122	3.5	367	4.7
1-EPZ	54	109	3.1	327	4.2
EDA	53	106	3.1	106	1.4
1-MPZ	21	41	1.2	103	1.3
Formate	108	0	-	108	1.4
Total Acetate	36	0	-	71	0.9
TOTAL		2561.1	74.1	4904.0	62.8

The distribution of N-containing degradation products is compared with the unrecovered (or “missing”) N from the degradation of PZ in Figure 6.9. In this figure, the generation of each of the prominent N-containing degradation products is shown through the course of the experiment. HEP, 1-EPZ, EDA, and 1-MPZ are plotted together in order to see their concentration on this scale. At 1 and 3 weeks, the PZ data had some scatter, creating an excess of missing PZ N. All of the major degradation products are continually increasing without any delay indicating a secondary mechanism.

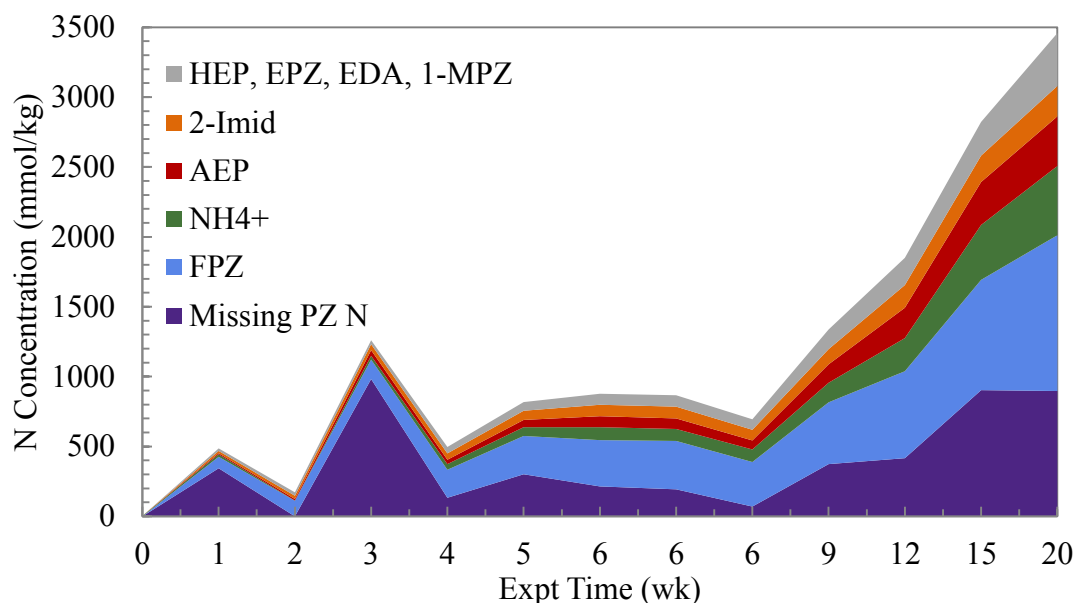


Figure 6.9: Distribution of recovered N during thermal degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 165 °C (TE44)

The loss of CO₂ is a unique observation that has not been seen for amine thermal degradation before. CO₂ is lost during thermal degradation of PZ to generate formate, formyl amides, and ureas, as will be discussed in greater detail in section 6.4. A mass balance, shown in Table 6.2, can be made for all CO₂ containing degradation products in an attempt to trace CO₂ loss. Formate, N-formyl PZ, and 2-Imid all contain one CO₂ function in their structure and account for 87.2% of the lost CO₂. This balance indicates that there are likely unidentified molecules with urea or formyl amide structures that contain functionalities originally derived from CO₂.

Finally, a fourth balance on the alkyl portion of the PZ molecule can be estimated. This balance accounts for where the backbone carbons of the PZ end up and is shown in Table 6.3. This was calculated as an “ethyl” balance where the every two-carbon chain was calculated separately. For example, every mole of EDA, 2-Imid, and acetate had one “ethyl”, each mole of PZ and FPZ had two “ethyls”, and each mole of HEP and AEP had

three “ethyls”. 1-MPZ was considered to have 2.5 “ethyls” for the balance. After 20 weeks of degradation, 60% of the lost backbone carbons of PZ are recovered in degradation products. This is similar to the overall C balance and has much worse closure than the overall N and CO₂ balances. This indicates that there are likely numerous carbon-based degradation products that have yet to be identified in the liquid phase.

6.2.4 Unidentified or unquantified products

Unfortunately, there were unidentified and unquantified peaks on all three of the major analytical tools used to analyze this example experiment. The mass balances discussed indicate that the major degradation products have been identified, but there is still room for further identification and mass balance closure. A comparison of the anion IC chromatogram for the initial and final sample for this experiment is shown in Figure 6.10 and with a magnified signal in Figure 6.11. From the magnified chromatogram, six unknown peaks are visible labeled with a “U” on the chromatogram. The peak at a retention time of 24 minutes is not nitrite, although the nitrite peak eludes just after it. The unidentified peaks are spread throughout the chromatogram and do not correspond to peaks identified in Chapter 8 as possible mono-amides of oxalate.

A comparison of the anion IC chromatogram for the original and NaOH treated final sample with a magnified signal is shown in Figure 6.12. The only change visible in the non-magnified chromatogram is the sizable increase in the formate peak. The alkaline treatment produced more formate and oxalate, but did not change the unidentified peaks. It is unlikely at this point that any of the unidentified peaks seen through anion IC are parts of amides.

Table 6.2: CO₂ mass balance for 8 m PZ with 0.3 mole CO₂ per mole alkalinity degraded at 165 °C for 20 weeks (TE44)

	Conc. mmol/kg	CO ₂ Balance	
		CO ₂ Conc. mmol/kg	Lost CO ₂ %
PZ Lost in 20 weeks	1729	0	-
CO ₂ Lost in 20 weeks	888	888	-
TOTAL Lost		888	
DEGRADATION PRODUCTS:			
N-Formyl PZ	557	557	62.8
NH ₄ ⁺	496	0	-
AEP	118	0	-
2-Imid	109	109	12.3
HEP	61	0	-
1-EPZ	54	0	-
EDA	53	0	-
1-MPZ	21	0	-
Formate	108	108	12.1
Total Acetate	36	0	-
TOTAL		774	87.2

Table 6.3: “Ethyl” mass balance for 8 m PZ with 0.3 mole CO₂ per mole alkalinity degraded at 165 °C for 20 weeks (TE44)

	Conc. mmol/kg	Ethyl Balance	
		Ethyl Conc. mmol/kg	Lost Ethyl %
PZ Lost in 20 weeks	1729	3458.1	-
CO ₂ Lost in 20 weeks	888	0	-
TOTAL Lost			
DEGRADATION PRODUCTS:			
N-Formyl PZ	557	1115	32.2
NH ₄ ⁺	496	0	-
AEP	118	355	10.3
2-Imid	109	109	3.2
HEP	61	184	5.3
1-EPZ	54	163	4.7
EDA	53	53	1.5
1-MPZ	21	51	1.5
Formate	108	0	-
Total Acetate	36	36	1.0
TOTAL		2065	59.7

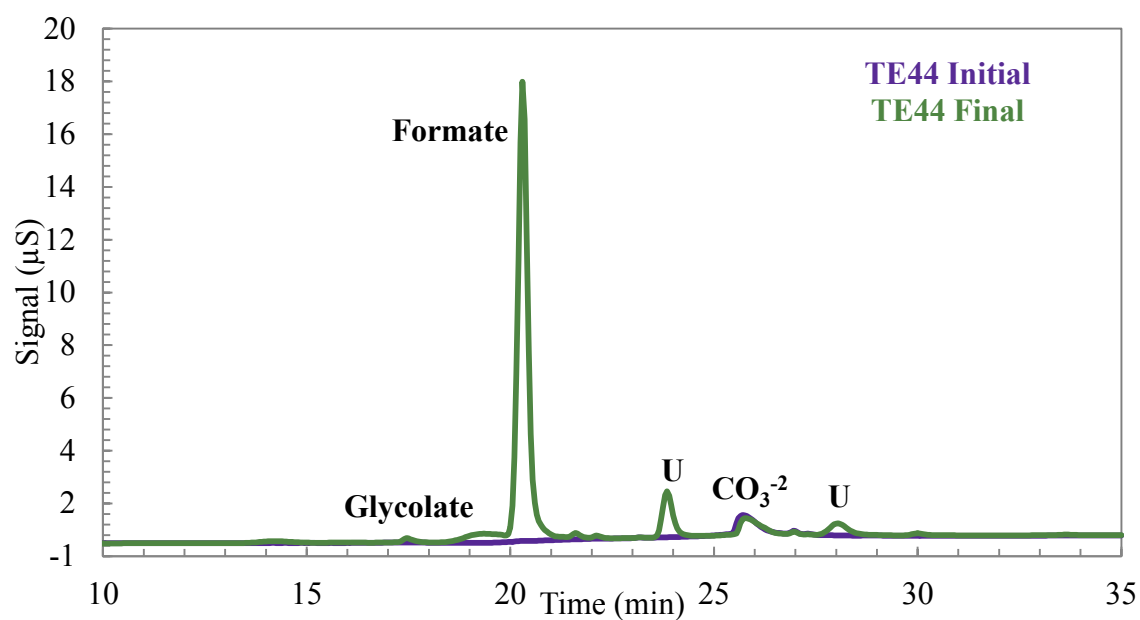


Figure 6.10: Anion IC chromatogram of initial and final sample of 8 m PZ with 0.3 mole CO_2 per mole alkalinity degraded at 165 °C (TE44)

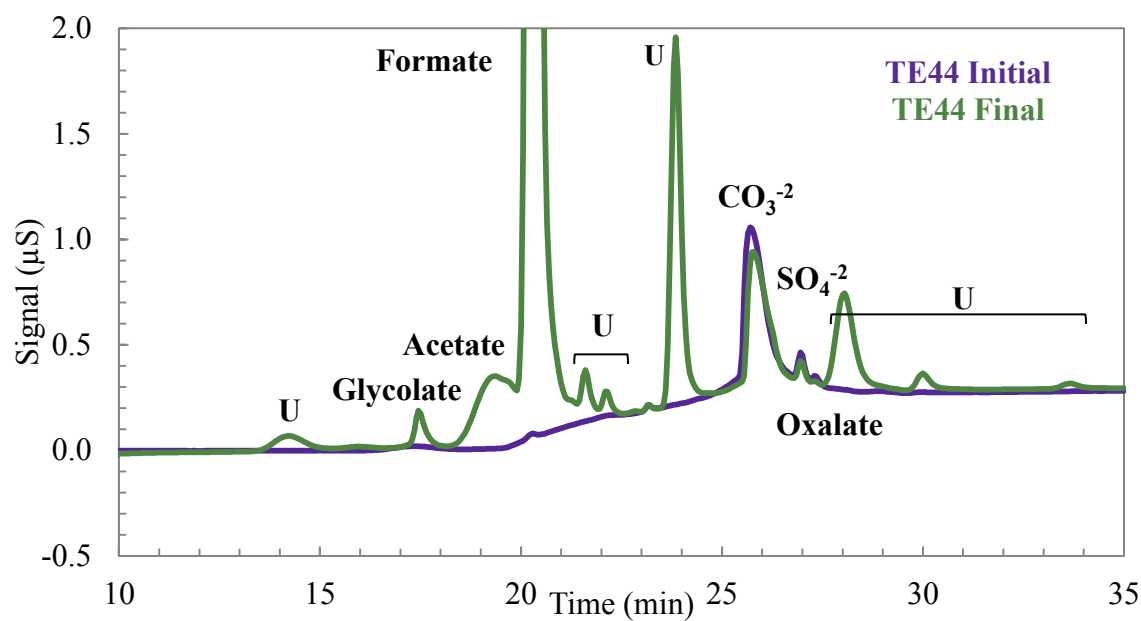


Figure 6.11: Anion IC chromatogram of initial and final sample of 8 m PZ with 0.3 mole CO_2 per mole alkalinity degraded at 165 °C with magnified signal (TE44)

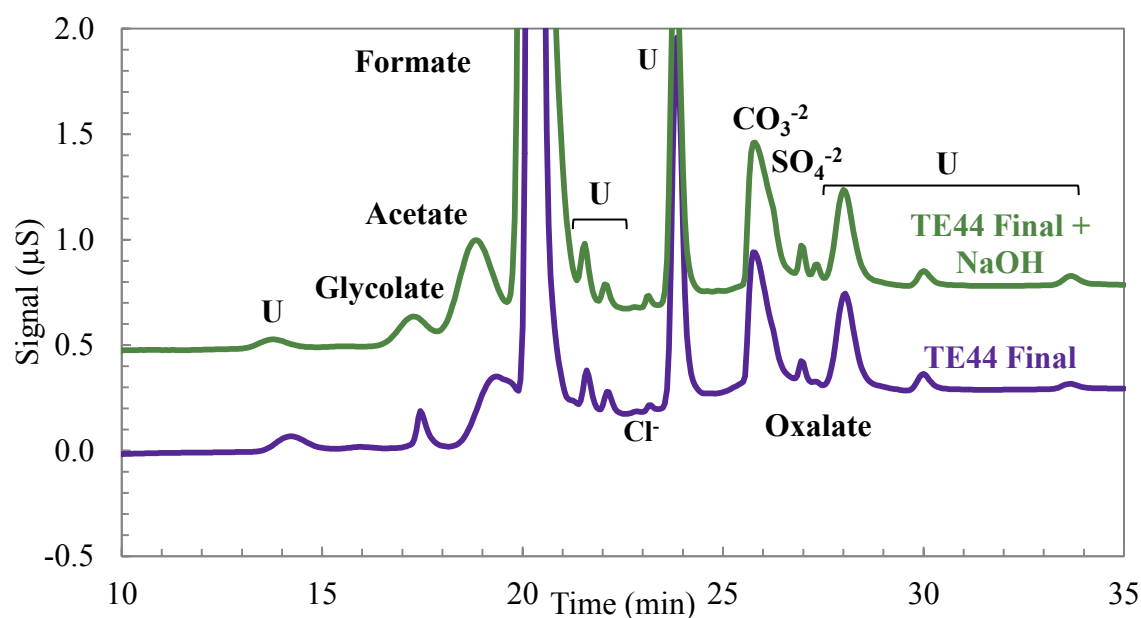


Figure 6.12: Anion IC chromatogram of original and NaOH treated final sample of 8 m PZ with 0.3 mole CO₂ per mole alkalinity degraded at 165 °C with magnified signal (Signal offset of 0.5 μS) (TE44)

There were also unidentified peaks on the Cation IC. The chromatogram for the final sample after 20 weeks of thermal degradation is shown in with a magnified signal in Figure 6.13. There were 5 major peaks at retention times of 18.0, 39.7, 42.0, 42.5, and 43.3 minutes that have yet to be positively identified and quantified. Suspected identities of these peaks are discussed in the following section. A comparison of the cation IC chromatograms for the original and NaOH treated final sample is made in Figure 6.14. The peak for N-formyl PZ is the only peak to disappear between the chromatograms indicating that none of the major unidentified peaks are also amides.

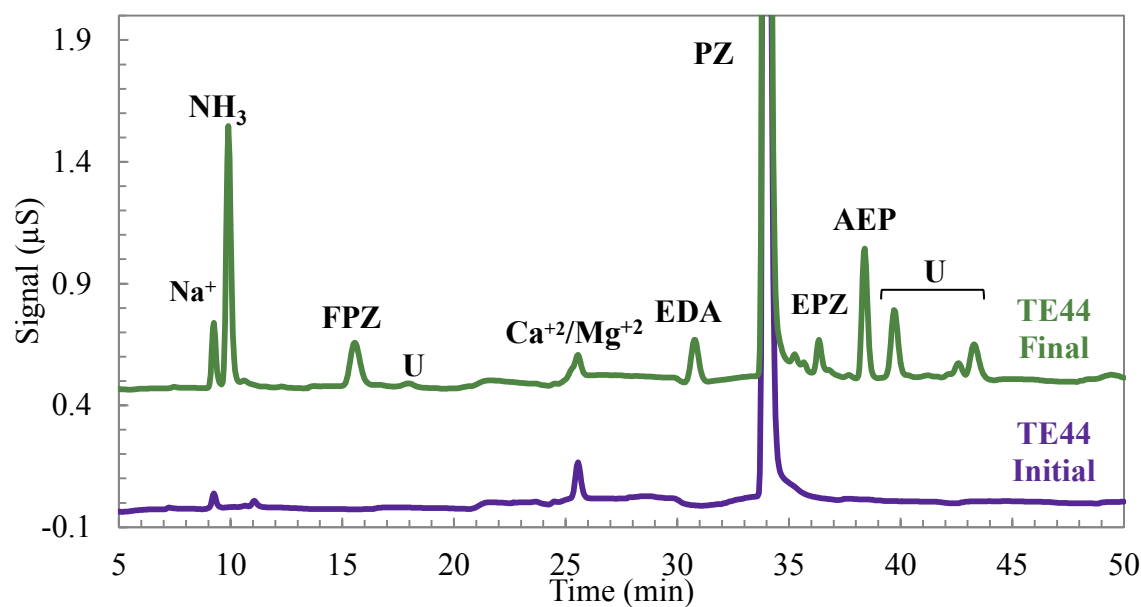


Figure 6.13: Cation IC chromatogram of the initial and final sample of 8 m PZ with 0.3 mole CO_2 per mole alkalinity degraded at 165 °C with magnified signal (Signal offset 0.5 μS) (TE44)

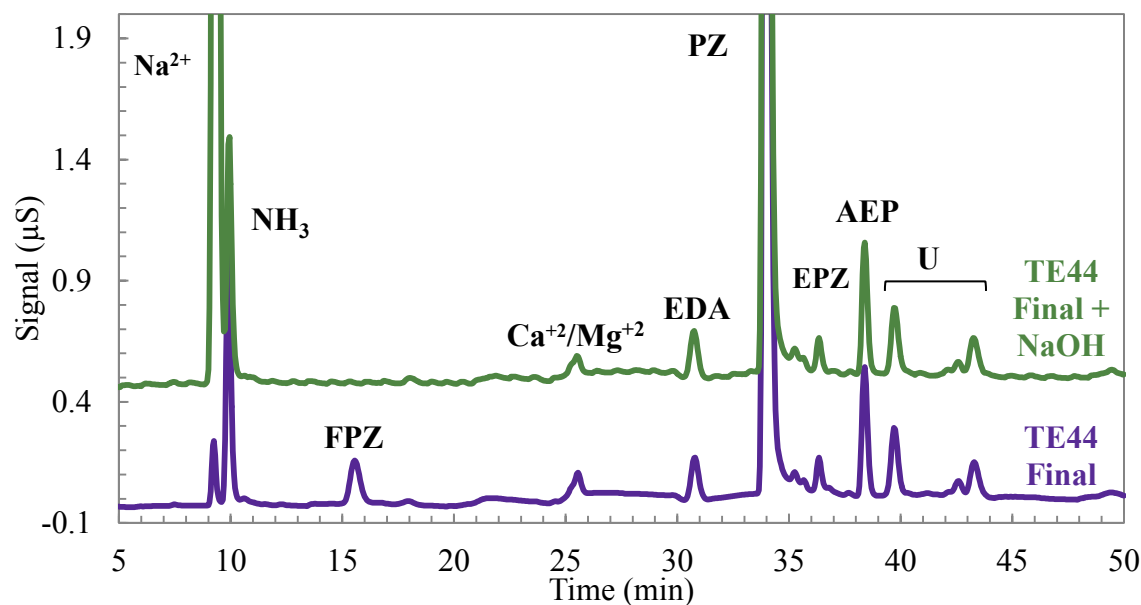


Figure 6.14: Cation IC chromatogram of original and NaOH treated final sample of 8 m PZ with 0.3 mole CO_2 per mole alkalinity degraded at 165 °C with magnified signal (Signal offset 0.5 μS) (TE44)

Finally, the HPLC also revealed multiple unidentified peaks that could correspond to major degradation products of PZ thermal degradation, as demonstrated in Figure 6.15. The only peak that was positively identified was 2-Imidazolidone (2-Imid), as labeled. The large peak between 16.5 and 22 minutes is an artifact of this particular run and did not occur in typical thermally degraded PZ samples. There are at least 8 significant, unidentified peaks but the relative importance in terms of concentration is not known due to possible differences in the response factor of each molecule with UV detection.

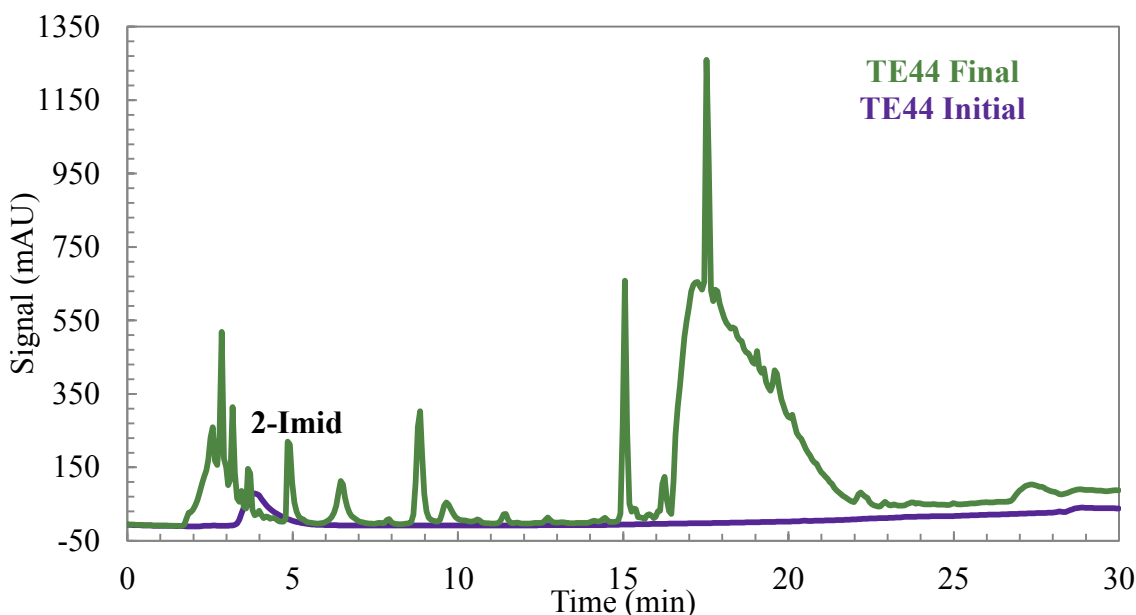


Figure 6.15: HPLC chromatogram of final sample of 8 m PZ with 0.3 mole CO₂ per mole alkalinity degraded at 165 °C (TE44)

6.2.5 Suspected thermal degradation products

The degradation products discussed in the previous sections have all been confirmed using commercially available standards and in the case of cations, confirmed with cation IC coupled with mass spectroscopy (IC-MS). An additional set of products have been suspected based on IC-MS or GC-MS results, but cannot be fully identified

due to a lack of a commercially available standard. Finally, a third category of molecules are suspected based on supposed mechanisms or other conjectures. In this project, no peak assignments were made without a positive match with a commercial standard, even if a GC-MS library match existed.

A number of molecules were unsuccessfully screened in an attempt to match unidentified peaks. Some molecules, such as 2-piperazinone, were screened on numerous analytical techniques to see if any response was registered. In a discussion of unknowns in regards to peak assignments, it is important to list what has been eliminated. All of these were tested as standards without alkaline reversal. For the anion analysis, common anions were screened to eliminate possible contamination. The anions screened included carbonate, bicarbonate, phosphate, thiosulfate, sulfite, persulfate, fluoride, iodine, iodate, bromide, bromate, metavanadate, permanganate, and borate. For cation IC, diethanolamine (DEA), methyldiethanolamine (MDEA), triethanolamine (TEA), dimethylaminoethanol (DMAE), methylaminoethanol (MAE), monoethanolamine (MEA), N,N'-bis(2-hydroxyethyl)piperazine (bHEP), diethylenetriamine (DETA), N,N'-diethylpiperazine (DEPZ), N-(2-Hydroxyethyl)-N'-methylpiperazine (HEMP), N-(2-aminoethyl)-N'-methylpiperazine (AEMP), N-(2-Hydroxyethyl)ethylenediamine (HEEDA), N,N'-diformylpiperazine (DFPZ), N-acetylpiperazine (AcPZ), 2-piperazinone, 2,5-piperazinedione, 2-imidazolidone (2-Imid), 2-methyl-2-imidazolidone, pyrazine, and N-(2-aminoethyl)glycine (AEG) were among those compounds tested as standards but not found as peaks in thermal degraded PZ.

6.2.5.1 Molecules identified through MS techniques

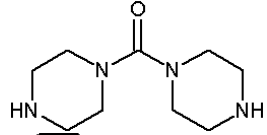
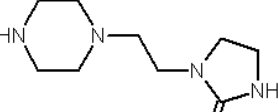
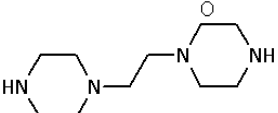
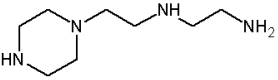
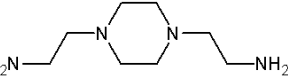
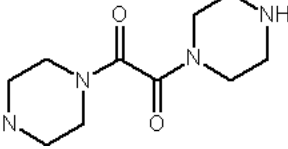
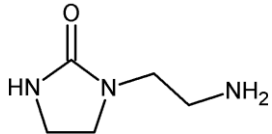
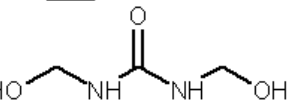
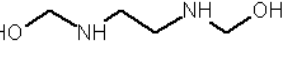
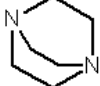
In this section, molecules that are suspected based on results from IC-MS and GC-MS techniques are discussed in terms of their possible contribution to the thermal

degradation mixture. LC-MS analyses were not successful at identifying any unique molecules. All of the molecules suspected, as discussed below, are shown with their structure and pertinent data in Table 6.4. An example of IC-MS analysis for a thermally degraded sample is shown in Appendix G. The technique used for each suspected molecule is specified in the last column and refer to either IC-MS with chromatographic separation in single quad mode with electrospray ionization (IC), GC-MS with chromatographic separation on a semi-polar column with electron ionization (GC), GC-MS with chromatographic separation, chemical ionization, and high resolution mass readings (HRGC). No results were obtained using direct injection into an MS in this project.

The most important unknown cation peaks are those at retention times of 39.7 and 43.3 minutes, as demonstrated in the magnified chromatogram shown in Figure 6.16 below. The first peak at 39.7 is suspected to be 1,1'-carbonyl-bis-piperazine (diPZ urea; CAS 17159-16-9) or 1-[2-(piperazinyl)ethyl]-2-imidazolidinone (the urea of AEAEPZ; CAS 104087-61-8). The IC-MS results indicated a molecule with a molecular weight of 198.2 grams per mole (m/z 199.2) which could be either of these molecules. Both are ureas and are suspected because of the known reaction of CO_2 with amines to create imidazolidones or oxazolidones as part of degradation pathways in other amines. There is also an abundance of PZ and CO_2 in solution due to the high PZ concentration and CO_2 loading in most solutions. Both of these ureas have two active amino functions that will respond in the diamine region of the cation. The results of acidified PZ experiments discussed in section 6.3 shed light on the identity of this peak and the urea of AEAEPZ is more likely. Pharmacological studies have investigated molecules with AEAEPZ side chains that react to form a side chain of AEAEPZ urea in the presence of urea and heat,

similar to the high temperature reactions in the presence of CO₂ studied in this project, so this product is highly likely (Bøgesø et al., 1988).

Table 6.4: Molecules identified with various MS-based techniques for thermally degraded concentrated PZ

Name	Abb.	Structure	CAS No.	MW (g/mol)	Basis*
1,1'-carbonylbis-piperazine	diPZ urea		17159-16-9	198.2654	HRGC
1-[2-(piperazinyl)ethyl]-2-imidazolidinone	AEAEPZ Urea		104087-61-8	198.2654	IC
1,1'-(1,2-ethanediyl)bis-piperazine	PEP		19479-83-5	198.3085	HRGC
1-[2-[(2-aminoethyl)amino]ethyl] piperazine	AEAEPZ		24028-46-4	172.2736	IC
N,N'-di(2-aminoethyl) piperazine	DAEP		6531-38-0	172.2736	IC
1,1'-(1,2-dioxo-1,2-ethanediyl)bis-piperazine			105807-56-5	226.28	IC
1-(2-Aminoethyl)-2-imidazolidone	AEI		6281-42-1	129.16	IC
1,3-bis(N-hydroxymethyl) urea			140-95-4	120.11	IC
N,N'-di(2-hydroxymethyl) EDA			70495-38-4	120.15	IC
Triethylenediamine	TEDA		280-57-9	112.17	GC

*IC = Ion chromatography separation coupled with mass spectroscopy; GC = gas chromatography separation coupled with mass spectroscopy; HRGC = High Resolution GC-MS

Another molecule that shares this molecular weight (198.2 gram per mole) is 1,1'-(1,2-ethanediyl)bis-PZ (PEP; CAS 19479-83-5), a polymeric quadramine of two PZ molecules. High resolution GC-MS analysis of thermally degraded 8 m PZ confirmed that the molecular weight for this molecule (198.3085 gram per mole) or an isomer and either of the other two molecules (diPZ urea and AEAEPZ; both 198.2654 gram per mole) are present in degraded solution. It is not expected that this molecule is present in any significant concentration.

The small peak at 42.0 minutes was found to have a molecular weight of 172.2 grams per mole (m/z 173.2) and likely corresponds to 1-[2-[(2-aminoethyl) amino]ethyl] PZ (AEAEPZ; CAS 24028-46-4). In loaded PZ degradation, this peak is minor, but is prominent in acidified PZ degradation and is discussed further in section 6.3. Another suspected degradation product with that molecular weight is N,N'-di(2-aminoethyl) piperazine (DAEP; CAS 6531-38-0) which was suspected in the degradation of AEP, but a standard was not available. In solution, a small concentration of this molecule is expected through S_N2 arm switching mechanism, similar to those discussed in section 7.3.1, but not at any great concentration.

The larger peak at 43.3 minutes was found to have strong signals corresponding to molecular weights of 99.2 and 198.2 grams per mole (m/z 100.2 and 198.2) and a weaker signal indicating a molecular weight of 226.2 grams per mole (m/z 227.2) on the IC-MS analysis. A molecular weight of 198.2 grams per mole could indicate any of the three molecules described above with this molecular weight (AEAEPZ, diPZ urea, or PEP). Given the retention time of the molecule, the best candidate is PEP, a quadramine. AEAEPZ has already been assigned as the most likely candidate for the peak at 39.7 minutes and the diPZ urea would respond as a diamine on the cation. The trace of a 226.2 gram per mole could correspond to 1,1'-(1,2-dioxo-1,2-ethanediyl)bis PZ (CAS:

105807-56-5), which is the oxalyl diPZ amide, although this would be expected to elude as a diamine, usually before this peak retention time. A good candidate for the mass of 99.2 gram per mole that co-elutes is not known.

The peak at 18.0 minutes was found to have a molecular weight of 129.2 gram per mole (m/z 130.2), according to IC-MS, and elutes in the region of monoamines. The peak grows with time, indicating it is a degradation product but not an amide. It was found that this peak corresponds to 1-(2-aminoethyl)-2-imidazolidone (AEI; CAS 6281-42-1), the internal amide of DETA. Despite being a triamine, the urea function makes only the terminal amino function responsive to cation IC and it should elute in this region of the chromatogram. This peak was identified, but not quantified for any experiment.

Finally, the peak at 42.5 minutes was determined to have a molecular weight of 120.7 grams per mole (m/z 121.7) on IC-MS. This does not correspond to any strong candidates for likely degradation products. The molecular weight matches N,N'-di(2-hydroxymethyl) EDA (CAS 70495-38-4) and N,N'-bis(2-hydroxymethyl) urea (CAS 140-95-5), but neither of these are strongly suspected.

Triethylenediamine (TEDA) is a molecule is suspected to be present based on proposed reactions and was identified with low resolution GC-MS with library matching of a thermally degraded PZ sample. TEDA elutes just after 1-EPZ on the IC-MS, but was not matched to any major peaks. It is suspected that TEDA is being produced and may react to other related forms, such as 1-piperazineacetic acid (1-PA), as is discussed in the next section.

High resolution MS of thermally degraded PZ also found peaks corresponding to N,N'-diformylpiperazine (DFPZ, CAS 4164-39-0), a molecular formulas of $C_7H_{14}N_2O$, and a molecular formula of $C_9H_{19}N_3O$. These molecular formulas to not match any suspected products and are not present in large concentrations. Standard (low resolution)

GC-MS analysis of thermally degraded 8 m PZ confirmed the presence of AEP, FPZ, and 1-MPZ through library matching. The same data also suggested TEDA, 2-methyl piperazine (2-MPZ), 2,5-dimethyl piperazine, and tetraethylenepentamine (TEPA, CAS 112-57-2), but only TEDA is believed to be a potentially important product based on the proposed mechanisms.

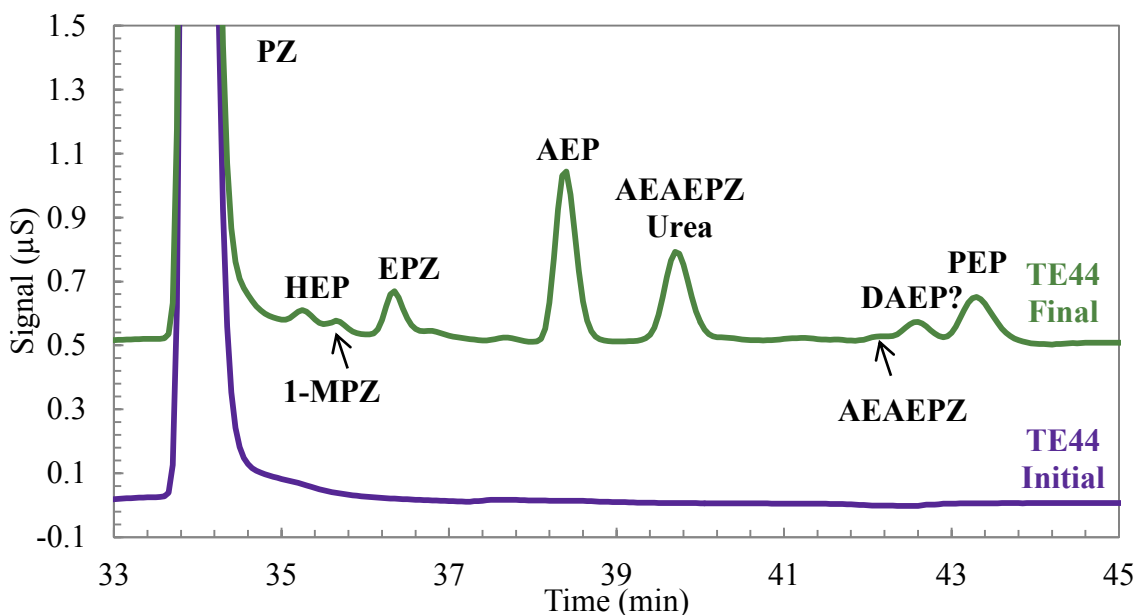


Figure 6.16: Cation IC chromatogram of initial and final sample of 8 m PZ with 0.3 mole CO₂ per mole alkalinity degraded at 165 °C with magnified signal (Signal offset 0.5 μS) (TE44)

6.2.5.2 Relative abundance of suspected products

For the unknown peaks that have suspected identities, the relative abundance of each can be approximated by analyzing the peak area from the cation IC chromatograms. The molecules tentatively assigned to the important unquantified peaks are the urea of AEAEPZ, AEAEPZ, PEP, and DAEP, although the assignment of DAEP is the least confident. The area of each unknown peak is compared to the peak area of AEP, a prominent degradation product, in Figure 6.17. This comparison should provide the

relative importance of each peak and give an idea as to the impact of the unknown molecules on the mass balances. It is important to note that molecules can have varying response factors during chromatography, so for the same concentration, peaks areas could be significantly different. This analysis does not attempt to predict the response factors of each molecule, but assume they are similar to the response factor of AEP to allow a relative comparison. This assumption could be disproven by running standards of each molecule to allow direct calibration and quantification of each molecule.

The urea of AEAEPZ is a prominent degradation product that appears with a larger peak area, and therefore larger assumed concentration than AEP. This molecule is expected to have a large impact on the mass balance based on relative peak area and the size of the molecule, which includes nine carbons and four nitrogens. The PEP peak area is very similar to the AEP peak area throughout the experiment indicating this may also be significant to the mass balance due to the importance of AEP to the mass balance. The concentration of AEAEPZ remains low throughout the experiment as it is suspected to react quickly with CO₂ to form its internal urea. The peak assigned to DAEP, if that is correct, is generated at low concentrations after an initial lag in production. This peak represents a product that is generated after initial degradation mechanisms by second order processes.

6.2.5.3 Other molecules suspected based on reactions

Additional reaction products are suspected to be formed during thermal degradation despite a lack of analytical evidence of their presence. These suspected molecules are summarized in Figure 6.18. Formaldehyde and other reactive aldehydes such as acetaldehyde or hydroxyethylacetaldehyde are suspected to be present and active

in the thermal degradation of concentrated PZ. A colorimetric approach to quantify aldehydes in thermally degraded PZ was attempted without success (Fregert et al., 1984).

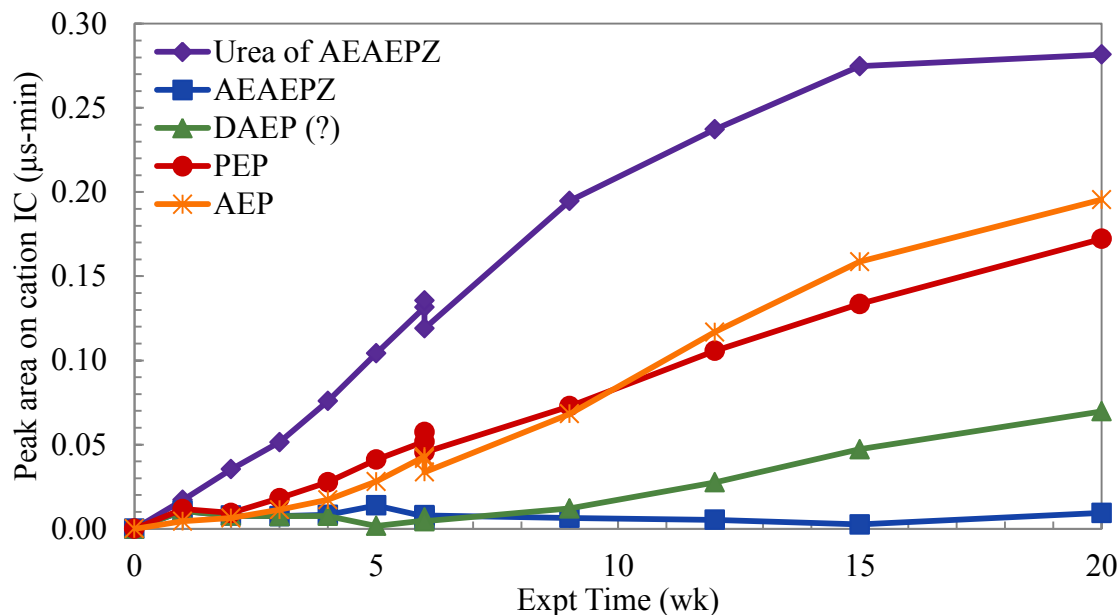


Figure 6.17: Relative abundance of suspected degradation products in the thermal degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 165 °C (TE44)

A variety of oxidized forms of PZ are suspected because of the formate generation mechanism. In some way, CO₂ is reduced to formate or formyl species and it is believed that another molecule must be oxidized at the same time in a redox-type reaction scheme. Possible oxidized forms of PZ or substituted PZ include 1-PA, the ketone form of TEDA, the enamine form of TEDA, or the hemiaminal (carbinolamine) form of TEDA, which is the hydrated form of the enamine. If 1-PA is produced, it is also possible to imagine two amide forms of that molecule, 1,4-Diazabicyclo[2.2.2]octan-2-one and 1-(1-Piperazinylacetyl)-piperazine. The discussion of oxidized products in Chapter 8 can be extended to thermal degradation because of the suspected redox reaction responsible for formate and formyl amide production.

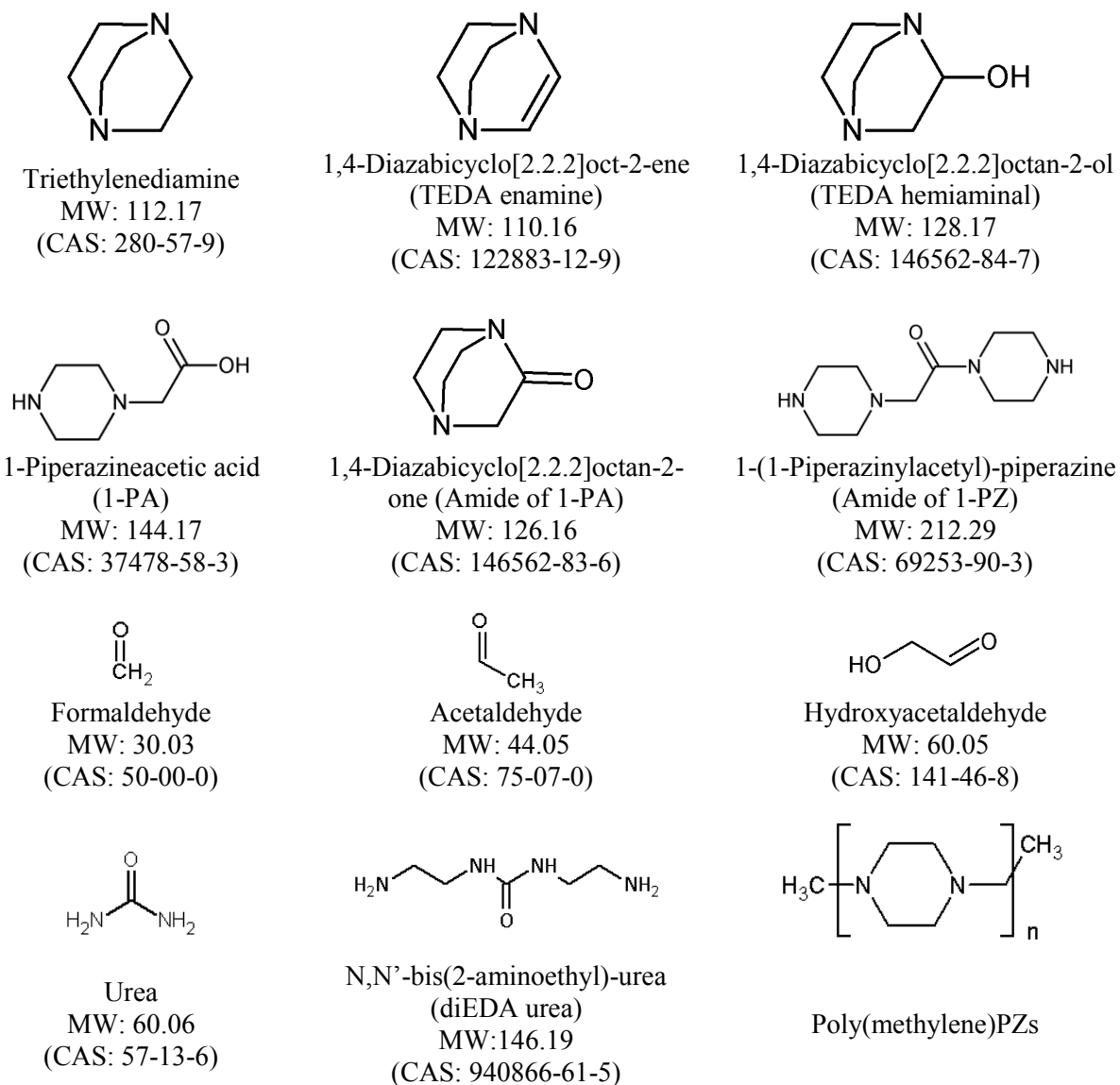


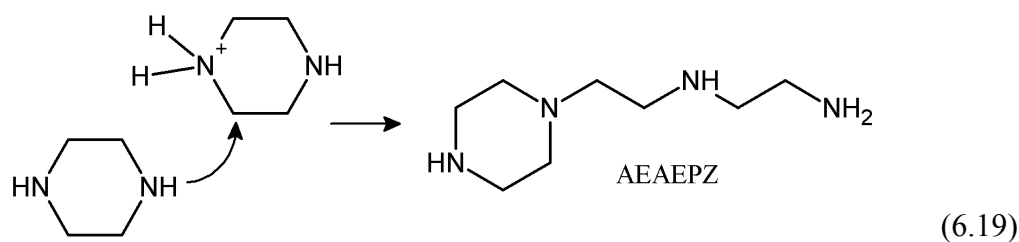
Figure 6.18: Structures of other suspected thermal degradation products

The presence of CO₂ and quantified production of 2-Imid indicate that other ureas are likely being created in solution. Simple urea (the urea of ammonia), PZ urea structures, or additional EDA urea structures are possible since there is a significant concentration of CO₂ left in solution after degradation.

Polymeric PZ structures are also suspected to be formed during thermal degradation of concentrated PZ. If formaldehyde is present, as believed, PZ and formaldehyde can react and form polymerized PZ products through condensation reactions (Iovu et al., 1994; Sandler and Delgado, 1969). Sandler and Delgado found that changing the ratio of formaldehyde to PZ could produce either polymethylene PZs or N,N'-(2-hydroxymethyl) PZ in water (Sandler and Delgado, 1969). Later research suggested that PZ and formaldehyde polymerization was catalyzed by metals such as complexes of nickel and other amines, which is pertinent since thermal degradation experiments were performed in stainless steel cylinders where iron (II), chromium (III), and nickel (II) are expected to be present due to mild corrosion (Ukrainsev and Krasnov, 1997).

6.3 ROLE OF H^+PZ AS AN ACTIVE SPECIES

Concentrated, loaded PZ solutions contain numerous species that could participate in thermal degradation reactions over a range of CO_2 loadings. Protonated PZ (H^+PZ) and PZ carbamate ($PZCOO^-$) are created from the initial reaction of PZ with CO_2 . A series of experiments were performed in order to determine if H^+PZ or $PZCOO^-$ is the active species for degradation. It is hypothesized, and shown in section 6.1 above, that H^+PZ plays an important role in the initial thermal degradation pathways. When PZ is protonated, the α -carbon is subject to attack by another nucleophilic PZ, creating ring-opening products. The suspected reaction is shown below in Equation 6.19. Other products are possible through a similar reaction or series of reactions where the α -carbon next to a protonated amino function is subject to attack by any nucleophile in solutions.



To test the behavior of H^+PZ , concentrated PZ in the absence of CO_2 was acidified to generate H^+PZ and then degraded under standard conditions. The goal was to examine H^+PZ degradation in the absence of any CO_2 -containing species such as PZCOO^- , H^+PZOO^- , or $\text{PZ}(\text{COO}^-)_2$. Experiments exploring the effects of temperature, PZ concentration, and acid concentration were performed. Oppositely, to test the behavior of PZCOO^- , concentrated PZ was spiked with KHCO_3 to generate PZCOO^- in the absence of H^+PZ and then degraded under standard conditions.

6.3.1 Thermal degradation of acidified, concentrated PZ

The baseline experiment for acidified PZ was 8 m PZ with 0.3 mole H^+ per mole alkalinity degraded at 175°C . This H^+ concentration was chosen to mimic the concentration of H^+PZ in 8 m PZ with CO_2 loading of 0.3 moles CO_2 per mole alkalinity is used. The experimental design assumed that loading created the same concentration of H^+PZ and PZCOO^- at this lean loading. Modeling of the system shows that this assumption is valid, as there is only slightly more H^+PZ than PZCOO^- at this CO_2 loading because PZCOO^- is beginning to react to form H^+PZCOO^- (Frailie and Rochelle, 2011).

The PZ loss and generation of total formate and EDA are compared in Figure 6.19, Figure 6.20, and Figure 6.21, respectively, for 8 m PZ with 0.3 moles CO_2 or H^+ mole per alkalinity degraded at 175°C . In the acidified experiment, PZ loss is decreased to only 34% of the initial PZ compared to 68% in the loaded experiment after 15 weeks. CO_2 is known catalyst for thermal degradation (section 5.3.3), and these results indicate

that degradation can occur in the absence of CO₂ with H⁺PZ present. H⁺PZ is, therefore, an active species for thermal degradation and may initiate the first mechanisms for PZ thermal degradation. Degradation in loaded PZ solutions is likely a combination of the initiating action of H⁺PZ and the reaction of CO₂-containing species with the products of H⁺PZ initiated reactions.

The production of total formate and EDA in acidified solutions indicates the importance of CO₂ in degradation product generation. Negligible concentrations of formate were produced in the absence of CO₂ while EDA concentrations were higher than loaded solutions. As discussed in the next section, formate is generated directly from CO₂ or CO₂-containing species during thermal degradation and in the acidified experiments, no CO₂ was available to be reduced to formate. During loaded degradation of PZ, EDA is generated through initial degradation mechanisms and then reacts with CO₂ to form 2-Imid. In the acidified experiments, no CO₂ is available to form 2-Imid so EDA accumulates and acquires larger concentrations, even with less overall degradation. EDA appears to have a slightly higher initial rate of generation in the presence of CO₂ which may indicate the fact that PZ degradation is occurring faster, or that the formate generation mechanism may help stimulate EDA generation in some way.

6.3.2 Effect of temperature, PZ concentration, and H⁺ concentration

The degradation of acidified PZ was investigated from 150 to 175 °C, 4 to 12 m PZ, and 0.2 to 0.6 mole H⁺ per mole alkalinity. These experiments were intended to determine if H⁺PZ initiated degradation in the absence of CO₂ responded similarly to changes in temperature, PZ concentration, and H⁺ concentration as CO₂-loaded degradation.

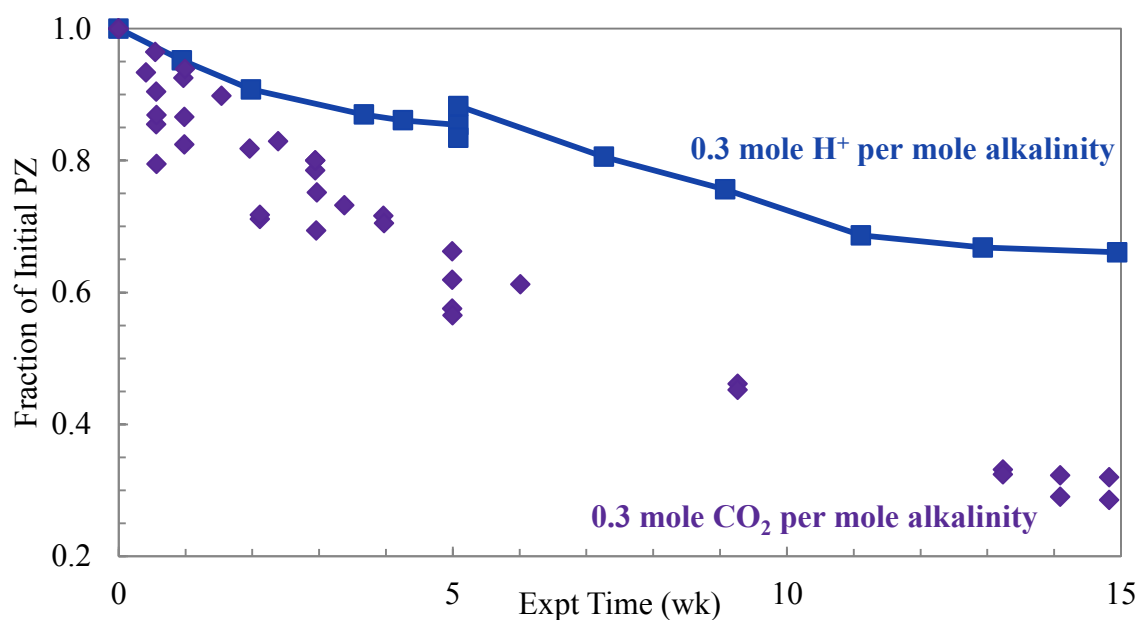


Figure 6.19: PZ loss in 8 m PZ at 175 °C with 0.3 mole CO₂ or H⁺ per mole alkalinity

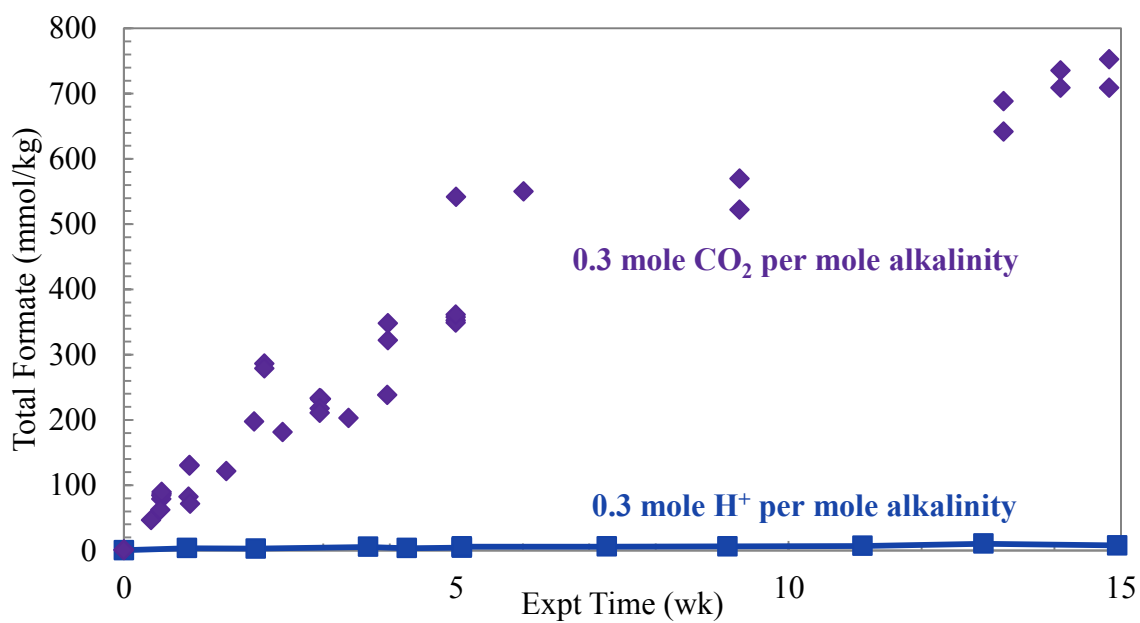


Figure 6.20: Generation of total formate in 8 m PZ at 175 °C with 0.3 mole CO₂ or H⁺ per mole alkalinity

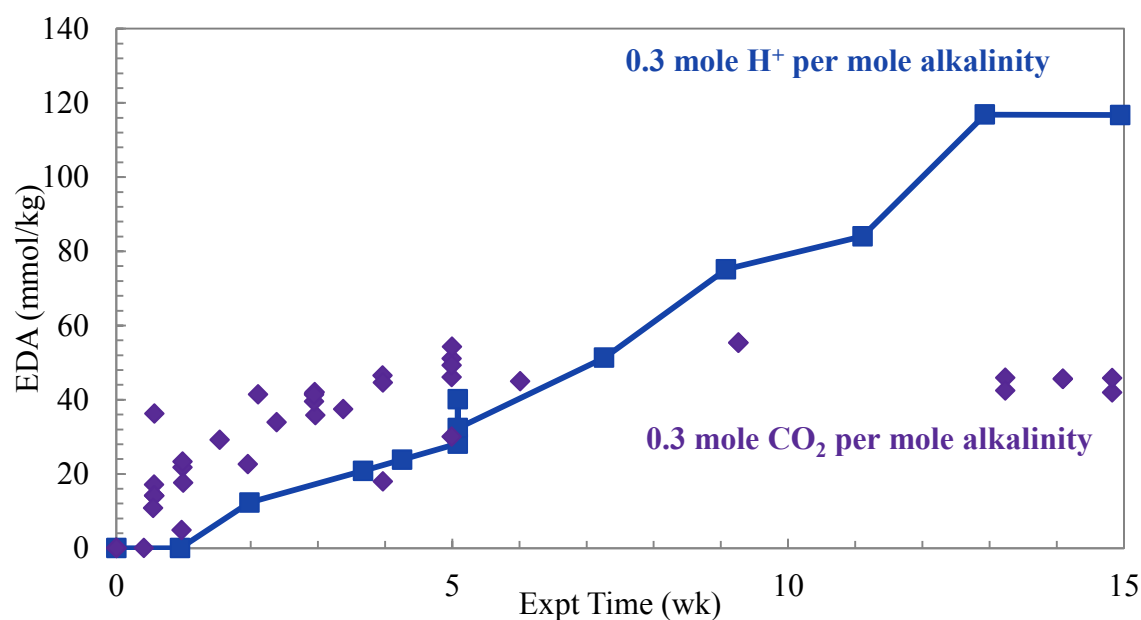


Figure 6.21: Generation of EDA in 8 m PZ at 175 °C with 0.3 mole CO₂ or H⁺ per mole alkalinity

6.3.2.1 Effect of temperature on acidified PZ degradation

The k_1 for PZ loss in acidified PZ is compared to loaded solutions over 150 to 175 °C in Figure 6.22. At each temperature, the CO₂-loaded solution degrades at least twice as fast as the acidified experiment. The production of EDA for the same six experiments is compared in Figure 6.23. The three CO₂-loaded experiments have larger initial rates of EDA generation due to enhanced rates of thermal degradation. As EDA accumulates, it reacts with CO₂ in these loaded cases to form 2-Imid and EDA reaches a maximum concentration. In the acidified experiments, the EDA is generated faster as temperature increases, as expected and accumulates as a final product of thermal degradation.

This observation of the acidified production of EDA can shed light on the suspected mechanisms involved. First, CO₂ is not required to make EDA. The presence of CO₂, however, may accelerate its production or just accelerates the overall thermal

degradation rate. This could indicate, for example, that EDA is more readily produced from the urea of AEAEPZ than from AEAEPZ itself. Secondly, there appears to be a slight delay in the production of EDA in the absence of CO₂, so the generation of EDA may be a second order reaction. There was not enough data at very short times in the loaded experiments to confirm that in EDA generation is a second order product in the presence of CO₂.

6.3.2.2 Effect of PZ concentration on acidified PZ degradation

The k_1 for PZ loss in acidified 4 to 12 m PZ is compared to loaded solutions from 150 to 175 °C in Figure 6.24. As with 8 m PZ, both 4 and 12 m PZ with 0.3 mole H⁺ per mole alkalinity degrade more than twice as slow as the loaded solutions. The PZ concentration behavior is similar for both CO₂-loaded and acidified solutions as the rates are slightly more than first order in PZ concentration. The production of EDA for the same six conditions at 175 °C is compared in Figure 6.25. As expected, the three loaded experiments have higher initial rates of EDA generation. In the acidified experiments, the EDA is generated at the same initial rate from 4 to 12 m PZ, while the experiments with CO₂ had increasing initial EDA production rates with increased PZ concentration. This indicates that the mechanism for EDA generation is rate limited by something other than PZ concentration because increasing the concentration of free PZ does not accelerate the EDA generation mechanism in the absence of CO₂.

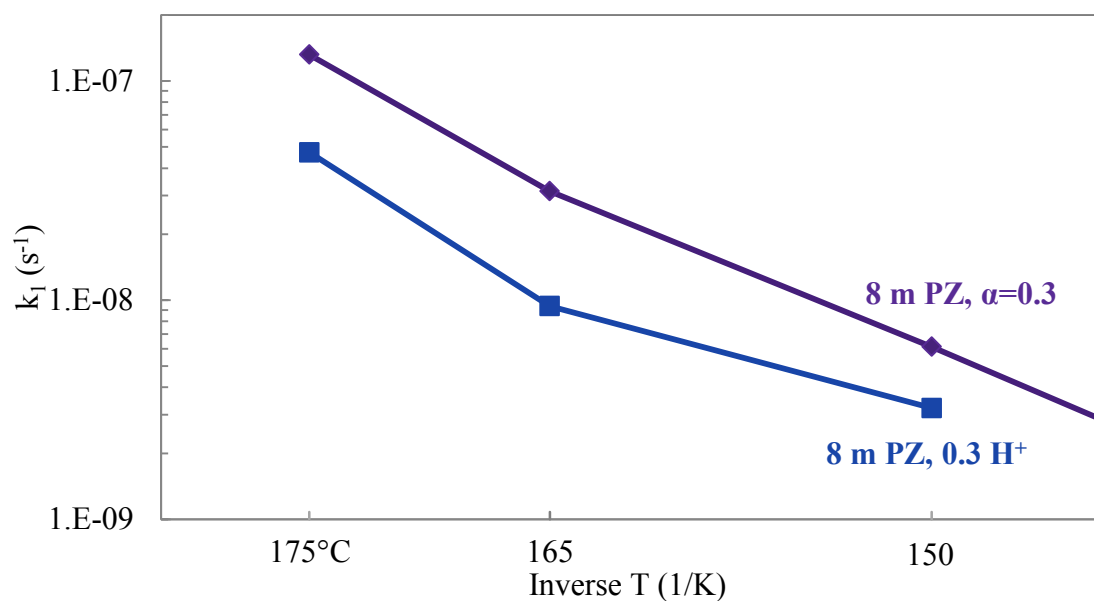


Figure 6.22: Comparison of k_1 values for PZ thermal degradation of acidified and loaded 8 m PZ

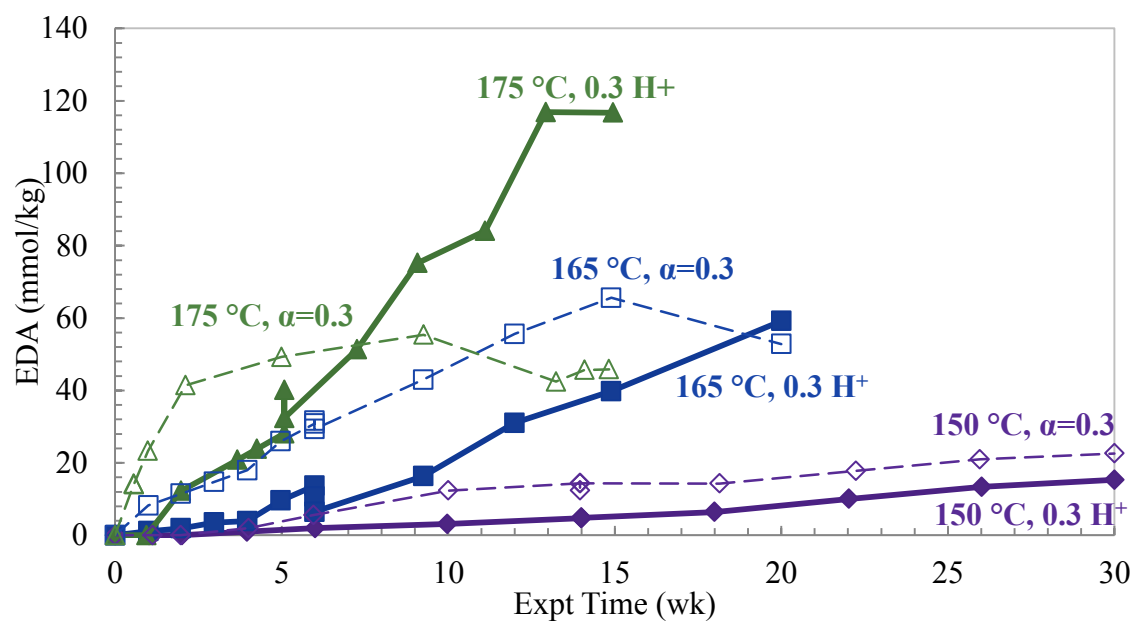


Figure 6.23: Generation of EDA for thermal degradation of 8 m PZ with 0.3 mole H⁺ (solid) or CO₂ (dashed) per mole alkalinity from 150 to 175 °C

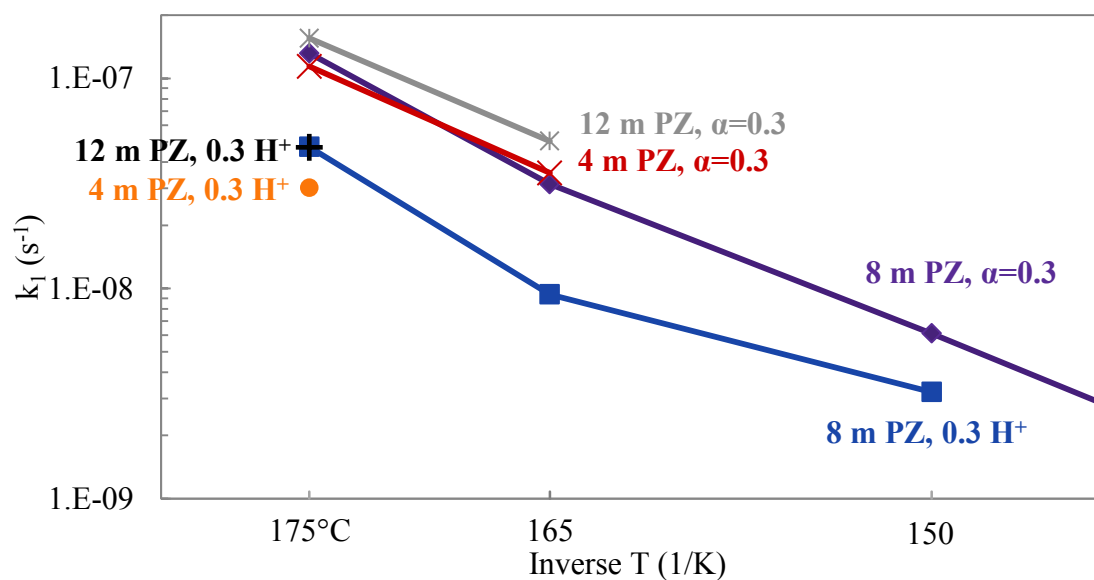


Figure 6.24: Comparison of k_1 values for thermal degradation of acidified and loaded 4 to 12 m PZ

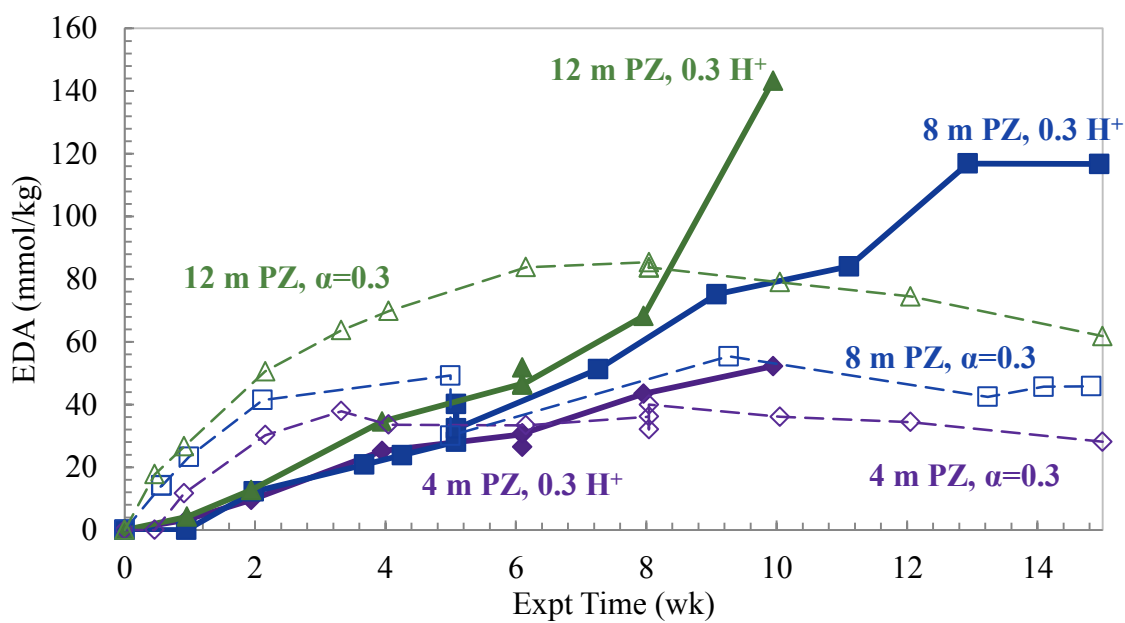


Figure 6.25: Generation of EDA for thermal degradation of 4 to 12 m PZ with 0.3 mole H⁺ (solid) or CO₂ (dashed) per mole alkalinity at 175 °C

6.3.2.3 Effect of H^+ concentration on acidified PZ degradation

Finally, the k_1 for PZ loss in 8 m PZ with 0.2 to 0.6 mole H^+ per mole alkalinity and 0.3 mole CO_2 per mole alkalinity are compared in Figure 6.26. Both concentrations of 0.2 and 0.6 mole H^+ per mole alkalinity decreased PZ loss compared with 0.3 mole H^+ per mole alkalinity. A maximum in PZ loss was also observed in loaded experiments and the acidified data appear to mimic that behavior. The production of EDA for the same three H^+ concentrations at 175 °C is compared in Figure 6.27. Interestingly, the generation of EDA proceeds at the same initial rate in the presence of all three H^+ concentrations, indicating that the EDA generation mechanism is not directly dependent on the concentration of H^+PZ in solution.

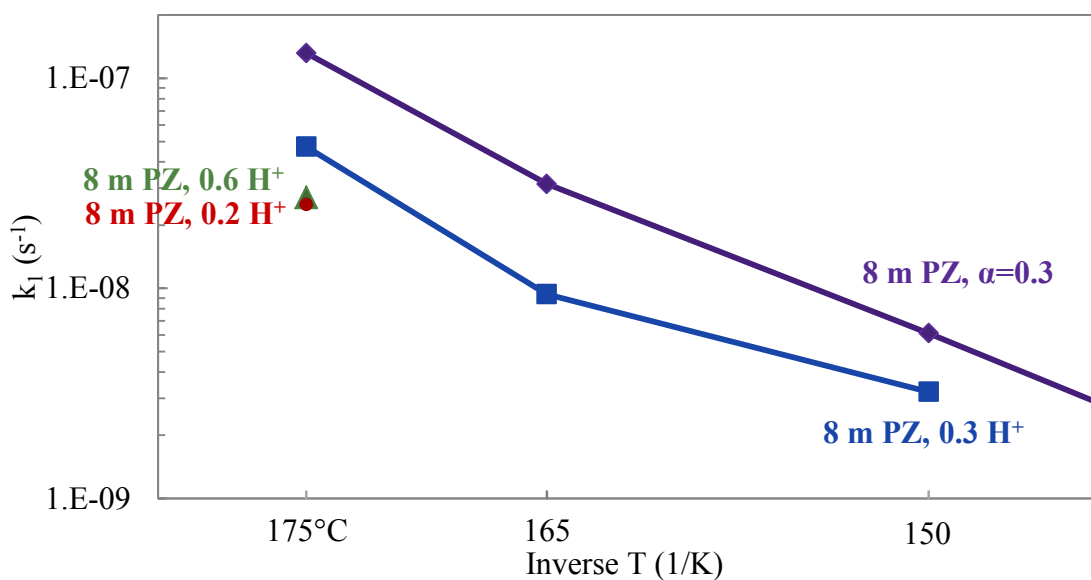


Figure 6.26: Comparison of k_1 values for thermal degradation of 8 m PZ with 0.2 to 0.6 mole H^+ or 0.3 mole CO_2 per mole alkalinity

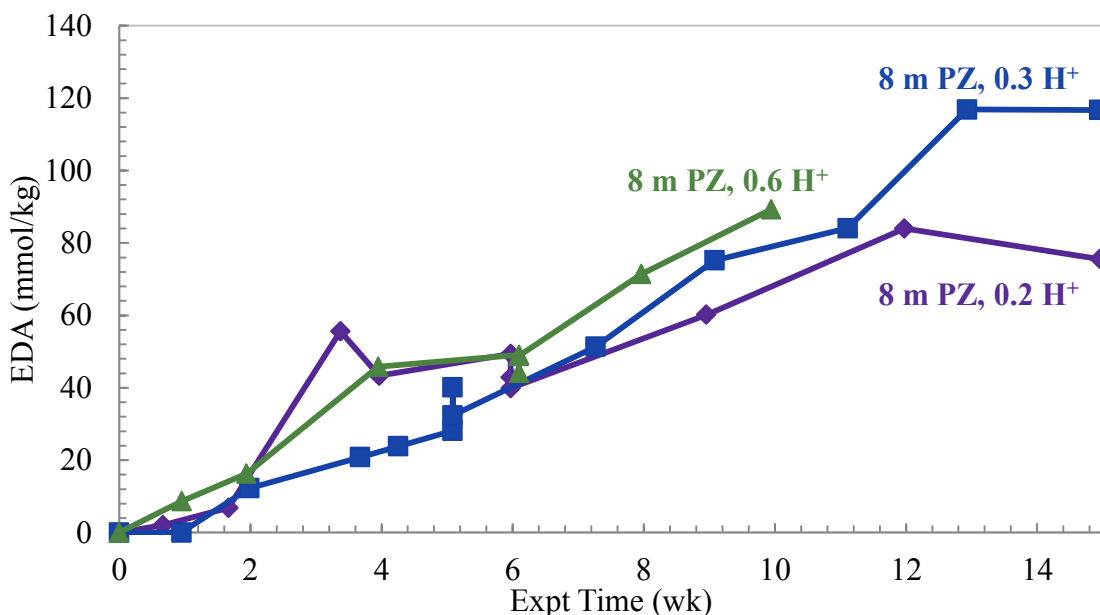


Figure 6.27: Generation of EDA for thermal degradation of 8 m PZ with 0.2 to 0.6 mole H⁺ per mole alkalinity at 175 °C

6.3.3 Thermal degradation of PZ with KHCO₃

A solution of 8 m PZ with 0.1 mole KHCO₃⁻ per mole alkalinity was degraded at 175 °C in an effort to determine if degradation would occur in the absence of H⁺PZ. It was assumed that the present of KHCO₃⁻ would react to create PZ carbamate (PZCOO⁻) and other CO₂-containing molecules without significant concentrations of H⁺PZ. The PZ loss in this experiment is compared to the complementary loaded experiment (0.1 mole CO₂ per mole alkalinity) in Figure 6.28. The generation of formate and EDA in these two experiments is compared in Figure 6.29. The absence of H⁺PZ severely limits overall degradation of PZ and generation of both formate and EDA compared to a loaded solution. H⁺PZ is a crucial species in the degradation mechanisms for PZ.

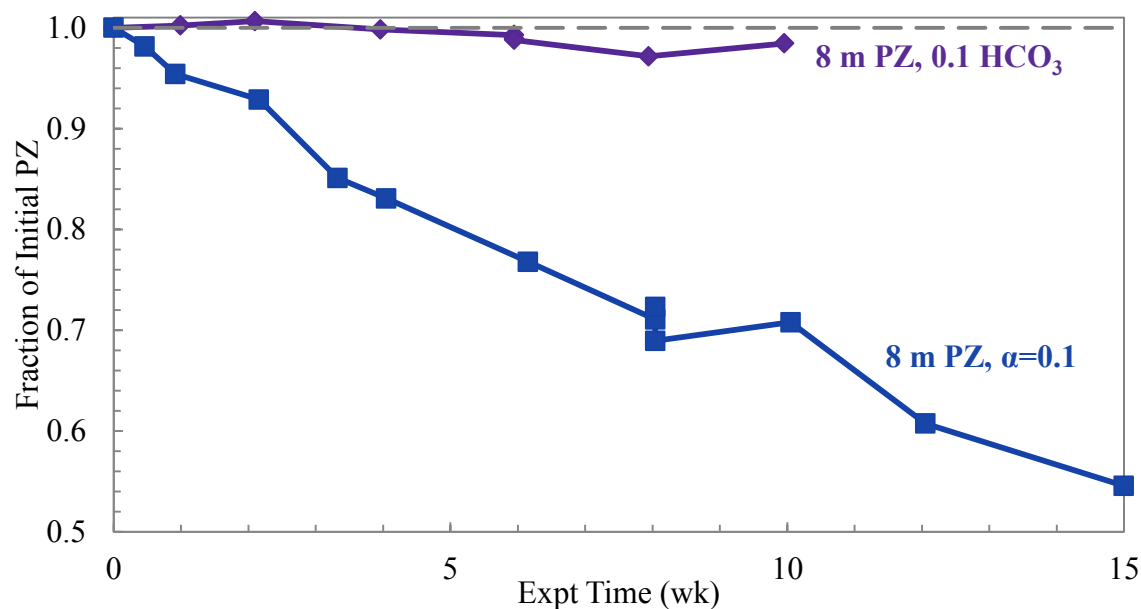


Figure 6.28: PZ Loss for thermal degradation of 8 m PZ with 0.1 mole CO₂ or KHCO₃⁻ per mole alkalinity at 175 °C

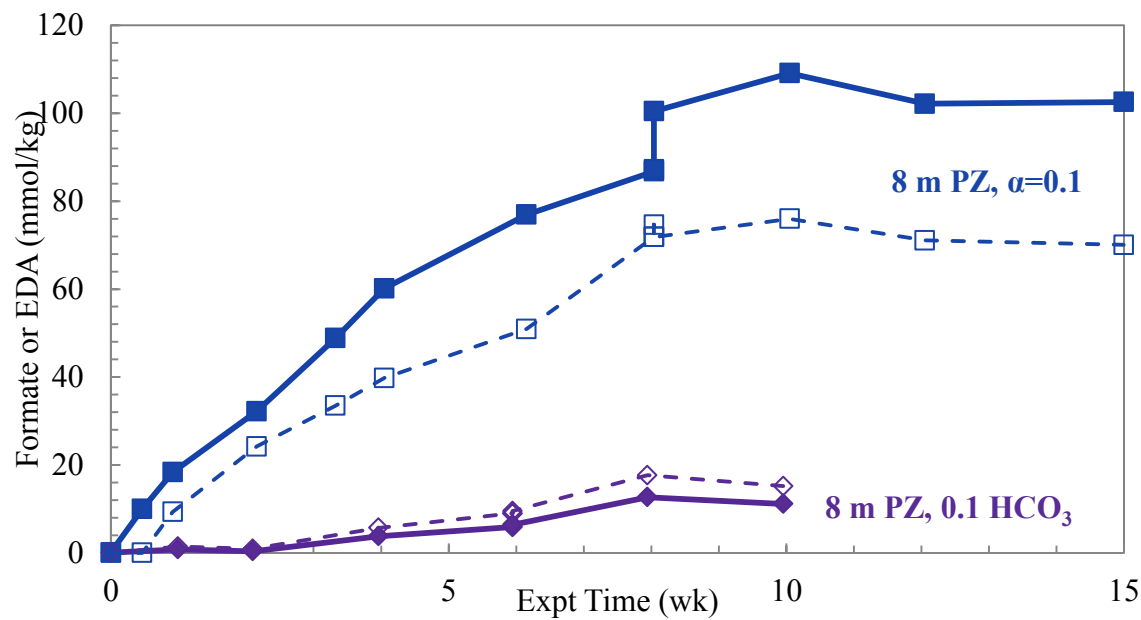


Figure 6.29: Generation of formate (solid) and EDA (dashed) for thermal degradation of 8 m PZ with 0.1 mole CO₂ or KHCO₃⁻ per mole alkalinity at 175 °C

6.3.4 Difference in degradation products in acidified PZ

Changes in EDA and formate generation during acidified PZ degradation were discussed in the preceding sections. Additional changes occur to the other degradation products in the absence of CO₂ that are observable when the cation IC chromatograms for 8 m PZ with 0.3 mole CO₂ (TE44) or H⁺ (TE48) per mole alkalinity degraded at 175 °C are compared. A 15-minute portion of the cation IC chromatograms for the final samples of these two experiments are compared in Figure 6.30. The acidified experiment had half as much degradation as the loaded experiment, so peak sizes are reflective of product rates relative to the overall level of degradation. EDA was shown to accumulate in the acidified degradation experiments due to a lack of CO₂ to react with and this observation will be extended to other species in solution. As an additional note, there were not significant changes between the original and alkaline treated samples for the acidified experiment, indicating that amides were not produced in any significant concentration.

The unidentified peaks in both samples can be analyzed in terms of the known reactions occurring in each sample and the MS results discussed above in section 6.1.4. The major unidentified peaks occur at retention times of 39.7, 42.0, 42.5, and 43.3 minutes. The peak at 42.0 minutes is a large peak in the acidified experiment, indicating it is a species that does not contain CO₂ (i.e. not an urea or imidazolidone) and not generated from a mechanism that requires CO₂ or CO₂-containing species. The peaks at 39.7 and 42.5 minutes are only significant in the loaded experiment, indicating CO₂ is involved in their structure or generation mechanisms. Based on the aforementioned observations and IC-MS data, suspected identities of these peaks can be assigned.

The peak at 42.0 minutes is believed to be 1-[2-[(2-aminoethyl)amino]ethyl]piperazine (AEAEPZ) (CAS 24028-46-4; N1-[2-(1-piperazinyl)ethyl]-1,2-Ethanediamine). This molecule is believed to be created from the S_N2 reaction of PZ

with H^+PZ in the initial stages of degradation. This molecule was also suspected for a peak in this region during thermal degradation screening of AEP performed by Davis (2009) and was supported by IC-MS molecular weight measurements.

The peak 39.7 is suspected to be the urea of AEAEPZ urea, which is dominant in CO_2 -loaded degradation. It is believed that in the presence of CO_2 , AEAEPZ would rapidly react with CO_2 to form the AEAEPZ urea leaving only trace amounts of unreacted AEAEPZ. The molecular weight of the peak at 39.7 minutes was also determined to be 198.2 gram per mole using IC-MS, which matches the AEAEPZ urea. It is possible that this peak is the diPZ urea since the molecular weights are the same, but provided the presence of an AEAEPZ peak in the acidified experiment and the elution position in the quada mine region of the chromatogram, AEAEPZ urea is a more likely molecule. The last two peaks at 42.5 and 43.3 minutes have not been positively identified but their suspected molecules are discussed in section 6.1.4.

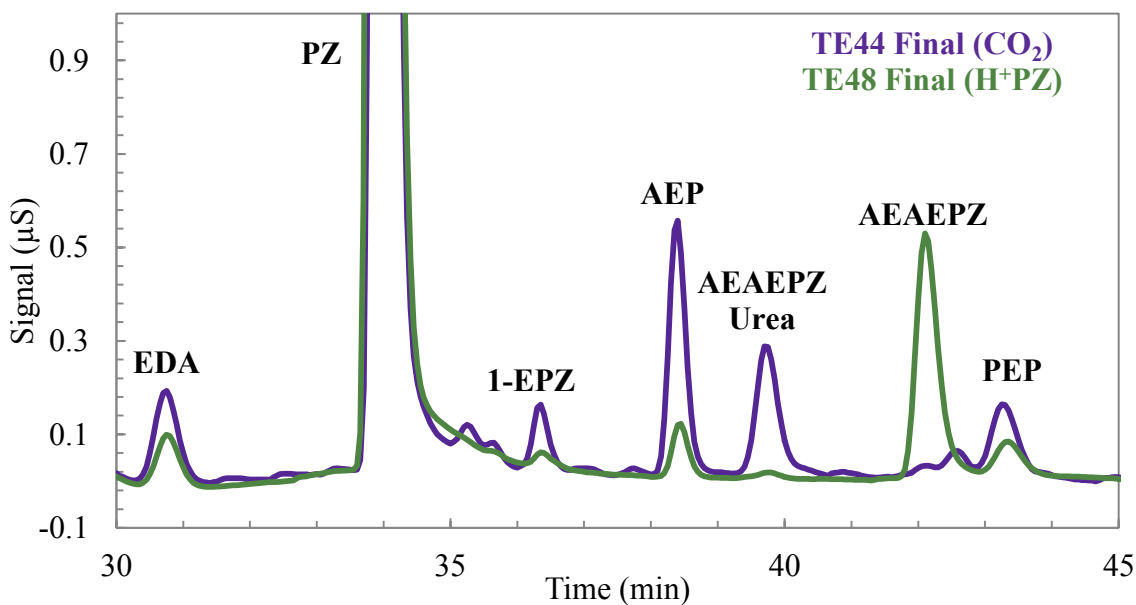


Figure 6.30: Cation IC chromatogram for the final sample of TE44 and TE48

6.4 MECHANISM FOR THE GENERATION OF FORMATE

6.4.1 Degradation of 8 m PZ in the presence of $^{13}\text{CO}_2$

In order to understand the generation of formate in oxygen-poor thermal degradation of concentrated PZ, an experiment was devised using ^{13}C -labelled CO_2 ($^{13}\text{CO}_2$) and NMR analysis. A solution of 8 m PZ was loaded with 0.3 mole CO_2 per mole alkalinity with $^{13}\text{CO}_2$. This solution was then degraded at 175 °C in thermal cylinders for six weeks. The degraded solutions were analyzed using ^1H and ^{13}C NMR in order to determine if the CO_2 lost during degradation ends up as formate or other products. A complimentary experiment with 8 m PZ with 0.3 mole natural CO_2 per mole alkalinity was performed in parallel as a control. Both sets of cylinders were degraded under the same conditions and analyzed in parallel.

The PZ loss and formate generation for the $^{13}\text{CO}_2$ -loaded and natural CO_2 experiments are compared to collated data for 8 m PZ with 0.3 mole CO_2 degraded at 175 °C (TE4, TE12, and TE18) in Figure 6.31 and Figure 6.32, respectively. The PZ loss is consistent between the collated reference data, $^{13}\text{CO}_2$ experiment, and natural CO_2 experiment, while the formate data contains some scatter in the collated reference data. These comparisons demonstrate that the $^{13}\text{CO}_2$ and natural CO_2 reference experiments match previously collected data for thermal degradation at these conditions and NMR analysis of these samples should be representative of expected degradation.

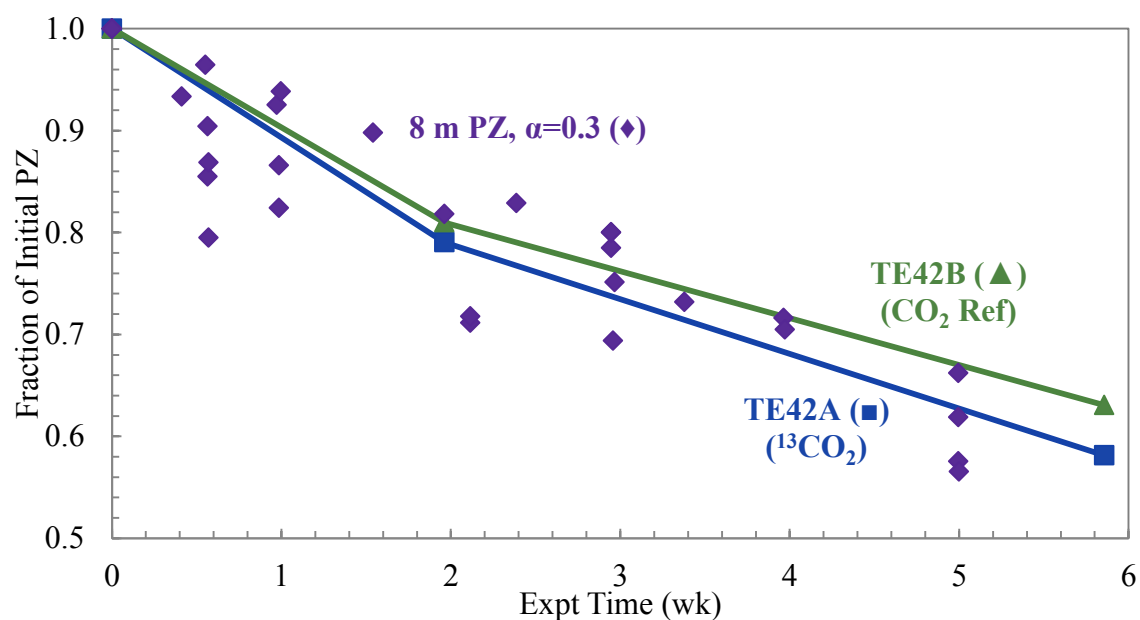


Figure 6.31: Comparison of PZ loss for 8 m PZ with 0.3 mole CO₂ or ¹³CO₂ per mole alkalinity at 175 °C

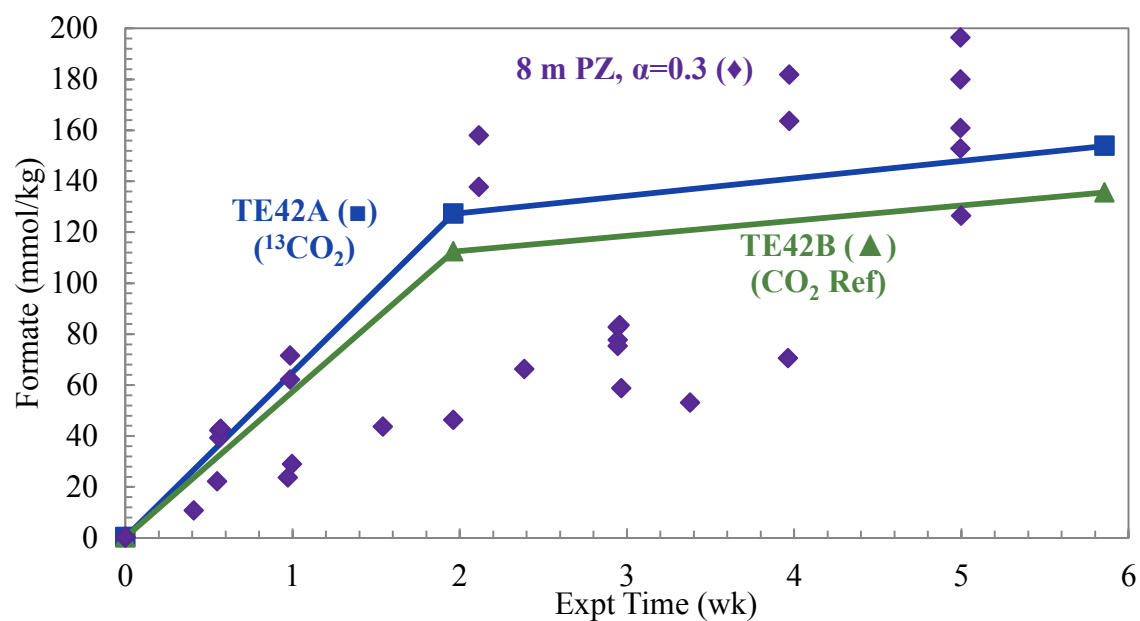


Figure 6.32: Comparison of formate generation for 8 m PZ with 0.3 mole CO₂ or ¹³CO₂ per mole alkalinity at 175 °C

6.4.2 NMR analysis of $^{13}\text{CO}_2$ degradation study

Degraded samples from the $^{13}\text{CO}_2$ and natural CO_2 experiments were analyzed using ^1H and ^{13}C NMR. The goal of the NMR work was to confirm the hypothesis that formate is generated during degradation from CO_2 , not carbons of the PZ backbone. The NMR results would indicate if formate contained ^{13}C from ^{13}C -labelled CO_2 , therefore indicating a mechanism for formate generation in an oxygen-poor environment. All NMR analysis was conducted at the NMR Laboratory at the University of Texas at Austin (Wallin and Storey, 2010).

To prepare for the NMR, background samples were analyzed to determine where formate generally appears in NMR spectra. The Spectral Database for Organic Compounds (SDBS) has a ^{13}C reference spectrum for formic acid (AIST, 2010). This spectrum was analyzed in the presence of CDCl_3 and shows the formic acid peak at 166.22 ppm (Figure 6.33). The peak expected for sodium formate in D_2O would be at 171.67 ppm (Gottlieb et al., 1997). The difference between these two chemical shifts is due to the pH of the solution in which formate was detected and demonstrates the range of shift for formate ions in aqueous solution that may be expected. The region where formate is seen is the downfield range of the ^{13}C spectrum where carbons that are part of a carbonyl ($\text{C}=\text{O}$) generally appear. In loaded PZ samples, the carbons of carbamate carbonyls and carbonate/bicarbonate carbonyls will also appear. In degraded solutions, it is expected that carbons of aldehyde carbonyls, ketone carbonyls, and amide carbonyls would appear in the same downfield area of the spectrum.

In order to anticipate what may be seen in degraded PZ solutions, two aliquots of loaded 8 m PZ were spiked with 38 and 305 mM formic acid and analyzed. The resulting downfield ^{13}C NMR spectra are shown in Figure 6.34 and Figure 6.35 below. In these two samples, the formate peak appears at a chemical shift of 170.191 and 170.296 ppm,

respectively. Both spectra also show peaks for the carbonyl in PZCOO^- (162.334 and 162.375 ppm, respectively) and the carbonyl in $\text{CO}_3^{2-}/\text{HCO}_3^-$ (162.796 and 162.838 ppm, respectively) in the same downfield view. The sample with 38 mM also registered a peak for the $\text{PZ}(\text{COO}^-)_2$ at 163.135 ppm and it is not clear why that did not show up in the 305 mM sample. In loaded PZ solutions, the chemical shift of the carbon in formate is not quite as great as that of sodium formate reference spectrum, but should occur around 170 ppm. This test also demonstrates that the formate peak does not overlap with any of the carbonyl peaks expected in neat and CO_2 -loaded PZ.

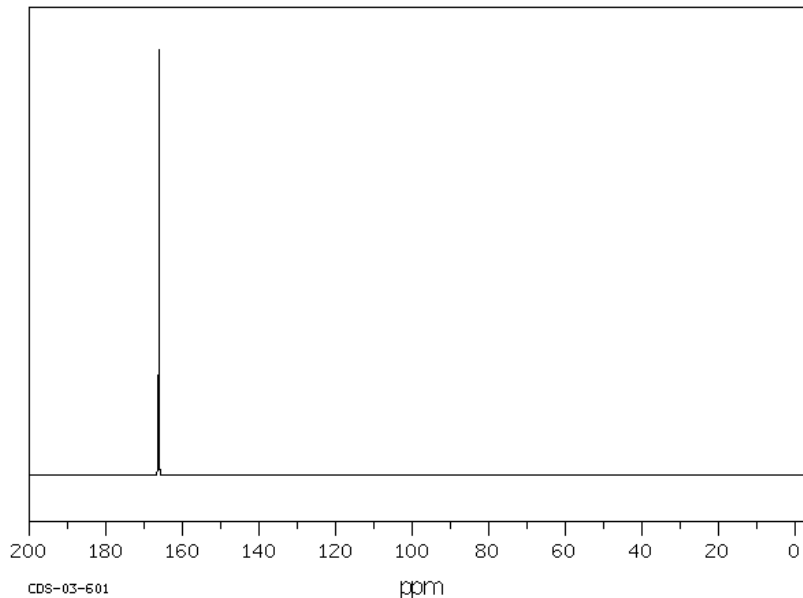


Figure 6.33: Reference ^{13}C spectrum for formic acid showing a major peak at 166.22 ppm (AIST, 2010)

In the degradation experiments, the ^{13}C -labelled CO_2 is used to amplify the NMR signal. ^{13}C NMR, as the name indicates, only detects ^{13}C isotopes of carbon. In standard samples, the signal is generated from the naturally occurring ^{13}C that is present in all matter, approximately 1% of all carbon. The effect of loading a PZ solution with $^{13}\text{CO}_2$

is seen when panels A and B of Figure 6.36 are compared. Panel A is a ^{13}C NMR spectrum of loaded PZ with natural CO_2 while Panel B is a ^{13}C NMR spectrum of $^{13}\text{CO}_2$ -loaded PZ. It is important to note the relative size of the group of peaks upfield (right side of spectrum, ~ 40 ppm) and downfield (left side of spectrum, ~ 160 ppm). The upfield peaks represent naturally occurring ^{13}C in the carbons on the PZ backbone and are the same size in Panels A and B, despite the difference in the ordinate scale. The downfield peaks represent carbonyl carbons (PZCOO^- , $\text{PZ}(\text{COO}^-)_2$, and $\text{CO}_3^-/\text{HCO}_3^-$). The effect of $^{13}\text{CO}_2$ is clearly visible in the increased size of the carbonyl peaks.

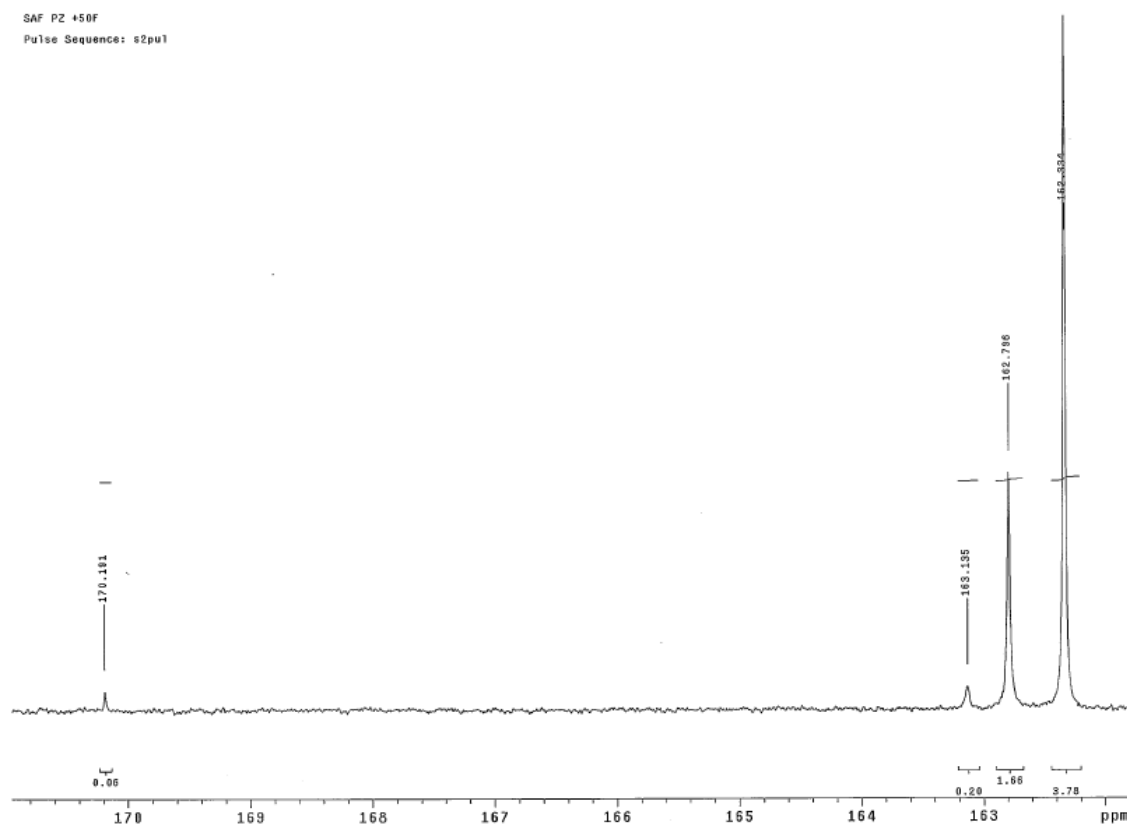


Figure 6.34: Downfield ^{13}C NMR spectrum for 8 m PZ with 0.3 mole CO_2 per mole alkalinity spiked with 38 mM formate

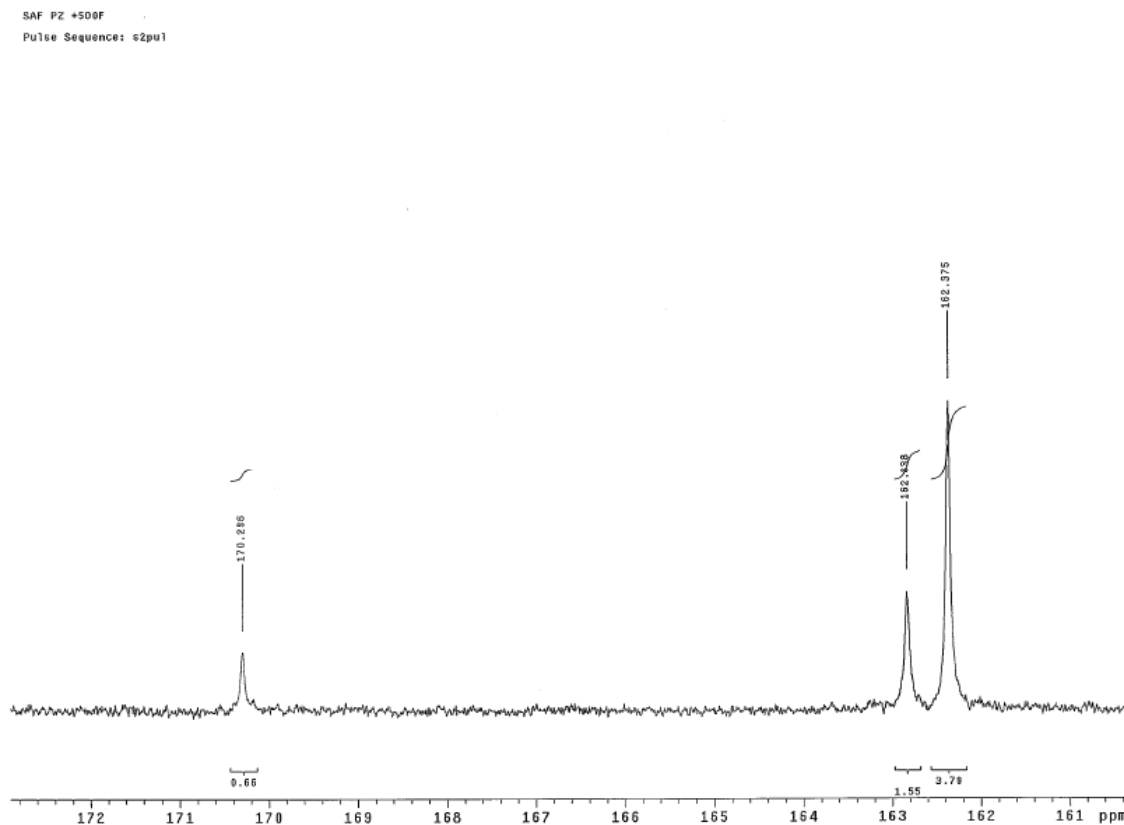


Figure 6.35: Downfield ^{13}C NMR spectrum for 8 m PZ with 0.3 mole CO_2 per mole alkalinity spiked with 305 mM formate

Samples of degraded PZ after 2 and 6 weeks of degradation at 175°C were analyzed with quantitative ^{13}C NMR. As expected, the ^{13}C NMR spectra for degraded PZ samples were very complex due to the high level of degradation. Examples of the downfield ^{13}C NMR spectrum for degraded solutions containing $^{13}\text{CO}_2$ and natural CO_2 after 6 weeks of degradation are shown in Figure 6.37 and Figure 6.38. The spectra are cropped to show between 160 and 172 ppm of the downfield ^{13}C spectrum for comparison purposes. The peak at the far left at 170.1 ppm in both figures correspond to formate based on the background spectra analyzed above.

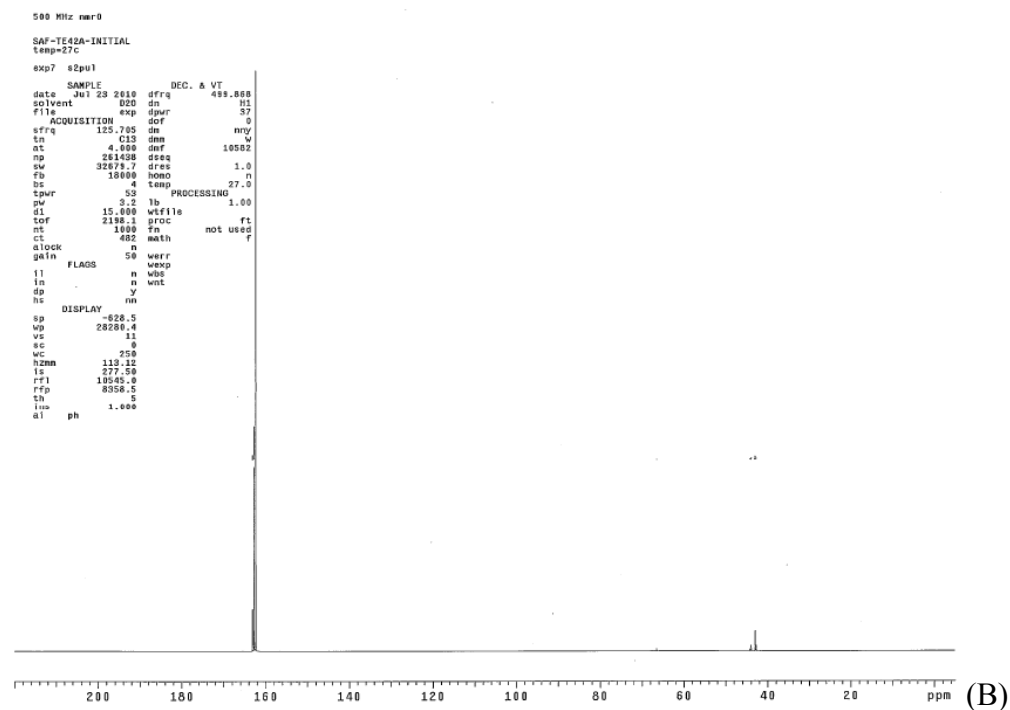
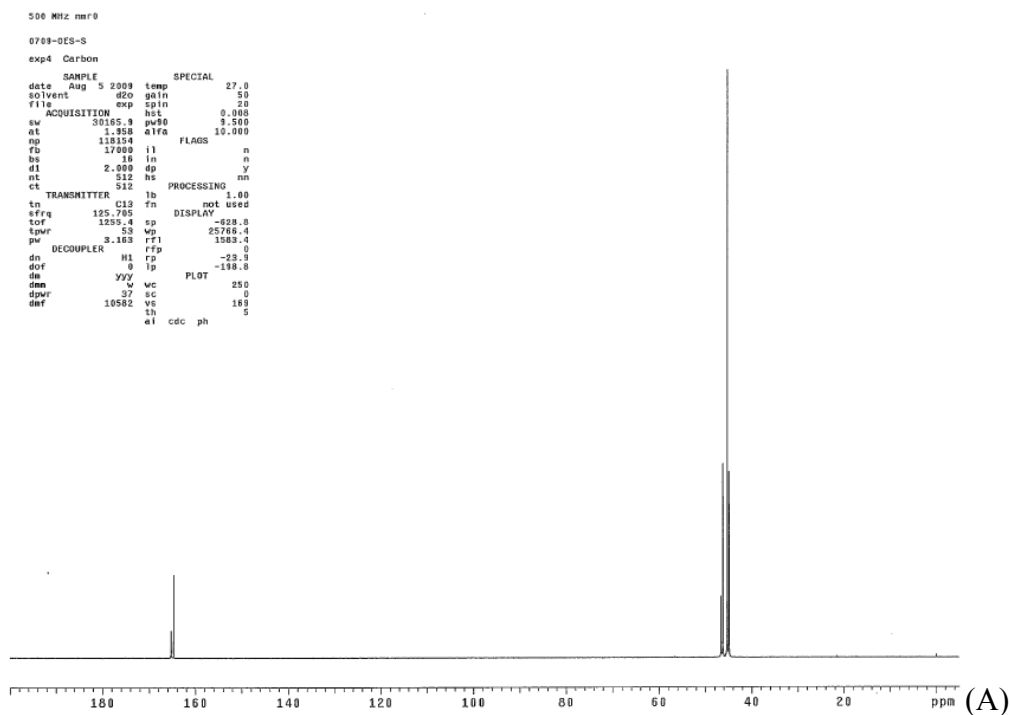


Figure 6.36: Comparison of ^{13}C NMR spectra for 8 m PZ loaded with (A) natural or (B) ^{13}C -labelled CO_2 (aligned on horizontal ppm scale)

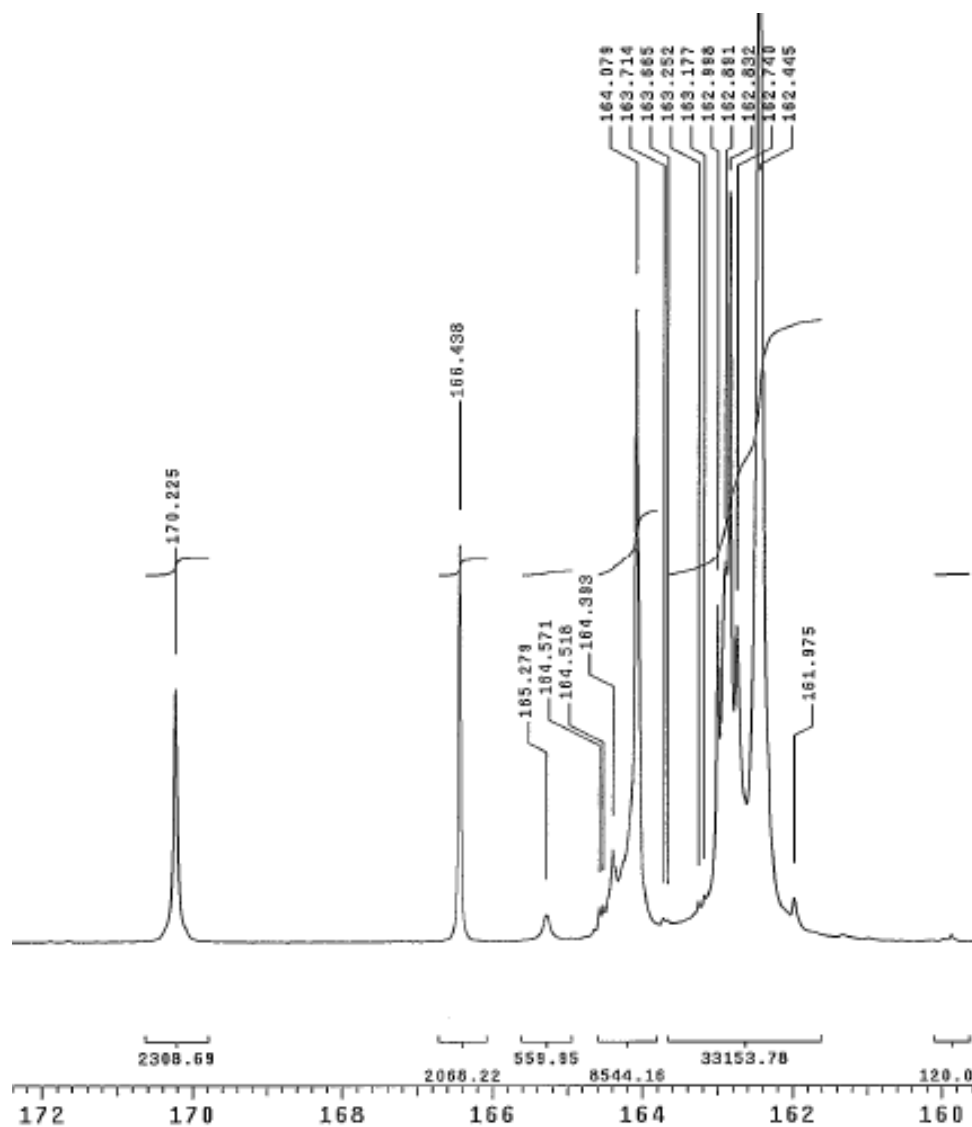


Figure 6.37: Downfield ^{13}C NMR spectrum for $^{13}\text{CO}_2$ loaded 8 m PZ after 6 weeks at 175°C

From these spectra, the concentration of formate was estimated using a reference standard of 1 wt % dioxane. The peak areas associated with dioxane (~ 3.5 ppm in ^1H and 66.5 ppm in ^{13}C) were then used to estimate the concentration of other species in solution. The calculation started by determining the concentration of dioxane, C_{Dioxane} , in the submitted sample in units of moles dioxane per kg of total solution (Equation 6.20).

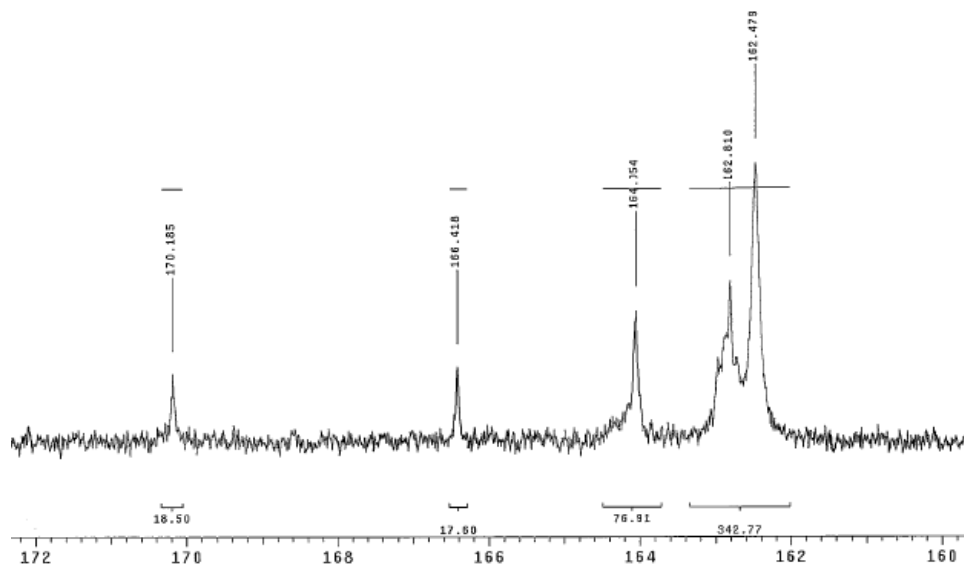


Figure 6.38: Downfield ^{13}C NMR spectrum for natural CO_2 loaded 8 m PZ after 6 weeks at 175°C

$$C_{\text{Dioxane}} = \frac{\text{g Dioxane}}{\text{g total}} \times \frac{\text{mol Dioxane}}{88.11 \text{ g Dioxane}} \times \frac{1000 \text{ g total}}{1 \text{ kg total}} \quad (6.20)$$

Then, a response factor, $\text{RF}_{\text{Dioxane}}$, was calculated using that concentration of dioxane, the number of carbons in dioxane, and the area from the ^{13}C NMR spectrum, $\text{Area}_{\text{Dioxane}}$ (Equation 6.21).

$$\text{RF}_{\text{Dioxane}} = \frac{\text{mole Dioxane}}{\text{kg soln}} \times \frac{4 \text{ Carbons}}{\text{mole Dioxane}} \times \frac{1}{\text{Area}_{\text{Dioxane}}} \quad (6.21)$$

Finally, the concentration of the species of interest was calculated using $\text{RF}_{\text{Dioxane}}$, the area of the peak, and the number of carbons of the species. When calculating concentrations for species that are assumed to contain only ^{13}C , the ratio of ^{13}C to ^{12}C must be applied since the reference chemical, dioxane contains only naturally occurring

^{13}C . The concentration of formate, C_{Formate} , which is assumed to contain only ^{13}C , was calculated using Equation 6.22.

$$C_{\text{Formate}} = \text{RF}_{\text{Dioxane}} \times \text{Area}_{\text{Formate}} \times \frac{\text{mole Formate}}{1 \text{ Carbon}} \times \underbrace{\frac{0.0107 \text{ mole } ^{13}\text{C}}{0.9893 \text{ mole } ^{12}\text{C}}}_{\text{Ratio of natural CO}_2} \quad (6.22)$$

Using Equation 6.22, the concentration of formate was calculated from the ^{13}C NMR spectrum for the degraded PZ. The calculated concentrations are compared with anion IC data of the same samples in Table 6.5. The formate concentration, not the total formate or formyl amide concentration was used because any amides would appear as separate peaks in the downfield region of the ^{13}C NMR. One set of calculations assumed that the formate peak in the $^{13}\text{CO}_2$ experiment contained all ^{13}C to match the hypothesis of the experiment. The final column in the table estimates the formate concentration from assuming it only contained natural ^{13}C . This would indicate a scenario where the formate carbon was produced from the PZ carbon backbone, rather than CO_2 . It is clear from comparing the last two columns of Table 6.5 that the assumption that formate contains only ^{13}C is valid. The formate estimated from assuming only naturally occurring carbon is up to 80X larger than the anion IC measurement. This comparison confirms the hypothesis that formate is generated from CO_2 , not the carbons on the PZ backbone.

Overall, the NMR analysis underestimated the formate concentration compared to the anion IC results. The NMR estimate is within 15% of the anion IC results for the final sample after 6 weeks of degradation. Given the nature of the NMR estimate, it is expected that the formate concentration contains more error when calculated this way compared to the direct measurement through anion IC.

Table 6.5: Comparison of formate quantified using anion IC and NMR in degraded PZ with $^{13}\text{CO}_2$ and natural CO_2

Expt.	Deg. Time weeks	Formate Concentration		
		Anion IC mmol/kg	NMR – ^{13}C mmol/kg	NMR – Natural C mmol/kg
$^{13}\text{CO}_2$ (TE42A)	0	0.27	0	0
	2	127.2	66	6120
	6	153.9	132	12,160
Natural CO_2 (TE42B)	0	0.21	0	0
	2	112.4	-	-
	6	135.6	-	101

The NMR analysis shows conclusively that the formate generated in degraded PZ solutions is from the CO_2 molecule. Formate contains the CO_2 carbon and is not generated through break-up of the PZ molecule itself. The mechanism for this CO_2 -reduction is not clear at this time.

This finding is notable since CO_2 is the only significant source of oxygen besides water in oxygen-poor thermal degradation. In addition, formate and formyl amides are found as a dominant degradation product in the thermal degradation of a variety of amines. This is primarily true in systems that do not undergo carbamate polymerization since that pathway uses the CO_2 molecule to create oxazolidones (Davis, 2009). The amines that produce significant formate concentrations during thermal degradation include: cyclic diamines (PZ, 1-MPZ, 2-MPZ), cyclic amines (piperidine, morpholine, pyrrolidine, hexamethyleneimine), straight chain amines (EDA, hexamethylenediamine), and some alkanolamines (MDEA). The presence of CO_2 is common in every experiment while the structures of the amine are very different including primary, secondary, and tertiary amines, linear amines, cyclic amines, monoamines, and diamines.

To demonstrate this, the generation of formate and total formate are compared for a variety of amines in Figure 6.39 and Figure 6.40, respectively. The degradation

conditions for the amines shown are different, but demonstrate the generation of formate and formyl amides in all solutions where data is available. The amines plotted are 8 m PZ, 7 m MEA (Davis, 2009), 8 m EDA (Zhou et al., 2010), 9 m 3-(methylamino) propylamine (MAPA) (Vevelstad, 2010), 8 m Mor, 7 m MDEA, 7/2 MDEA/PZ (Closmann, 2011), and 8 m 1-MPZ. CO₂ loadings were 0.2 mole per mole alkalinity for MDEA and MDEA/PZ, 0.3 mole per mole alkalinity for PZ, Mor, and 1-MPZ, and 0.4 mole CO₂ per mole alkalinity for MEA, EDA, and MAPA. Data shown represents thermal degradation at 135 °C for MEA, EDA, MAPA, MDEA, and MDEA/PZ, 150 °C for 1-MPZ, and 175 °C for PZ, Mor, and 1-MPZ. It is expected that all amines thermally degraded in the presence of CO₂ will produce both formate and formyl species, even if these products have not yet been quantified.

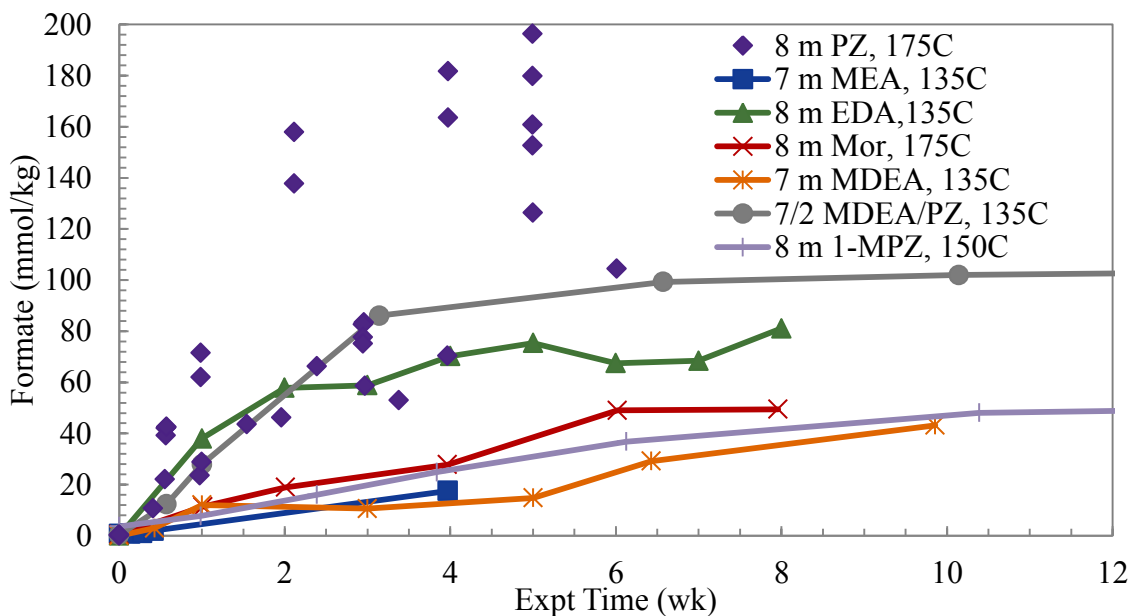


Figure 6.39: Comparison of formate generation for a variety of CO₂ capture amines

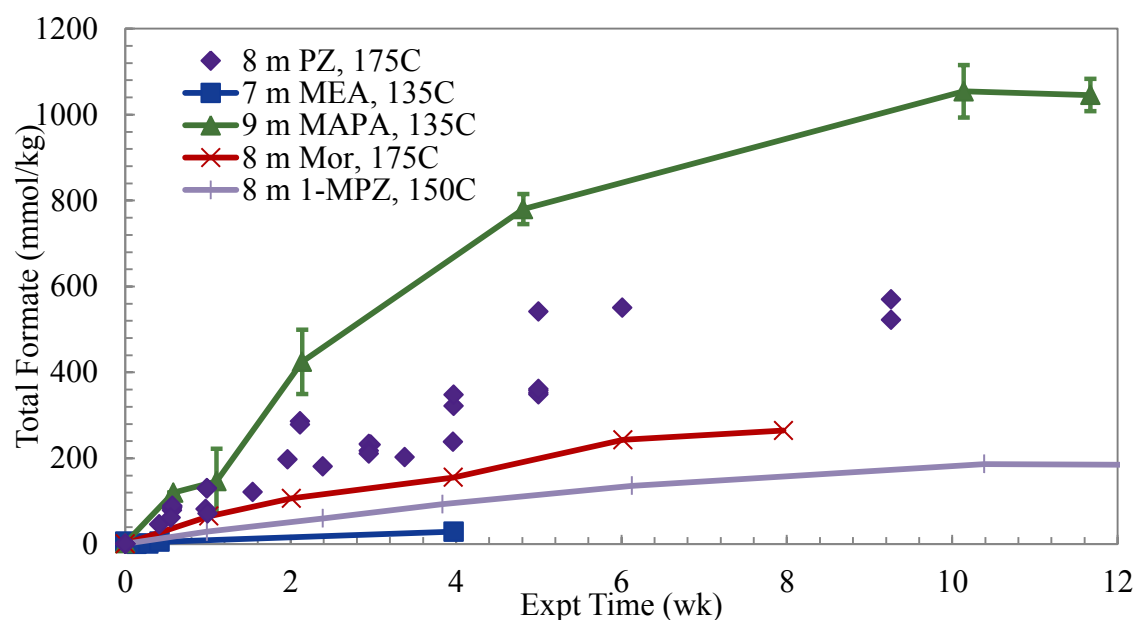
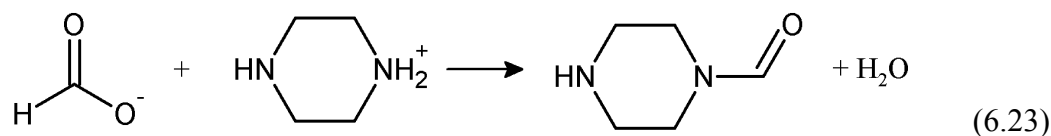


Figure 6.40: Comparison of total formate generation for a variety of CO₂ capture amines

6.4.3 Relationship of formate, PZ, and N-formyl PZ

The generation of formate, formyl amides, and FPZ is a crucial part of the thermal degradation of concentrated, aqueous PZ. Formate and formyl amides were generated in every thermally degraded solution containing CO₂ and are used as tracer compounds to track PZ degradation. The mechanism for the generation of formate from CO₂ has not been elucidated and it is not known whether formate ion or FPZ is produced first. All that is known is that both species are generated in the initial mechanisms of degradation products without a lag in the production. Most likely, one is generated first and reacts quickly with water or PZ to produce the complementary species. An equilibrium reaction appears to be occurring between the molecules where both are final products and the concentrations depend on degradation conditions (Equation 6.23). This equilibrium is complicated by the speciation of PZ into a variety of molecules including H⁺PZ and PZCOO⁻. It is not clear which form prefers to take part in the equilibrium.



Amides can be converted to their respective carboxylate ion and amine through a hydrolysis, which is the basis of the alkaline treatment for quantifying amides (Koike et al., 1987). This reaction can be catalyzed by either acid or base and could occur readily in either direction at high temperature (Brown, 1994). It well established that FPZ can be produced through the reaction of PZ with active reactants in high temperature environments. For example, Horrom and colleagues produced FPZ by combining methyl formate and PZ while Duranleau reacted CO with catalyst at high temperature to produce FPZ and N,N'-diformyl PZ (Duranleau et al., 1986; Horrom et al., 1954). The same has been observed for other amides where research has shown that equimolar amounts of oxalate and PZ react to create N-oxalyl PZ (Mislyuk et al., 1985).

The interconversion of formate and FPZ was tested by spiking loaded 8 m PZ with either 200 mM formate or FPZ. The ratio of these species was monitored over 5 days at 175 °C, as shown in Figure 6.41. In both solutions, the spiked component reacted with either PZ or water to produce the other, indicating that neither is an intermediate for the other, but both are final products that can interconvert.

Other amides are created during thermal degradation of PZ, but FPZ is the first amine created and accumulates to significant concentrations before additional amides are formed. This is illustrated in Figure 6.42 where the concentration of formyl amides quantified using alkaline reversal and the anion IC tracks with the concentration of FPZ for the first 6 weeks of degradation. After that, the concentration of FPZ plateaued while the total formyl amides concentration continues to increase, indicating the production of different amides.

In all thermal degradation experiments with concentrated PZ, more formyl amides are generated than formate. The ratio of formyl amides to formate that is generated, however, appears to depend on solution speciation. The ratio of formyl amides to formate in degraded 4 to 20 m PZ with 0.3 mole CO₂ per mole alkalinity is compared in Figure 6.43. The ratio increases with increased PZ concentration, which is expected with higher concentrations of free PZ according to Le Chatelier's principle. The ratio of formyl amides to formate in degraded 8 m PZ with 0 to 0.47 mole CO₂ per mole alkalinity are compared in Figure 6.44. Increased CO₂ concentration also increases the ratio of formyl amides to formate. There is a larger amount of CO₂ in solution at higher loadings which can lead to more formate or formyl amides through the formate generation mechanism. Interestingly, the high loading experiment with 0.47 mole CO₂ per mole alkalinity did not lose as much PZ as lower loadings, but produced larger ratios of formyl amides to formate.

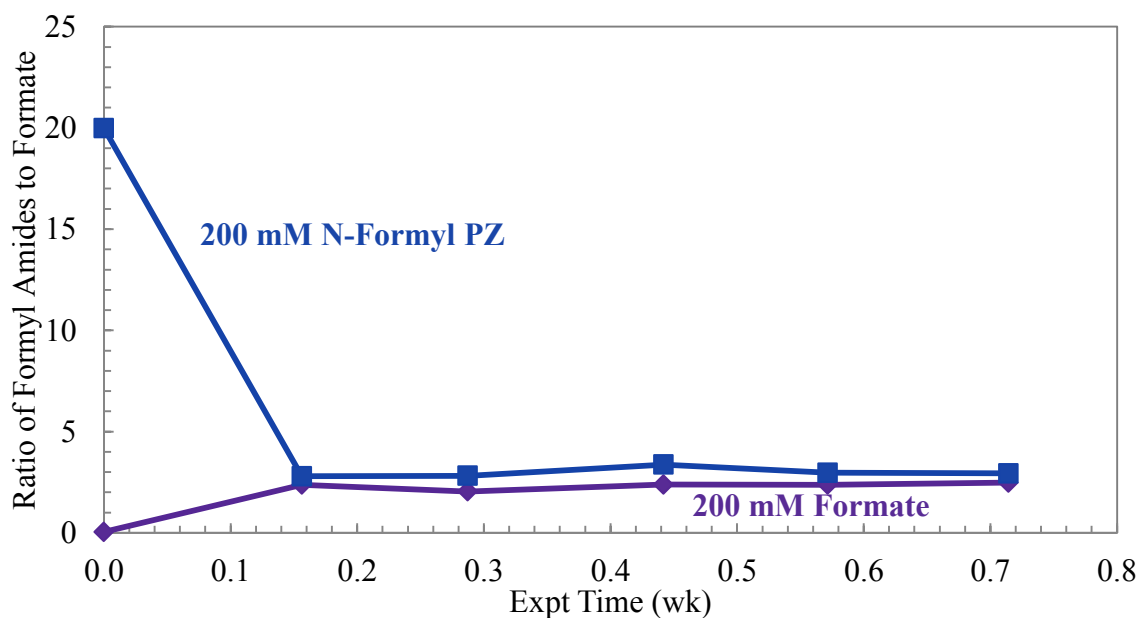


Figure 6.41: Equilibrium of formyl amides and formate at 175 °C in 8 m PZ spiked with 200 mM formate (TE66) or N-formyl PZ (TE67)

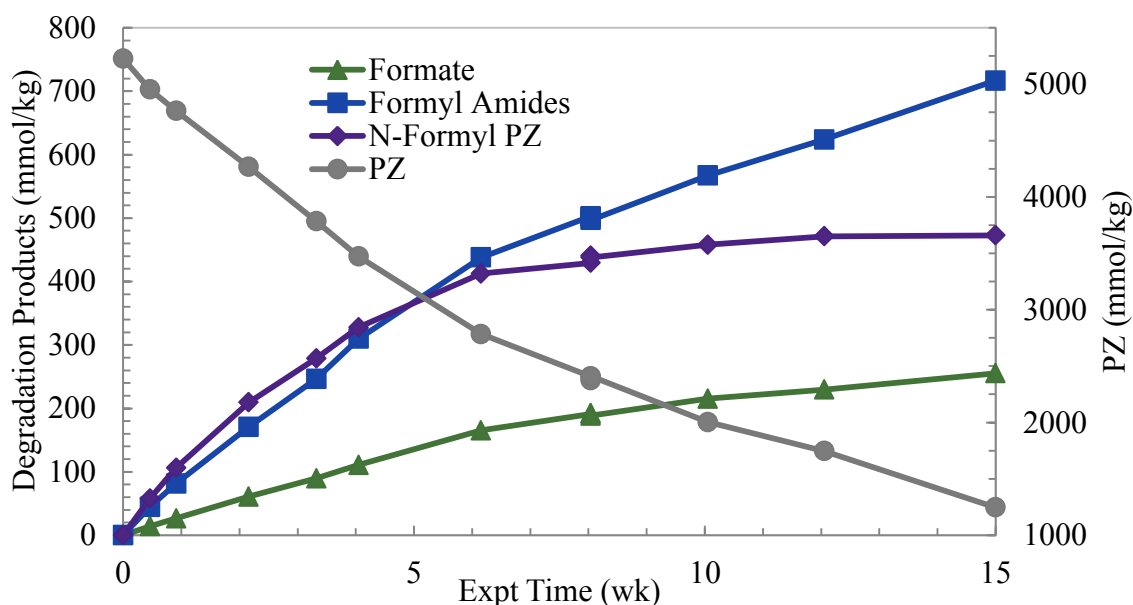


Figure 6.42: Concentration profiles for PZ loss and generation of degradation products for 12 m PZ with 0.3 mole CO₂ per mole alkalinity at 175 °C (TE33)

The effect of temperature on the equilibrium ratio of formyl amides to formate from 55 to 175 °C is shown in Figure 6.45. The experiment at 55 °C is oxidation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity in the presence of 4 mM Cu²⁺ (OE25) while the remaining data sets are thermal degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity (TE10, TE12, TE14, and TE44). Although oxidation and thermal degradation occur through different processes and under different conditions, the equilibrium ratio of formyl amides to formate is not strikingly different. The oxidation experiment was not as long in duration, but the data obtain indicate the ratio is very similar to the range of data obtained with thermal degradation. There is not a clear trend in the ratio with changing temperature. In all cases discussed, it is clear that the equilibrium ratio for each condition is reached quickly and persists, despite changing levels of overall degradation.

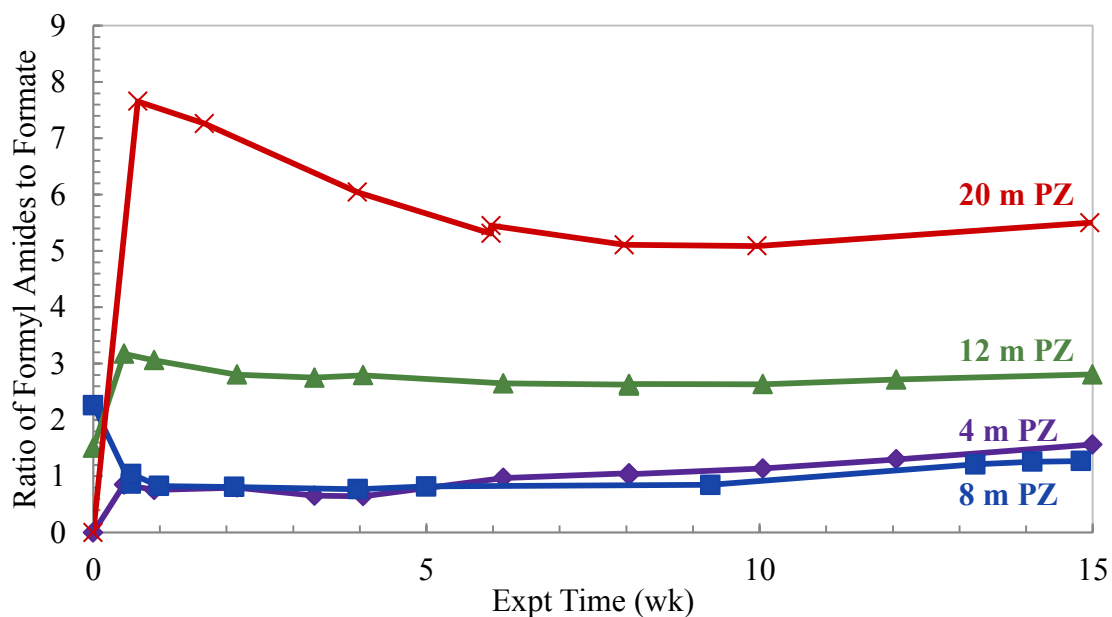


Figure 6.43: Ratio of formyl amides to formate produced during degradation of 4 to 20 m PZ with 0.3 mole CO₂ per mole alkalinity at 175 °C

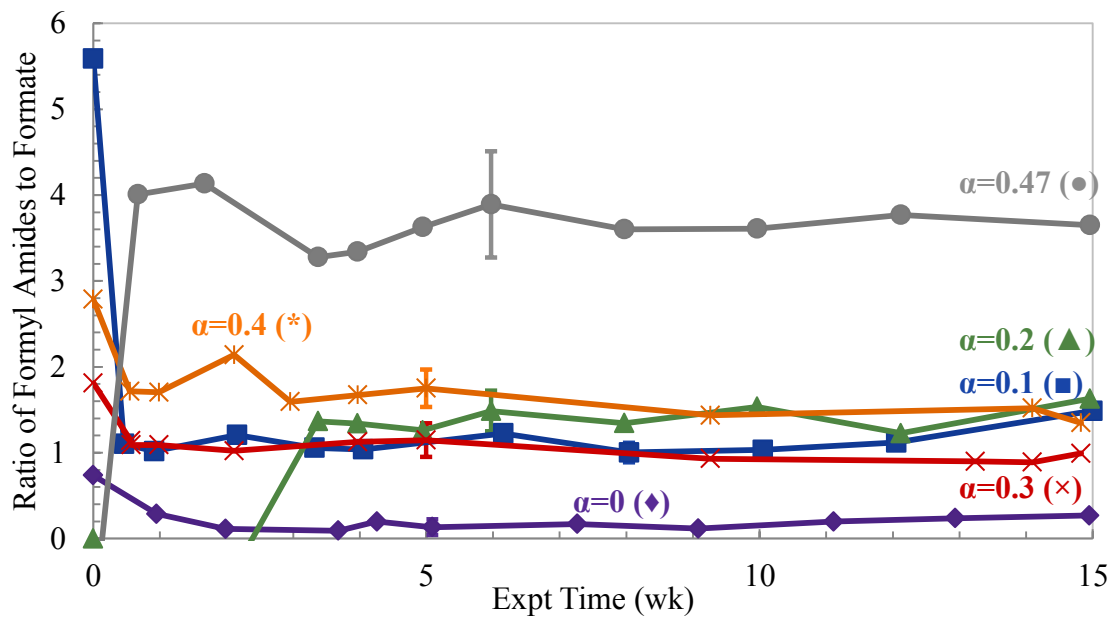


Figure 6.44: Ratio of formyl amides to formate produced during degradation of 8 m PZ with 0 to 0.47 mole CO₂ per mole alkalinity at 175 °C

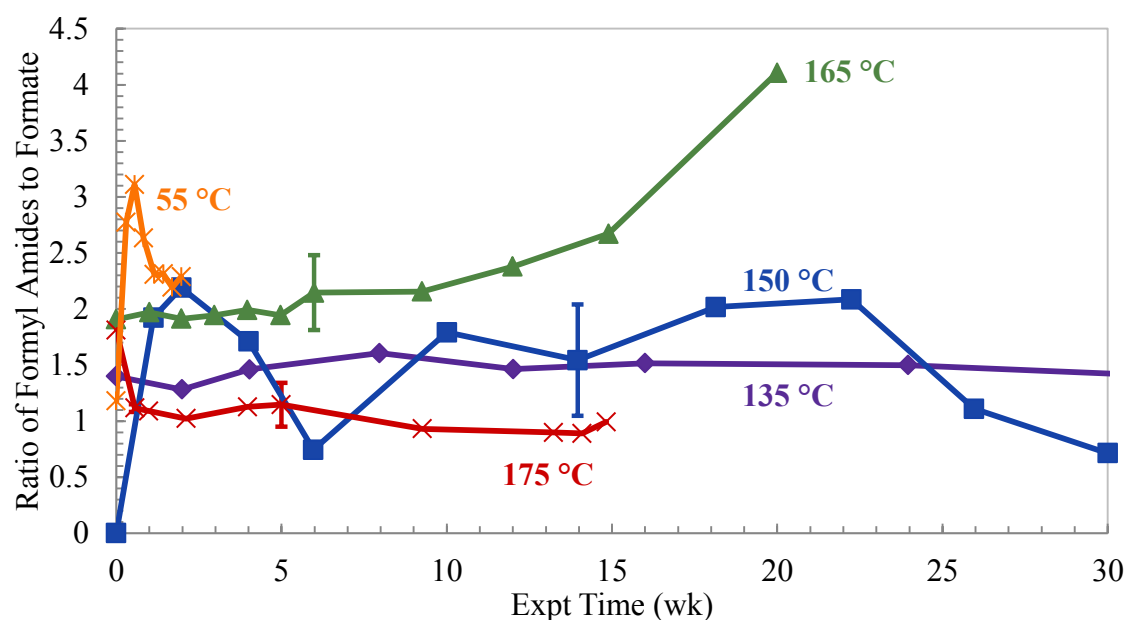


Figure 6.45: Ratio of formyl amides to formate produced during degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity from 55 to 175 °C (OE25, TE10, TE12, TE14, and TE44)

In order to understand the behavior of formyl amides and formate during thermal degradation, the average of the equilibrium ratio of formyl amides to formate was calculated for experiments ranging from 4 to 20 m PZ, 0 to 0.47 mole CO₂ per mole alkalinity, and 55 to 175 °C. As with Figure 6.45, the 55 °C data is from oxidation in the presence of 5 mM Cu²⁺ (OE25). If the ratio varied with time, the ratio toward the end of the experiment was taken to represent the equilibrium ratio expected. The ratios are shown for all conditions over a range of CO₂ loadings in Figure 6.46. The ratio increases with both PZ and CO₂ concentration, indicating a preference for producing amides at high PZ concentration and CO₂ loading. This result could be expected because increased concentrations of either free PZ or CO₂ would be expected to produce more amides.

Surprisingly, the effect of temperature is minimal, except for the two data points for 12 m PZ at 165 and 175 °C. This fact is demonstrated in Figure 6.47 where all of the

8 m PZ data are plotted as the same data set. In fact, a linear fit of all of the 8 m PZ data provides a reasonable regression that could predict the expected ratio of formyl amides to formate over a range of CO₂ loadings. The regression is shown in the figure and is as follows where the concentration of formyl amides, C_{FA}, and concentration of formate, C_F, are related to the CO₂ loading, α (mole CO₂ per mole alkalinity), by Equation 6.24. For 20 m PZ at 175 °C, the ratio can be described by Equation 6.25). Data for 4 and 12 m PZ were not gathered at varied CO₂ concentrations so the same regression cannot be performed.

$$\frac{C_{FA}}{C_F} = 5.54 \times \alpha + 0.30 \quad (6.24)$$

$$\frac{C_{FA}}{C_F} = 7.73 \times \alpha + 3.10 \quad (6.25)$$

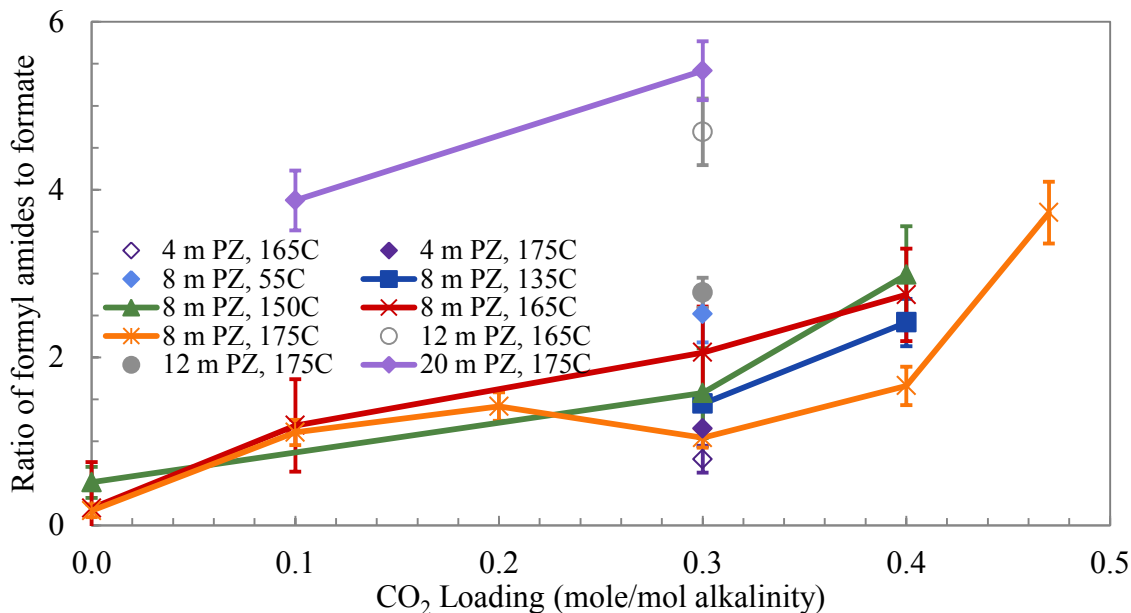


Figure 6.46: Ratio of formyl amides to formate generated during PZ thermal degradation of 4 to 12 m PZ at 135 to 175 °C

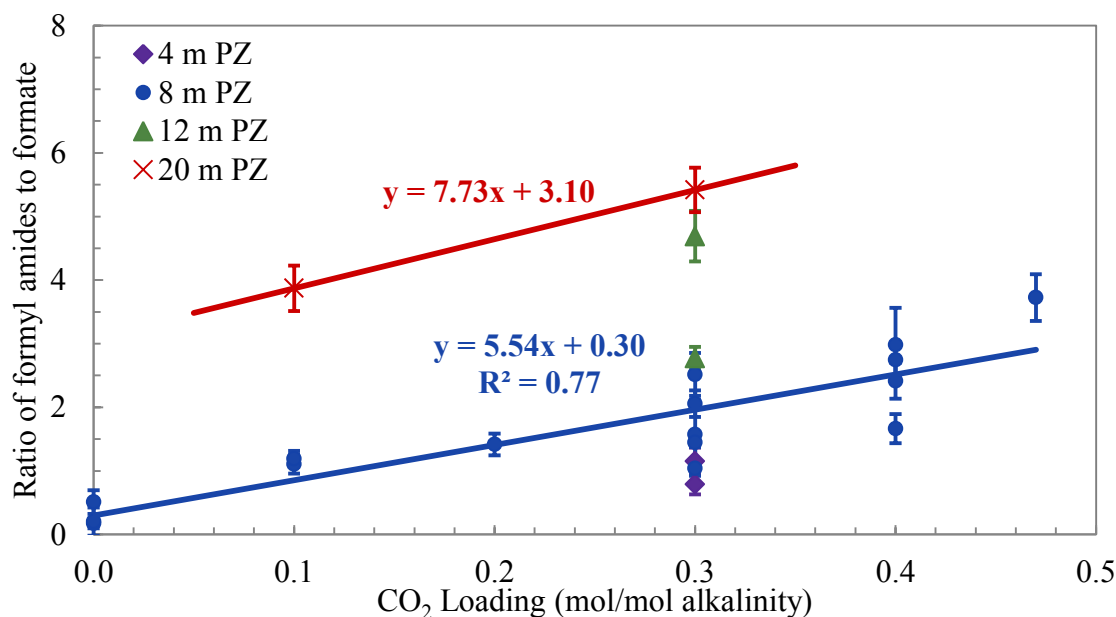


Figure 6.47: Ratio of formyl amides to formate generated during PZ thermal degradation of 4 to 12 m PZ without the effect of temperature

6.5 ROLE OF EDA IN PZ THERMAL DEGRADATION

EDA is a prominent thermal degradation product of PZ, but is known to degrade rapidly at temperatures lower than normal PZ degradation experiments (Zhou et al., 2010). During degradation, EDA produces both the cyclic EDA urea, 2-Imidazolidone (2-Imid), and the linear diEDA urea, N,N'-bis(2-aminoethyl)urea, whose chemical structures are shown in Figure 6.48 below. Zhou quantified 2-Imid using HPLC with UV detection while N,N'-bis(2-aminoethyl)urea was identified using cation IC-MS (Rochelle, 2009b). Since EDA is generated during PZ degradation, the thermal degradation of EDA is important to understand.

Three experiments were performed with the aim of highlighting the behavior of EDA in thermally degraded PZ. Blends of 8 m PZ and 1 m EDA were degraded at 150 and 175 °C and 8 m PZ spiked with 1 m 2-Imid was degraded at 175 °C. It was

hypothesized that EDA reacts with CO₂ to rapidly form 2-Imid, so the equilibrium between the two molecules in the presence of high concentration PZ was investigated.

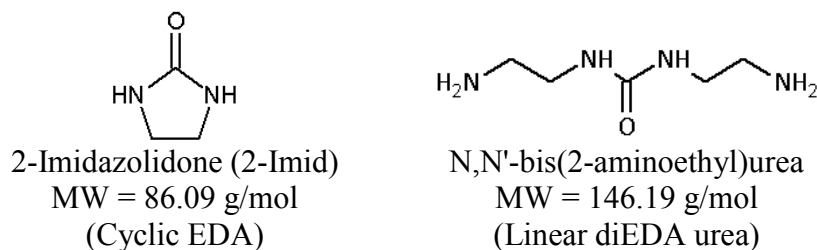


Figure 6.48: Chemical structures of EDA ureas produced during thermal degradation

The concentrations of PZ, EDA, 2-Imid, and EDA loss for the blend 8 m PZ + 1 m EDA at 150 °C is shown in Figure 6.49. EDA quickly reacted with CO₂ in this blend to form 2-Imid. It is not suspected that EDA reacted from any other product as the EDA loss tracks closely with the generation of 2-Imid, within the expected error of the two analytical methods. During the 4 weeks of degradation, both the EDA loss and 2-Imid generation level out indicating an equilibrium condition may have been reached where the EDA and 2-Imid have nearly the same concentration (approximately 225 mmole per kg). The loss of PZ is consistent through the experiment, with only 4% lost after 4 weeks at 150 °C. The equilibrium of EDA and 2-Imid occurs significantly faster than PZ loss and is likely not strongly affected by other PZ degradation products in this experiment.

The concentrations of PZ, EDA, 2-Imid, and EDA loss for the blend 8 m PZ + 1 m EDA at 175 °C are shown in Figure 6.50. The high reaction temperature produced a rapid equilibrium between EDA, CO₂ and 2-Imid where EDA and 2-Imid reached equilibrium concentrations within 1 week. As found in the lower temperature experiment, the EDA loss tracks closely with the generation of 2-Imid within the expected error of the two analytical methods. The difference in analytical technique used

for quantification or the presence of another EDA-based degradation product may account for the slight difference in the concentration of 2-Imid and EDA loss. After 1 week of degradation, the EDA and 2-Imid concentrations level out, but not to the same value as in the 150 °C experiment. The temperature dependence of the equilibrium or the presence of more degradation products may be influenced these equilibrium concentrations.

In an effort to understand the equilibrium between EDA and 2-Imid, a blend of 8 m PZ + 1 m 2-Imid was degraded at 150 °C. A secondary goal of this experiment was to determine if ureas switched arms rapidly in degrading solutions at high temperature. Since 2-Imid was added, it was hypothesized that PZ, being a stronger nucleophile and more concentrated in solution, would react and take the place of the EDA molecule in the urea structure to generate PZ-based ureas.

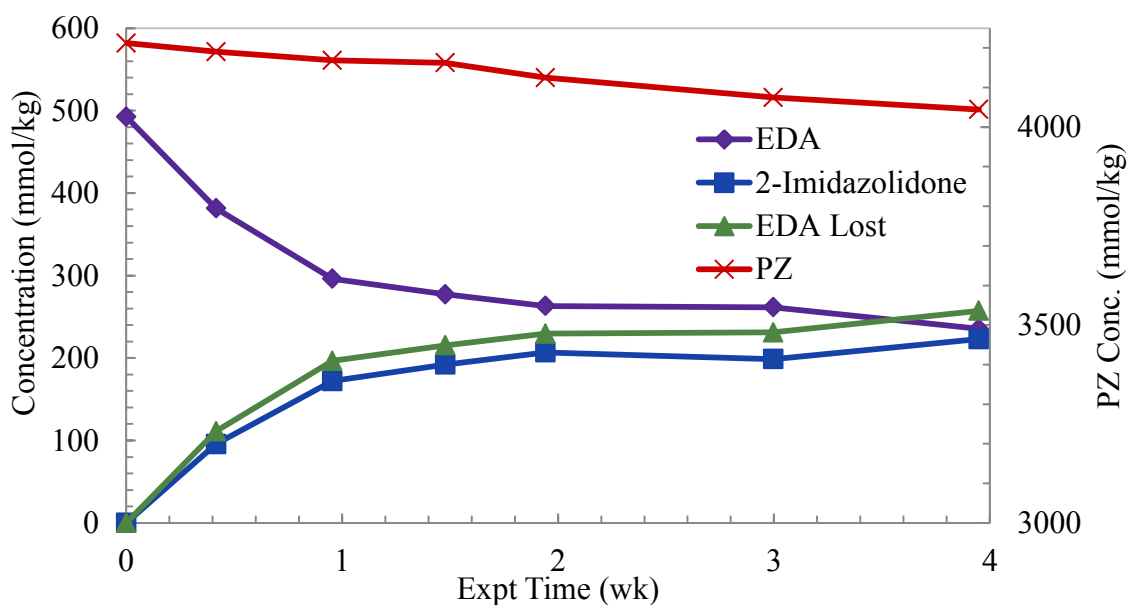


Figure 6.49: Concentration profiles for prominent amines in thermal degradation of 8 m PZ + 1 m EDA ($\alpha = 0.3$) at 150 °C

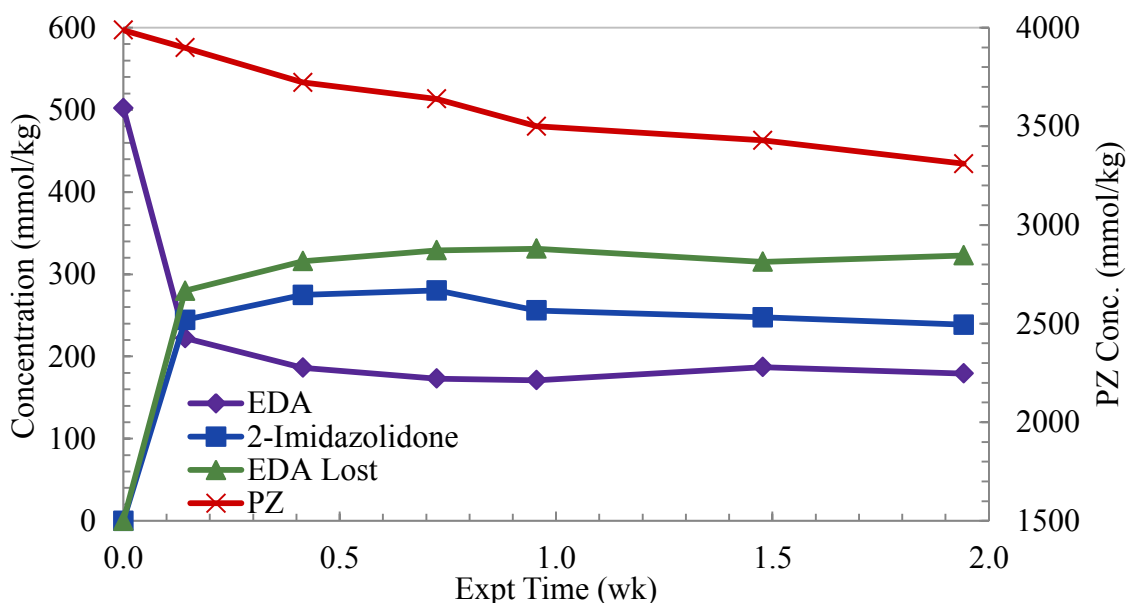


Figure 6.50: Concentration profiles for prominent amines in thermal degradation of 8 m PZ + 1 m EDA ($\alpha = 0.3$) at 175 °C

The concentrations for PZ, 2-Imid, EDA, CO₂, and lost 2-Imid are shown in Figure 6.51. As hypothesized, the loss of 2-Imid correlates with the production of EDA. A majority of 2-Imid loss ends up as EDA directly, with a smaller fraction being lost to other products or due to differences in analytical technique. The experiment was not long enough to establish equilibrium between the two compounds, if this would have occurred. A rise in CO₂ concentration is noticeable, but not as large as would be expected from the reaction of 2-Imid into EDA and CO₂, indicating that CO₂ is participating in other reactions as well. The cation IC did not show new, unidentified peaks indicating the presence of new ureas. The experiment was short, but it is clear that although PZ is a stronger nucleophile, it does not act to displace the EDA and form new ureas which would be seen on the cation IC due to second amino function on PZ. The 5-membered, cyclic urea structure of 2-Imid is like more thermodynamically stable than any other di-amine urea that may be produced from other amines, rather than internal ureas.

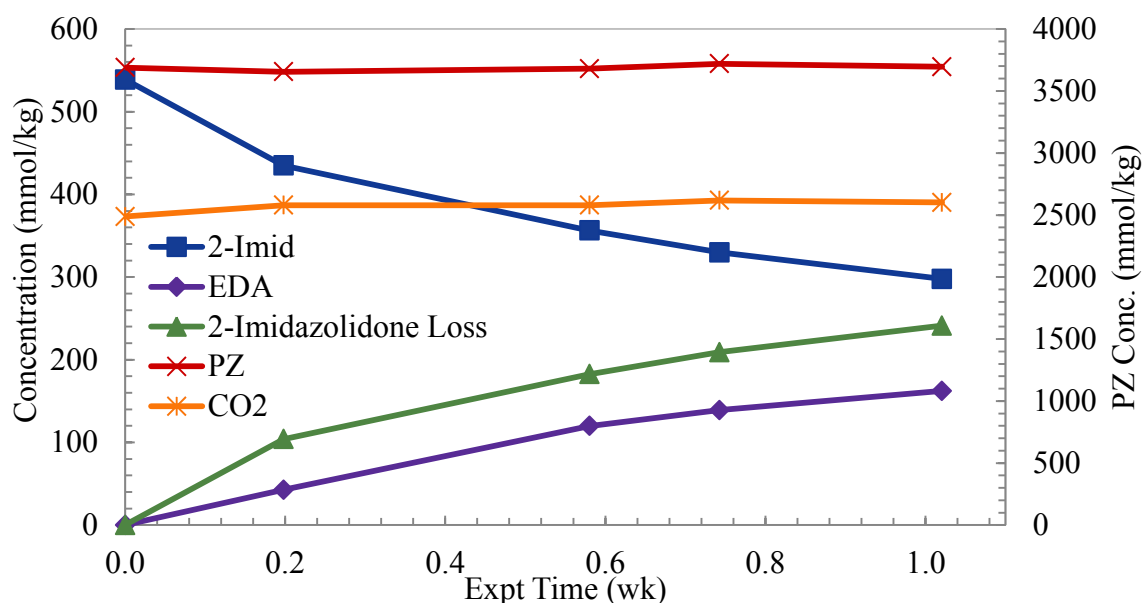


Figure 6.51: Concentration profiles for thermal degradation of 8 m PZ + 1 m 2-Imid ($\alpha = 0.3$) at 175 °C

The formate generation pathways discussed in section 6.1 suggested that formate and formyl amides could be produced from ureas in solution rather than carbamate species. This set of experiments with added EDA or 2-Imid would have increased concentrations of urea earlier in the experiment than PZ degrading on its own. If formate is generated from ureas like 2-Imid, the generation of formate should be increased, at least initially. The generation of total formate is compared for thermal degradation of 8 m PZ (represented as collated data from TE4, TE12, and TE18) and 8 m PZ/1 m EDA (TE59) at 175 °C in Figure 6.52. Formate is generated at the same rate as the experiment not spiked with EDA. At this temperature, 2-Imid and EDA reached equilibrium within 1 day, so there was an enhanced concentration of 2-Imid past this point in the spiked experiment. The presence of 2-Imid does not appear to enhance formate production at 175 °C.

Unexpectedly, this same observation was not made for the 150 °C data. The generation of total formate is compared for thermal degradation of 8 m PZ (represented as collated data from TE4, TE12, and TE18), 8 m PZ/1 m EDA (TE64), and 8 m PZ/1 m 2-Imid (TE64) at 175 °C in Figure 6.53. In this case, the addition of EDA enhanced formate generation compared to unspiked PZ and PZ spiked with 2-Imid. There are too few data to make a conclusive statement about the 2-Imid spiked experiment, but the enhancement due to EDA is unexpected. If formate is generated from 2-Imid, the EDA spiked experiment certainly has more 2-Imid present for the duration of the experiment. It is possible that at 150 °C PZ degradation is slow and does not produce significant 2-Imid within this time period. At 175 °C, PZ degradation is fast and makes 2-Imid at a rate that can compete with the spiked concentration of 2-Imid, so an enhancement in formate generation is not observed. The data is inconclusive at this point to determine if the presence of 2-Imid enhances formate generation across all temperatures.

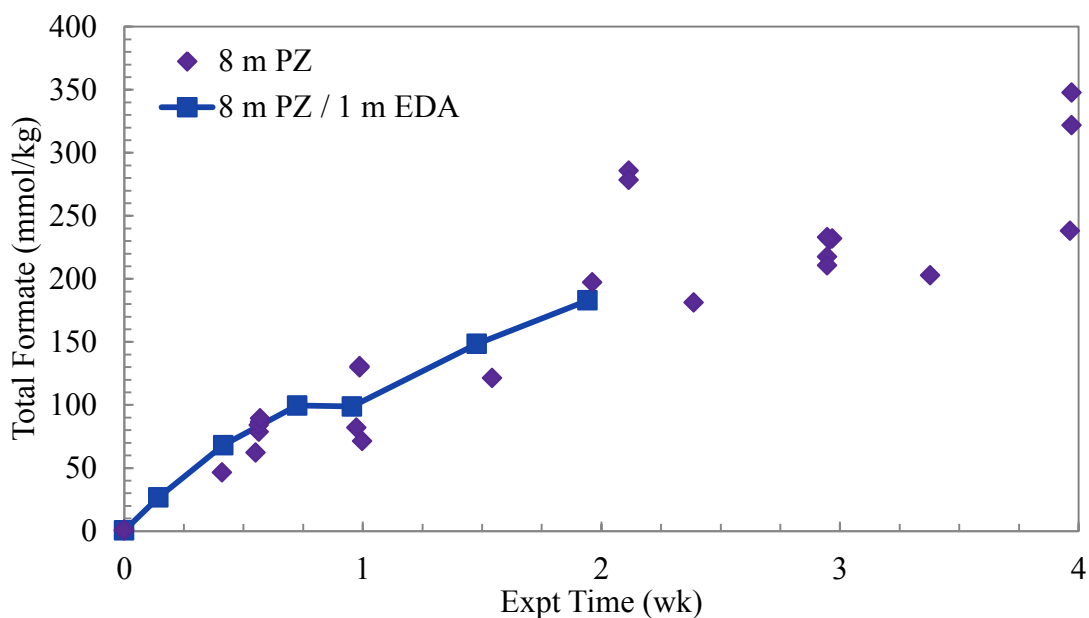


Figure 6.52: Comparison of total formate generation in thermal degradation of 8 m PZ and 8 m PZ/1 m EDA with 0.3 mole CO₂ per mole alkalinity at 175 °C

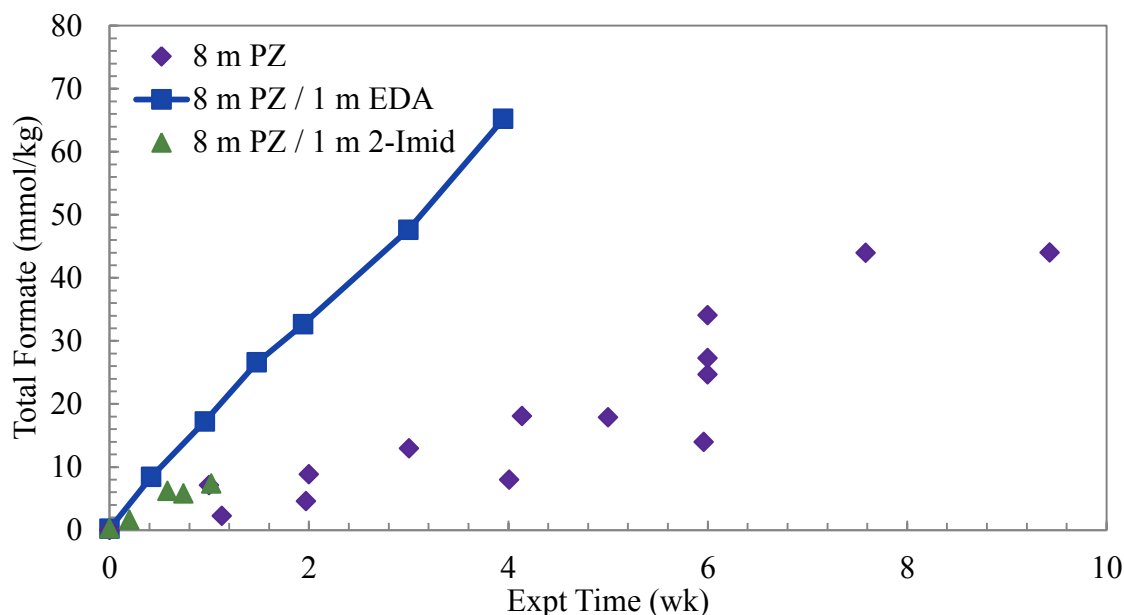


Figure 6.53: Comparison of total formate generation in thermal degradation of 8 m PZ, 8 m PZ/1 m EDA, and 8 m PZ/1 m 2-Imid with 0.3 mole CO₂ per mole alkalinity at 175 °C

The results of these experiments indicate that an equilibrium is occurring between EDA, CO₂ and 2-Imid. These match observations seen in all thermally degraded, loaded PZ where EDA is produced, but does not accumulate like other products. The reaction to form 2-Imid was written as follows (Equation 6.26).



The equilibrium constant, K_{EQ} , for the reaction could then be written to relate the concentrations of each species, indicated by brackets (Equation 6.27). In this equilibrium equation, the concentration of water is ignored since this reaction occurs in aqueous solution and its concentration is not limited.

$$K_{\text{EQ}} = \frac{[\text{2-Imid}]}{[\text{EDA}] \cdot [\text{CO}_2]} \quad (6.27)$$

The K_{EQ} was calculated at each time point for the three experiments discussed in this section and one baseline 8 m PZ experiment (TE44). The K_{EQ} is compared for all four in Figure 6.54 and the tabulated values are shown in Table 6.6. All four experiments demonstrate similar behavior of tending toward a K_{EQ} value of approximately 0.0005 kg per mole, even though experiments were performed at various temperatures.

Data past 12 weeks for the baseline 8 m PZ experiment show an increase in this value where the equilibrium is likely affected by the high levels of PZ degradation and presence of other degradation products. This analysis shows that the conversion of EDA to 2-Imid in loaded PZ solutions occurs with predictable behavior and makes 2-Imid an important final product of degradation while EDA is simply an initial indicator and intermediate product. Longer term experiments would be needed to differentiate the temperature dependence of the K_{EQ} .

Table 6.6: Calculated K_{EQ} for 8 m PZ with either 1 m EDA or 1 m 2-Imid with 0.3 mole CO_2 per mole alkalinity (TE59, TE60, and TE64)

Temp °C	8 m PZ / 1 m EDA		8 m PZ / 1 m 2-Imid	
	Time wk	K_{EQ} kg/mol	Time wk	K_{EQ} kg/mol
150	0.0	0	0.0	0
	0.4	0.000092	0.2	0.003702
	1.0	0.000215	0.6	0.001143
	1.5	0.000261	0.7	0.000839
	1.9	0.000307	1.0	0.000683
	3.0	0.000096		
	3.9	0.000377		
175	0.0	0		
	0.1	0.000248		
	0.4	0.000377		
	0.7	0.000411		
	1.0	0.000404		
	1.5	0.000391		
	1.9	0.000437		

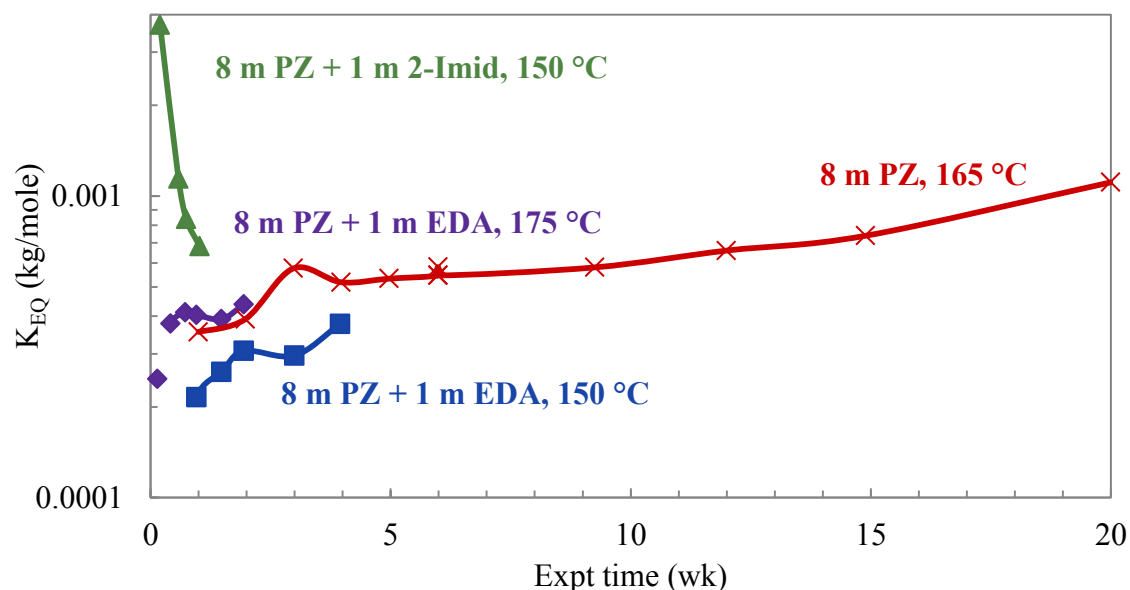


Figure 6.54: Equilibrium of EDA, CO₂, and 2-Imid in spiked thermal degradation experiments

6.6 ABSENCE OF OXYGEN AND CO₂ THROUGH NITROGEN PURGE

It has been suggested that the production of formate during thermal degradation experiments is due to the presence of oxygen (O₂) in the headspace of the thermal cylinders and dissolved O₂ in the amine solution at the start of thermal degradation experiments. The argument has been that the O₂ molecules in the formate and formyl amides must be due in part to the dissolved O₂ and water, rather than CO₂ as suggested by the mechanism discussed in section 6.3 above. A complimentary concept is that the presence of molecular O₂ activates or initiates the mechanisms that lead to PZ thermal degradation and the production of degradation products such as formate and formyl amides. In an effort to address these arguments, two thermal degradation experiments, one unloaded and one lean loaded (0.3 mole CO₂ per mole alkalinity), were conducted with an inert headspace in the cylinders at the start of the experiment. This circumstance was achieved by filling and sealing the thermal cylinders in a glove bag filled with

nitrogen (N_2) gas. The hypothesis of these experiments was that the replacement of O_2 and CO_2 in the headspace with inert N_2 would demonstrate the effect of those molecules, especially O_2 .

To create an inert environment, all of the materials needed for the task were first placed into the glove bag. Then, the glove bag was flushed with N_2 , sealed, and inflated to a reasonable working pressure with N_2 . The PZ solutions were not specifically purged or sparged with N_2 to remove O_2 since the process of loading the solution with CO_2 acts to strip out most of the other gases present in solution. The cylinders were filled in the glove bag and sealed according to Swagelok[®] specifications while under the presence of N_2 . The tightness of the cylinders was checked out of the glove bag to ensure the success of the experiment. For the unloaded experiment, cylinders were filled in the same fashion but with warm solution to maintain a liquid phase solution.

The PZ loss for the high temperature degradation of standard unloaded 8 m PZ is compared to the N_2 purged experiment in Figure 6.55. A third set of data from three separate repeated experiments exploring thermal degradation of 8 m PZ with 0.3 mole CO_2 per mole alkalinity at 175 °C is also included to place the unloaded degradation data in context. Both unloaded experiments suffered only a very slight loss of PZ compared with the loaded degradation rate. There was a small decrease in the PZ loss in the N_2 purged experiment indicating that ambient O_2 may, in fact, affect the overall degradation rate of thermal degradation experiments.

In order to further see the effect of the N_2 headspace, the production of total formate and EDA are compared in Figure 6.56 and Figure 6.57, respectively, for the same three conditions. There is a noticeable decrease in rate of total formate generated during the experiments as the concentration is decreased by 56 % from 18.3 to 8.1 mmole per kg. The loaded experiment generates formate concentration quickly due to the formate

generation mechanism discussed above. Total formate concentration is decreased under a N_2 atmosphere compared to the baseline unloaded experiment. The presence of O_2 could have activated mechanisms responsible for both the degradation of PZ and production of total formate. A decrease in rate can be observed in both PZ loss and formate production when O_2 was removed from the headspace. The O_2 does not appear to be required for either mechanism, since both proceed without it, but likely acts to activate or catalyze the mechanisms of degradation.

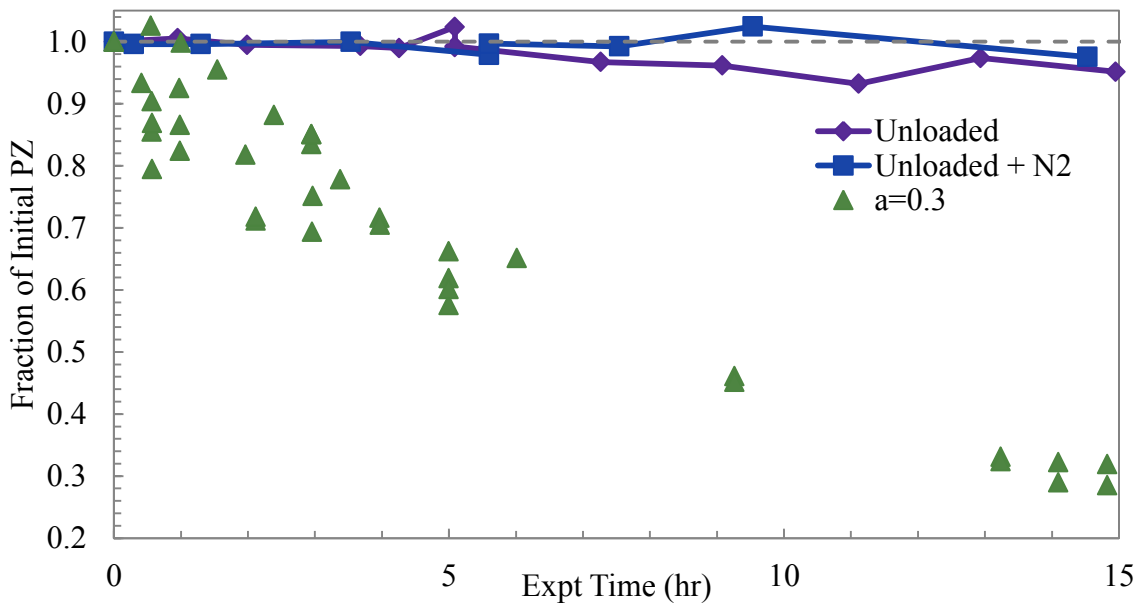


Figure 6.55: Comparison of PZ loss for degradation at 175 °C for unloaded 8 m PZ, unloaded and N_2 -purged 8 m PZ, and 8 m PZ with 0.3 mole CO_2 per mole alkalinity

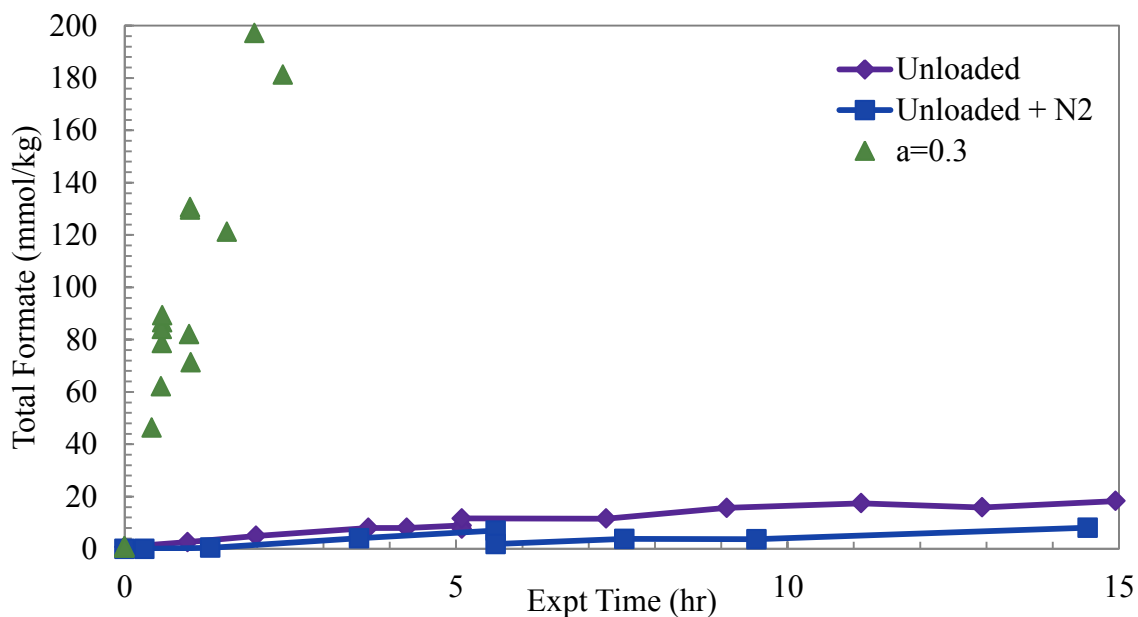


Figure 6.56: Generation of total formate in degradation at 175 °C for unloaded 8 m PZ, unloaded and N₂-purged 8 m PZ, and 8 m PZ with 0.3 mole CO₂ per mole alkalinity

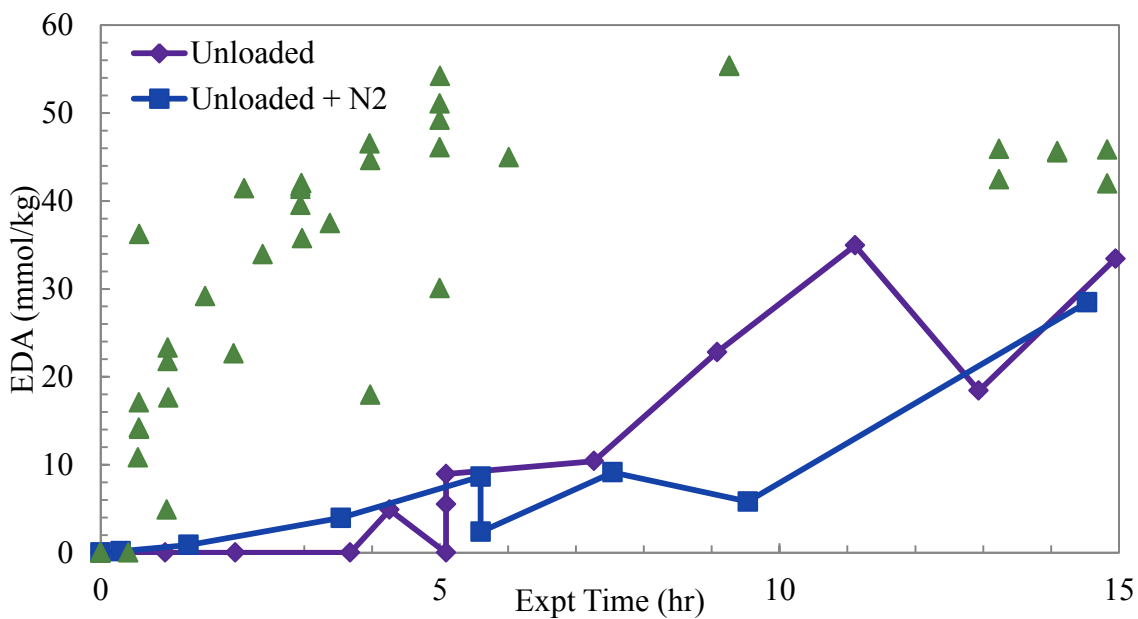


Figure 6.57: Generation of EDA in degradation at 175 °C for unloaded 8 m PZ, unloaded and N₂-purged 8 m PZ, and 8 m PZ with 0.3 mole CO₂ per mole alkalinity

A second important observation can be made from the EDA data in Figure 6.57. The generation of EDA between the standard and N₂-purged experiments is nearly identical, indicating the lack of O₂ and CO₂ in the headspace did not affect EDA formation. As detailed in previous sections, it is believed that EDA generation is due to the action of the H⁺PZ molecule and is separate from the formate generation mechanism. In these experiments, the concentration of H⁺PZ and, therefore, the production of EDA, should not have been affected by the presence or lack of O₂ or CO₂ in the headspace.

The PZ loss for 8 m PZ with 0.3 mole CO₂ per mole alkalinity with a N₂ purged headspace is compared to a standard experiment in Figure 6.58. The standard data are collated points from repeated experiments on 8 m PZ with 0.3 mole CO₂ per mole alkalinity degraded at 175 °C. The PZ loss is close between the two sets of data except for a slight deviation at the latter time points. After seven weeks, the loss of PZ in the N₂ experiment is less than the CO₂-loaded experiment. Again, this indicates that a lack of O₂ does decrease the loss of PZ during thermal degradation significantly.

The generation of total formate and EDA are compared in Figure 6.59 and Figure 6.60, respectively. The concentration of total formate is the same between the standard and N₂ experiments, while the EDA concentration is slightly increased the N₂ case. This is not expected given the decreased PZ loss. The reaction of EDA with CO₂ to form 2-Imid may be impacted and slowed by the reaction mixture present in the N₂ experiment. If that reaction were slowed by the lack of O₂ in some way, EDA would be allowed to accumulate to slightly higher concentrations than would be expected in a standard experiment. If O₂ typically activates or accelerates various mechanisms during degradation, the EDA/2-Imid equilibrium may rely on the presence of another species that is at a lower concentration due to the lack of O₂.

The N₂-purged experiments demonstrated that the presence of O₂ in the headspace of the thermal degradation experiments has a slight, but noticeable effect of PZ loss and the generation of degradation products in the absence of CO₂. The degradation mechanisms are not dependent on the presence of O₂ and are only minimally enhanced by O₂. It is not surprising that O₂ is reactive at these extreme temperatures. A likely hypothesis is that the small initial concentration of O₂ present from the headspace and any dissolved O₂ in solution react with the metal surfaces or dissolved metals in solutions through free radical mechanisms. Once the O₂ molecules are used up, the effect is lost and rates proceed as they would in the absence of O₂. Changes in the initial degradation rates were not directly observed in the aforementioned experiments, as would be expected with this hypothesis, but the expected error of the analytical tools would likely preclude this observation with the given data sets.

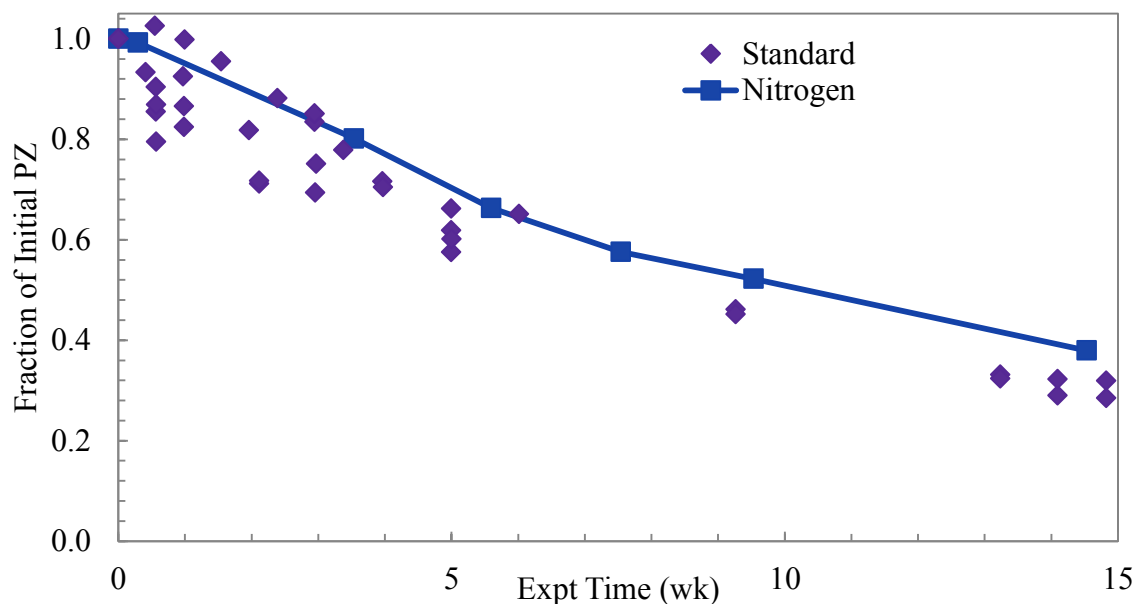


Figure 6.58: Comparison of PZ loss in degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 175 °C with a standard or N₂ headspace

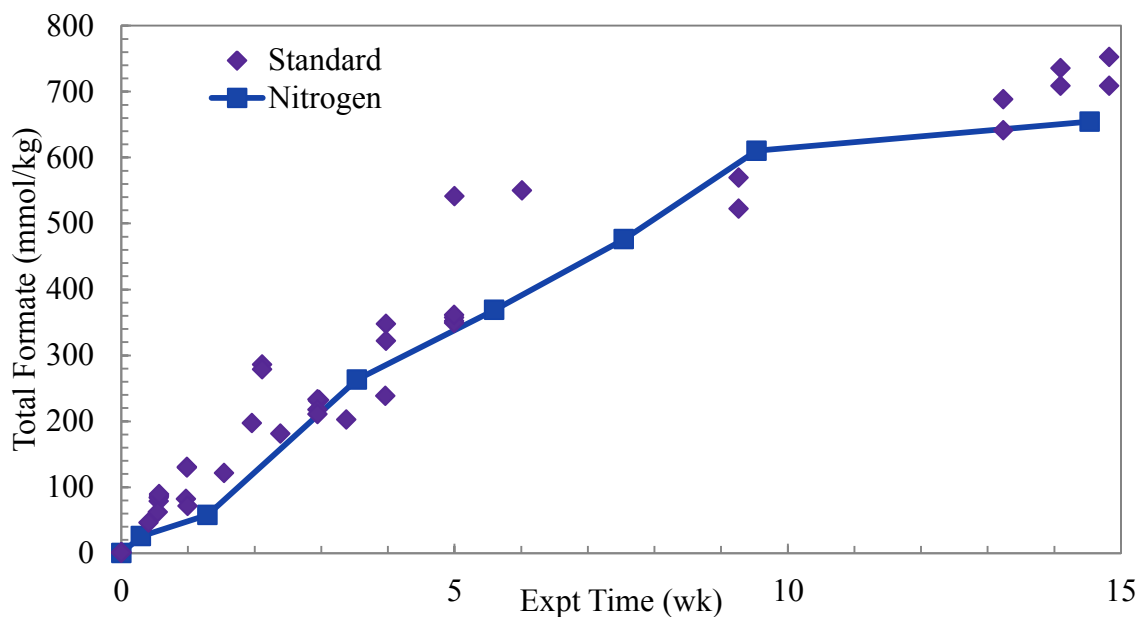


Figure 6.59: Generation of total formate in degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 175 °C with a standard or N₂ headspace

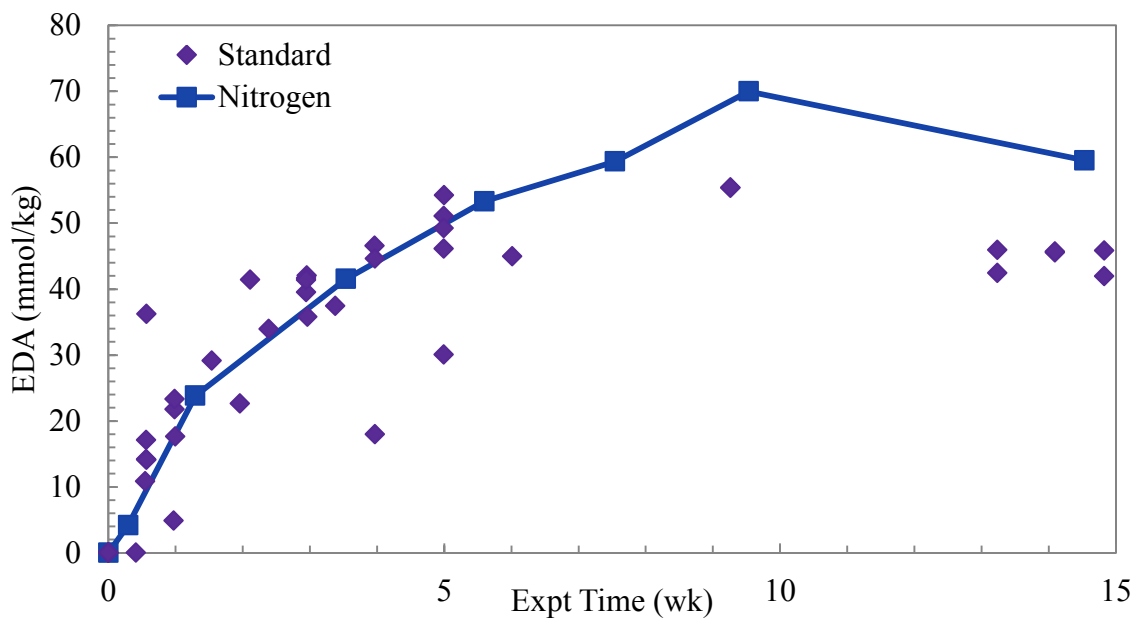


Figure 6.60: Generation of EDA in degradation of 8 m PZ with 0.3 mole CO₂ per mole alkalinity at 175 °C with a standard or N₂ headspace

6.7 CONCLUSIONS

The most abundant degradation products of thermally degraded 8 m PZ are N-formyl PZ (FPZ), ammonium (NH_4^+), and N-(2-aminoethyl)PZ (AEP). These molecules account for 57% of nitrogen and 45% of carbon lost during degradation as PZ and CO_2 . Other prominent products include, in order of decreasing impact on the nitrogen and carbon balance, 2-imidazolidone (2-Imid), N-(2-hydroxyethyl)piperazine (HEP), N-ethylpiperazine, ethylenediamine (EDA), 1-Methylpiperazine (1-MPZ), formate, acetate, and other heat stable salts (glycolate and oxalate) in small concentrations.

After 20 weeks of thermal degradation at 165 °C, 74% and 63%, respectively, of the nitrogen and carbon lost in the form of PZ and CO_2 was recovered in the form of quantifiable degradation products. For the same experiment, 87% and 60% of the lost CO_2 molecules and “ethyls” were recovered.

In the first step of the mechanism, 1-[2-[(2-aminoethyl) amino]ethyl] PZ (AEAEPZ) is believed to be formed from a ring opening $\text{S}_{\text{N}}2$ reaction of PZ with H^+PZ . The limiting rate was found to require protonated amine, but not CO_2 , which agrees with the proposed production of AEAEPZ from H^+PZ and PZ. Degradation of concentrated PZ in the presence of HCO_3^- demonstrated that PZ loss and generation of formate and EDA depend on the presence of H^+PZ to proceed. In the presence of CO_2 , AEAEPZ is expected to react to form its internal urea. Both molecules, AEAEPZ and its urea, are suspected to play major roles in thermal degradation pathways for concentrated PZ.

At 150 °C, EDA is in equilibrium with 2-Imid, the internal urea of EDA. The equilibrium constant, K_{EQ} , tends toward a value between 0.0004 and 0.0006 kg solution per mole.

Degradation of acidified PZ was shown to mimic what would occur in the absence of CO_2 and explained some behavior of the EDA generation mechanism. EDA

accumulates in the absence of CO₂ because it does not react to form the more preferred 2-Imid structure. CO₂ is not required in the degradation mechanism that generates EDA. EDA generation is not directly dependent on either PZ or H⁺PZ concentration.

NMR analysis of degraded ¹³CO₂-loaded PZ solutions conclusively showed that formate is generated directly from the CO₂ in solution. The mechanism is not clear at this point. Formate is not generated from the break-up of the PZ backbone itself. Formate is generated consistently as a major product in all oxygen-poor, CO₂ loaded amine thermal degradation where carbamate polymerization is not the major degradation mechanism.

During thermal degradation from 135 to 175 °C, and oxidation at 55 °C, formyl amides are in equilibrium with formate. Formyl amides were consistently produced at higher concentrations than formate. The ratio of formyl amides to formate produced was a strong function of PZ concentration and CO₂ concentration, but not temperature. For 8 m PZ from 55 to 175 °C, the ratio can be described as follows where the CO₂ loading, α , is in units of mole CO₂ per mole alkalinity (Equation 6.24). For 20 m PZ at 175 °C, the ratio can be described as follows (Equation 6.25).

$$\frac{C_{FA}}{C_F} = 5.54 \times \alpha + 0.30 \quad (6.24)$$

$$\frac{C_{FA}}{C_F} = 7.73 \times \alpha + 3.10 \quad (6.25)$$

The oxygen present as dissolved oxygen or in the headspace of the thermal cylinders was found to have a minimal effect that could not account for all quantified formate and formyl amides generated in typical thermal degradation experiments.

Chapter 7 – Thermal Degradation of Structural Analogs of Piperazine and Substituted Piperazines

The thermal degradation of structural analogs of PZ, substituted PZs, and PZ blends were explored in this chapter. Structural analogs of PZ were examined in an effort to understand the thermal stability of PZ. Substituted PZs were investigated as potential new solvents with advantageous characteristics for CO₂ capture applications. Blends of PZ with substituted PZs were also studied as a new solvent system with advantageous thermal equilibrium characteristics. Portions of this chapter are excerpted from a previous article (Freeman and Rochelle, 2011).

7.1 STRUCTURAL ANALOGS OF PIPERAZINE

One of the most important advantages of concentrated PZ over other well-studied, baseline alkanolamine solvents such as monoethanolamine (MEA), 2-amino-2-methyl-1-

propanol (AMP), or methyldiethanolamine (MDEA) is its exceptional resistance to thermal degradation. PZ has been found to be resistant to degradation up to 150 °C, well above the standard stripper operating conditions, as demonstrated in Chapter 5 of this dissertation and previously (Freeman et al., 2010a). At temperatures above 150 °C, PZ begins to degrade at rates similar to alkanolamines at temperatures between 100 and 135 °C.

The structural reasons for the resistance of PZ to thermal degradation is not clear when analyzing the degradation data obtained previously. PZ is 6-membered ring with two secondary amino functions. Six-membered cyclic alkanes are known to be stable due to minimized angle or torsional strain and six-member heterocycles, such as PZ, would benefit as well (McMurry, 2000). PZ does not have an alcohol function, which is known to enhance thermal degradation through well understood pathways (Davis, 2009; Dawodu and Meisen, 1996; Kennard and Melsen, 1985). It is also lacking any steric hindrance from alkane or hydroxyl groups on the amine or α -carbon that would interfere with reactions at the position of the amino function. The library of thermal degradation data available in literature includes studies on primary amines, secondary amines, tertiary amines, alkanolamines, hindered amines, long-chain amines, and other amines of interest to CO₂ capture applications. Despite the wide range of degradation data available, it is difficult to draw conclusions about the structural strength of PZ.

Thermal degradation of seven structural analogs of PZ was performed to determine the structural characteristics that provide thermal resistance. The structures of PZ, piperidine (PD), morpholine (Mor), pyrrolidine (Pyr), hexamethyleneimine (HMI), homopiperazine (HomoPZ), ethylenediamine (EDA), and hexamethylenediamine (HMDA) are shown in Figure 7.1. The molecules are arranged to demonstrate the comparisons developed in this paper. The effect of changing a secondary heteroatom,

ring size in monoamines, ring size in diamines, and methylene chain length are each analyzed using thermal degradation data. Thermal degradation data for EDA was taken from the work of Shan Zhou (Zhou et al., 2010). The first order rate, k_1 , constant analysis developed in section 5.2 will be used for comparison. The k_1 was calculated using the entire time series of data, unless otherwise indicated. When comparisons are made to 8 molal (m) PZ with 0.3 mole CO_2 per mole alkalinity, the data shown are collated from three separate, repeated experiments.

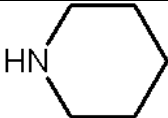
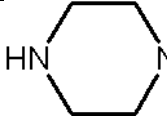
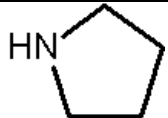
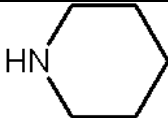
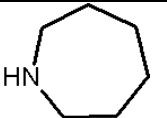
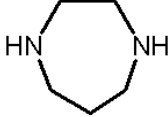
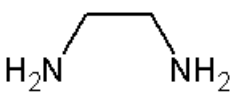
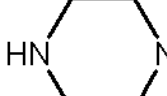
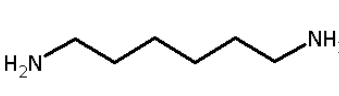
COMPARISON	Molecules Investigated		
Secondary Heteroatom	 Piperidine (PD)	 PZ	 Morpholine (Mor)
Ring Size in Monoamines	 Pyrrolidine (Pyr)	 Piperidine (PD)	 Hexamethyleneimine (HMI)
Ring Size in Diamines	 PZ	 Homopiperazine (PZ)	
Methylene Chain Length	 Ethylenediamine (EDA)	 PZ	 Hexamethylenediamine (HMDA)

Figure 7.1: Structures of amines investigated in thermal screening

7.1.1 Effect of second heteroatom in 6-member ring

The effect of changing the heteroatom in a six-member ring containing one amino function was investigated by degrading 8 m PD, 8 m PZ, and 8 m Mor with 0.3 mole CO₂ per mole alkalinity at 175 °C. This analysis compares the degradation rate achieved when the methylene group in the 4 position on PD is changed to an amino group (PZ) or oxygen (Mor). The fraction of the initial amine remaining after degradation at 175 °C is shown in Figure 7.2. Data were fit with an exponential regression and the calculated k_1 value is shown for each amine. For all three amines, total formate was a dominant degradation product and is compared in Figure 7.3.

Mor and PD both degraded more slowly than PZ. These are the first amines to be found to be more thermally stable than PZ, although Mor has been previously identified as thermally stable (Davis, 2009). The presence of a second amino function in the 6-member ring increases the thermal degradation rate of PZ. The k_1 value of PD, $8.41 \times 10^{-8} \text{ s}^{-1}$, is 1.7 times that of Mor, $4.97 \times 10^{-8} \text{ s}^{-1}$, while the k_1 of PZ, $1.32 \times 10^{-7} \text{ s}^{-1}$, is over 2.6 times that of Mor. The presence of multiple amino functions allows for more nucleophilic attack which increases degradation. This is especially important since PZ is unique in that even when PZ has reacted with CO₂ to form protonated PZ (H⁺PZ) and PZ carbamate (PZCOO⁻), there is another amino group that can be an attacking nucleophile or be subject to nucleophilic attack. The concentration of total formate in the PD and Mor experiments is half of that produced in the PZ experiments. The raw CO₂ concentration in the PZ experiment was double that of the other experiments due to the definition of CO₂ loading and directly caused the doubling of total formate generation.

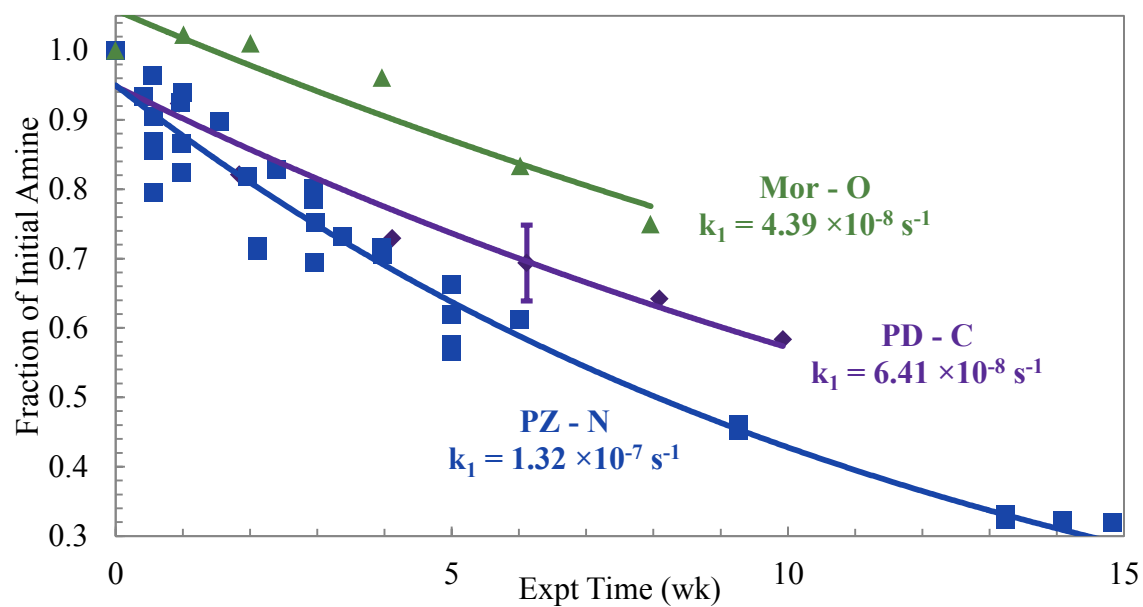


Figure 7.2: Amine loss in thermal degradation of 6-membered rings with varying heteroatoms at 175 °C

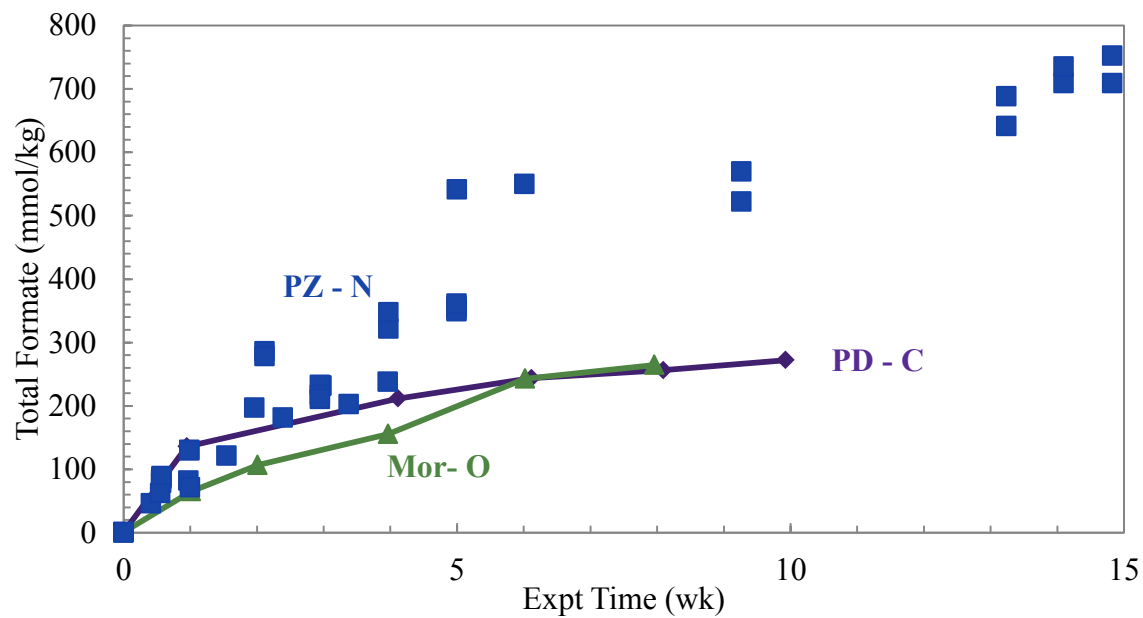


Figure 7.3: Production of total formate in thermal degradation of 6-membered rings with varying heteroatoms at 175 °C

The pK_a values for the amines studied in this paper are shown in Table 7.1. The pK_a values reported for PD, PZ, and Mor in Table 7.1 indicate that PZ has an intermediate base strength with PD having the highest pK_a for the amino group. From the low pK_a value of Mor, it was expected that it would act as a weak attacking group and have a lower degradation rate than PZ. Although PD has a higher pK_a than PZ, indicating it is a stronger base, the higher degradation rate in PZ is likely just due to the additional amino function available for nucleophilic attack reactions whereas PD has a portion of its molecules tied up as protonated PD (H^+PD) and PD carbamate ($PDCOO^-$) after reaction with CO_2 .

Table 7.1: pK_a values at 298 K

Molecule	$pK_{a,1}$	$pK_{a,2}$	Reference ^b
PD	11.22	-	S
PZ	9.71 - 9.73	5.33 - 5.41	Ha, He, K
Mor	8.36	-	H, Pa
Pyr	11.12-11.27	-	AS, S
HMI	11.07	-	Pe
HomoPZ ^a	10.09	6.67	Pa
1-MPZ	9.14	4.63	K
2-MPZ	9.57	5.24	K

^a Values listed for HomoPZ are at 303 K

^b Reference: AS = (Albert and Serjeant, 1971); H = (Hall, 1956); Ha = (Hamborg and Versteeg, 2009); He = (Hetzer et al., 1968); K = (Khalili et al., 2009); Pa = (Pagano et al., 1961); Pe = (Perrin, 1965); S = (Searles et al., 1956)

7.1.2 Effect of ring size in monoamines

The effect of ring size on thermal degradation of a monoamine was investigated by degrading 8 m Pyr, 8 m PD, and 8 m HMI with 0.3 mole CO_2 per mole alkalinity at 175 °C. The fraction of the initial amine remaining after 10 weeks at 175 °C is compared in Figure 7.4. An exponential regression was fit to each set of data and the calculated k_1 values are shown. For Pyr and HMI, where the degradation rate is clearly more than first

order in amine concentration, the k_1 was calculated using only the first week of data and should be considered an apparent k_1 . For all three amines, total formate was one of the dominant degradation product identified and the concentration is compared in Figure 7.5.

The most thermally stable amine of the three, as expected, is the six-membered PD. It is well known that 5- and 7-membered rings are not as stable as 6 membered rings and the thermal stability of these amines follows suit. Comparing the simplest cyclic alkanes, cyclopentane, cyclohexane, and cycloheptane, cyclohexane is considered to be free of strain while the cyclopentane and cycloheptane have 6.2 and 6.1 kcal/mol of torsional strain, respectively (McMurry, 2000). In amine heterocycles, the 7-membered HMI appears to be the least stable, losing nearly all the initial amine after one week of degradation compared to only 55% and 8% loss of Pyr and PD, respectively.

The production of total formate (Figure 7.5) does not track with the amount of amine lost for each despite having the same CO_2 concentration. PD produced the most formate while the least amount of amine was lost. Degraded solutions of both Pyr and HMI were found to contain polymeric substances. This was not observed thermally degraded PD or PZ. The mechanism for thermal degradation is certainly quite different from previous amines studied and the presence of polymeric substances after degradation does not lend itself for further study in the field of CO_2 capture.

7.1.3 Effect of ring size in diamines

The effect of ring size on thermal degradation of a diamine was investigated by thermally degrading 8 m PZ and 8 m HomoPZ with 0.3 mole CO_2 per mole alkalinity at 175 °C. The loss of amine and production of total formate is shown in Figure 7.6 and Figure 7.7. HomoPZ degrades rapidly in comparison with PZ, losing 98% of the initial amine within 4 weeks while PZ loses only 30%. Total formate is a dominant degradation

product for both amines, but in HomoPZ it is an intermediate. All previous work on PZ showed steady increases of total formate, indicating it was a final product of degradation (Freeman et al., 2010a).

The addition of one methylene group to a PZ molecule (HomoPZ) weakens the structure and the thermal resistance seen in PZ is lost. The degradation also proceeds through a different mechanism, as demonstrated by the presence of formate and formyl amides as intermediates, rather than final products. Although there are few data points in the region where HomoPZ is initially being degraded, the data indicates that the reaction is not first order in amine, as has been hypothesized for PZ thermal degradation (Freeman et al., 2010a).

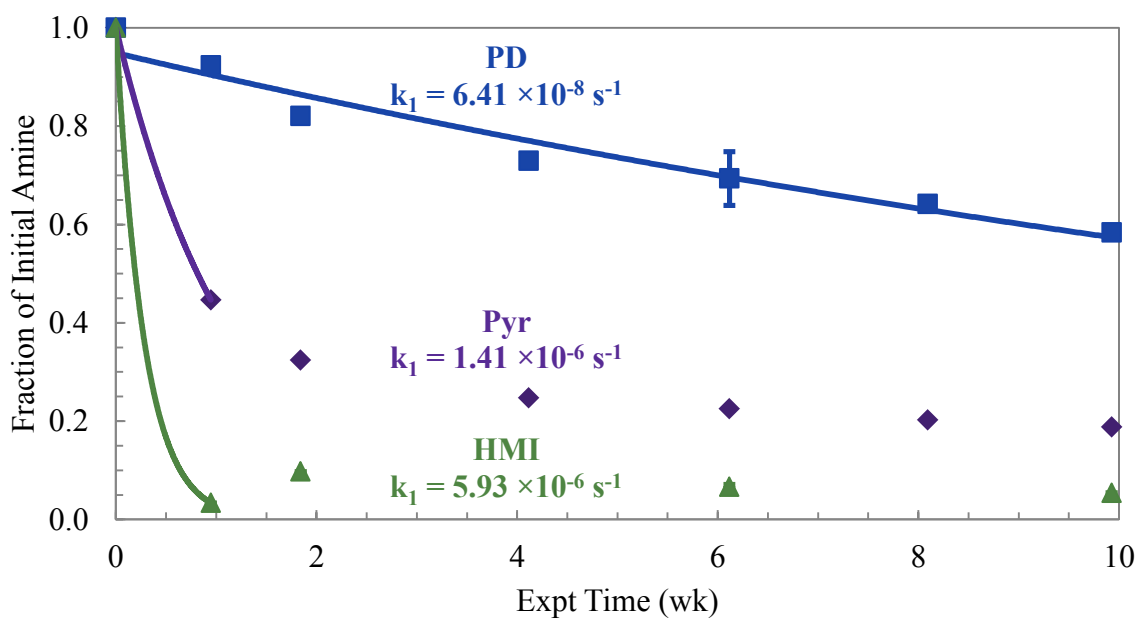


Figure 7.4: Amine loss in thermal degradation of monoamines at 175 °C

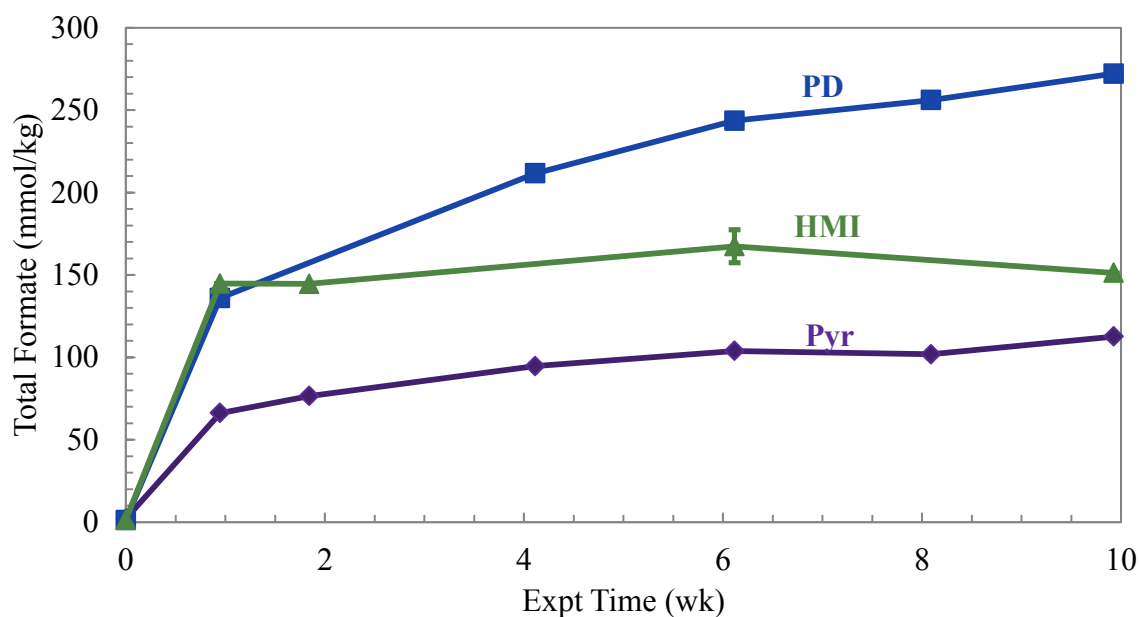


Figure 7.5: Production of total formate in thermal degradation of monoamines at 175 °C

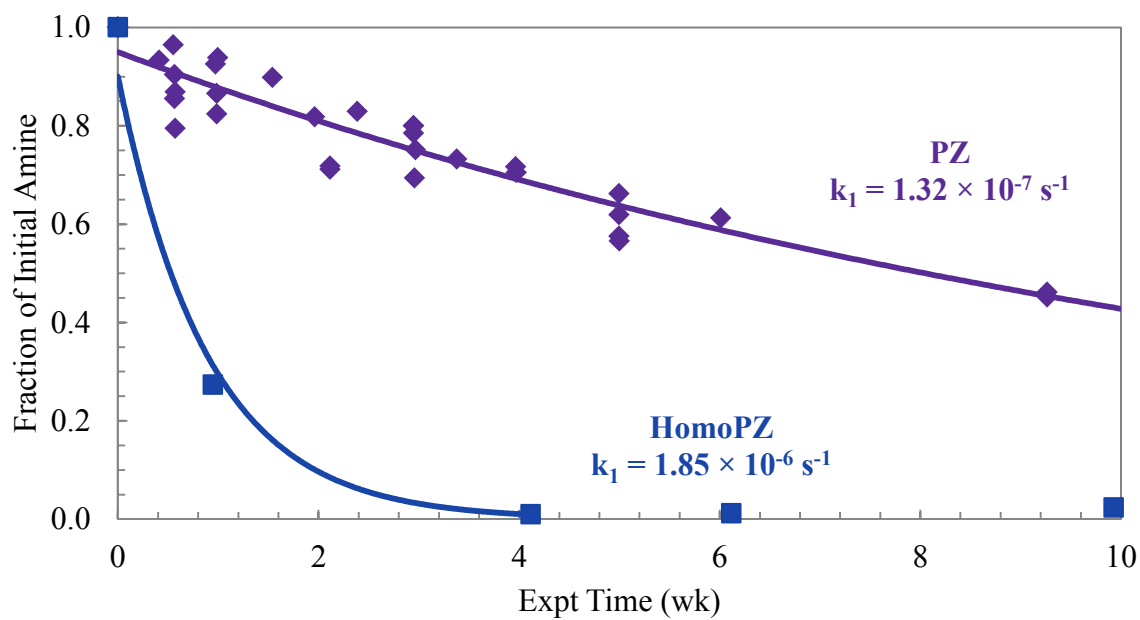


Figure 7.6: Amine loss in thermal degradation of diamines at 175 °C

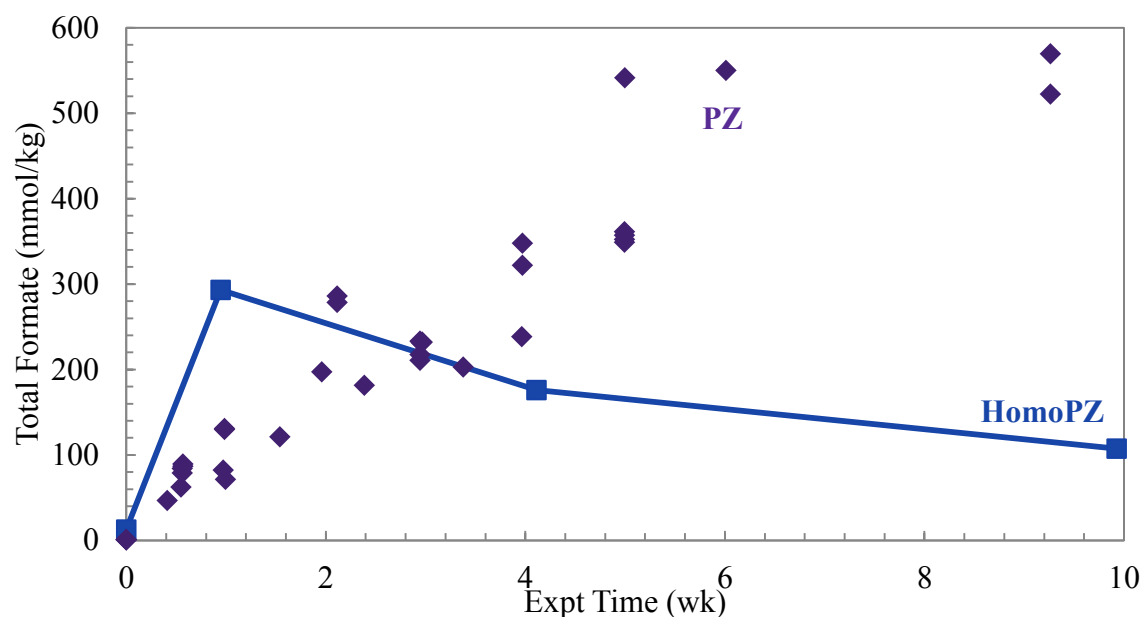


Figure 7.7: Production of total formate in thermal degradation of diamines at 175 °C

7.1.4 Effect of methylene chain length

The effect of methylene chain length on thermal stability of amines was investigated by degrading 8 m PZ and 8 m HMDA with 0.3 moles CO₂ per mole alkalinity at 175 °C. The thermal degradation of concentrated EDA was also investigated previously by Zhou and Eide-Haugmo (Eide-Haugmo et al., 2011; Zhou et al., 2010). The EDA data collected at various CO₂ loadings and lower temperatures due to the instability of EDA. Zhou (2010) investigated 8 m EDA with 0.2 or 0.4 mole CO₂ per mole alkalinity at 135 °C (Zhou et al., 2010). The study of Eide-Haugmo investigated 7.13 m EDA with 0.25 moles CO₂ per mole alkalinity degraded at 135 °C (Eide-Haugmo et al., 2011). Due to the differences in CO₂ concentration and temperature, the three amines will be analyzed using k_1 values alone, rather than the raw concentration data in order to understand the overall degradation effects.

Previous work on structural analogs of MEA found that amine stability was dependent on the stability of or inability to create the initial oxazolidone ring product (Davis, 2009). Davis found that increasing the length of the amine, and therefore, the ring size of the initial oxazolidone product, decreased degradation rates and prevented the carbamate polymerization pathway from proceeding past this initial product.

The k_1 values calculated from exponential regression of amine concentration data are compared in Figure 7.8 for all relevant data. PZ and HMDA demonstrate thermal stability compared to all three sets of EDA data. At 135 °C, where data overlaps, EDA degrades between 31 and 172 faster than PZ. HMDA is primarily stable because the internal urea that could be created with reaction with CO₂ would be an unstable 9-member ring. On the other hand, EDA can readily react with CO₂ to create the internal urea, 2-Imid (discussed in section 6.5). The cyclic structure of PZ prevents the formation of the internal urea of PZ, which would be too sterically strained to exist at significant concentrations. As with the conclusions of Davis, changes in amine structure that prevent the formation of stable or fast reacting intermediates slows overall thermal degradation rates.

7.2 METHYL-SUBSTITUTED PIPERAZINES

Four mono- and dimethyl substituted PZ structural analogs were analyzed for their thermal stability. The methyl-substituted PZs investigated were 1-methylpiperazine (1-MPZ), 1,4-dimethylpiperazine (1,4-DMPZ), 2-methylpiperazine (2-MPZ), and *trans*-2,5-dimethylpiperazine (t2,5-DMPZ), whose structures provided in Figure 7.9. Two enantiomers of 2-MPZ, (R)-(-)-2-MPZ and (S)-(+)-2-MPZ exist and the form used in this study was assumed to be a racemic mixture because it was not specified by the

manufacturer. The *trans* isomer of 2,5-DMPZ was used due to its availability compared to the *cis* isomer.

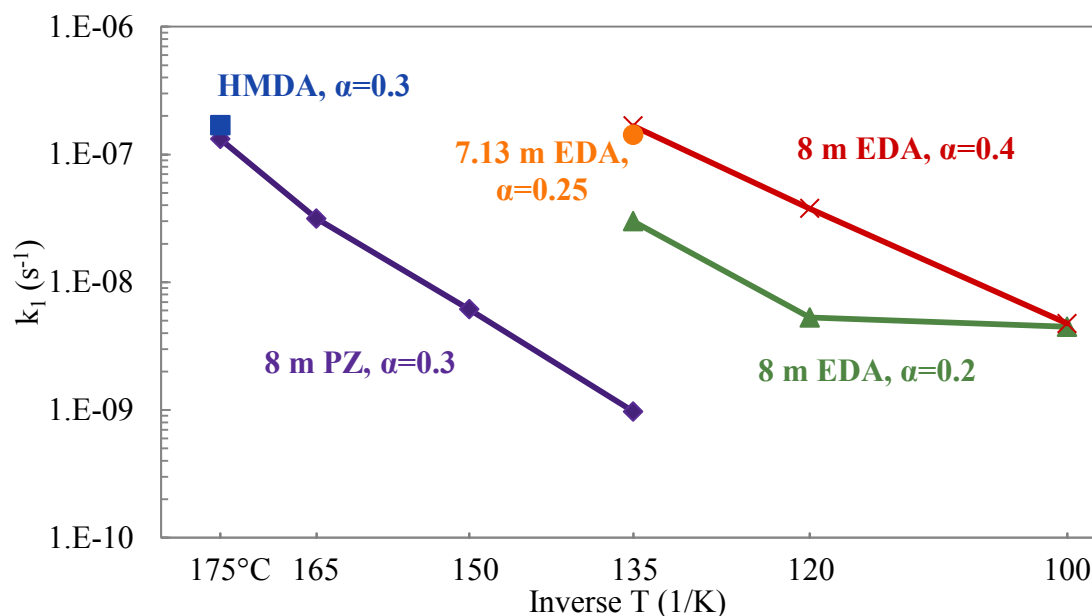


Figure 7.8: Comparison of k_1 values for thermal degradation of PZ, HMDA, and EDA from 100 to 175 °C

1-MPZ and 2-MPZ were both studied as 8 m solutions, and in a 4 m/4 m blend with PZ. 1,4-DMPZ was not studied alone or as a blend with PZ due to its inability to absorb CO₂. This amine was investigated as part of a blend of PZ, 1-MPZ, and 1,4-DMPZ that is discussed in detail in the next section. 2,5-DMPZ was studied as a 2 m solution, much lower than the other methyl-substituted amines, due to severe solubility issues and was studied in a 4 m /4 m blend with PZ. This blend also had solubility issues, but they were manageable using the same techniques used to investigate unloaded 8 m PZ.

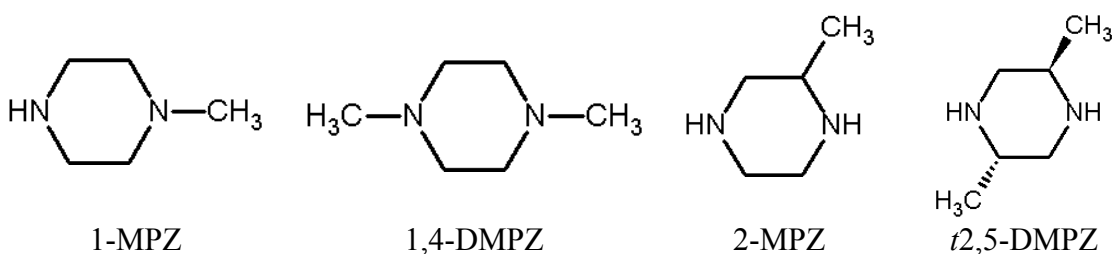


Figure 7.9: Structures of methyl-substituted PZs

Davis found that blending of amines caused more degradation of each constituent, in general (Davis, 2009). For example, when PZ is blended with another amine such as MEA or AMP, both the other amine and PZ are degraded faster than each alone. This has also recently been confirmed for blends of MDEA and PZ where degradation occurs at a ratio of one mole PZ alkalinity to one mole MDEA alkalinity until PZ is completely degraded (Closmann, 2011; Closmann et al., 2009). PZ is a strong nucleophile and can attack the other amines in solution and cause degradation outside of the usual pathways associated with MEA or AMP degradation. PZ can also attack itself, as it does in a solution by itself, but weaker nucleophiles such as MEA or AMP are more susceptible to PZ's attack, causing faster degradation for each than separate.

7.2.1 1-Methylpiperazine (1-MPZ) and PZ + 1-MPZ blend

The thermal degradation of 8 m 1-MPZ and 4 m PZ / 4 m 1-MPZ were studied at 150 °C. The loss of total starting amine in these experiments is compared with 8 m PZ with exponential regressions and the calculated k_1 values in Figure 7.10. For the blend, the sum of PZ and 1-MPZ at each time point is taken as a fraction of the initial total amine concentration to show the overall degradation during the experiment. The main degradation products of 1-MPZ degradation were found to be PZ, 1,4-DMPZ, formyl amides such as N-formyl PZ, and formate. Acetate and oxalate were found in very small, non-zero concentrations. Unfortunately, the blend experiment suffered from a large

percentage of failed cylinders so data was only obtained for the first 10 weeks. The main degradation products generated in the blend were formate, formyl amides, 1,4-DMPZ, and EDA. The generation of total formate and EDA are compared for degradation of PZ, 1-MPZ, and the blend in Figure 7.11 and Figure 7.12, respectively.

The effect of blending PZ with 1-MPZ in comparison to the thermal stability of the amines by themselves can be observed directly. Degradation occurs rapidly in the solution of 1-MPZ alone compared to both the blend and PZ alone. This is due to an equilibrium being established between PZ, 1-MPZ, and 1,4-DMPZ that is discussed in more detail in section 7.3 below. EDA was not produced in the degradation of 1-MPZ, which supports the presence of a separate, equilibrium mechanism that dominates reactions in this solution.

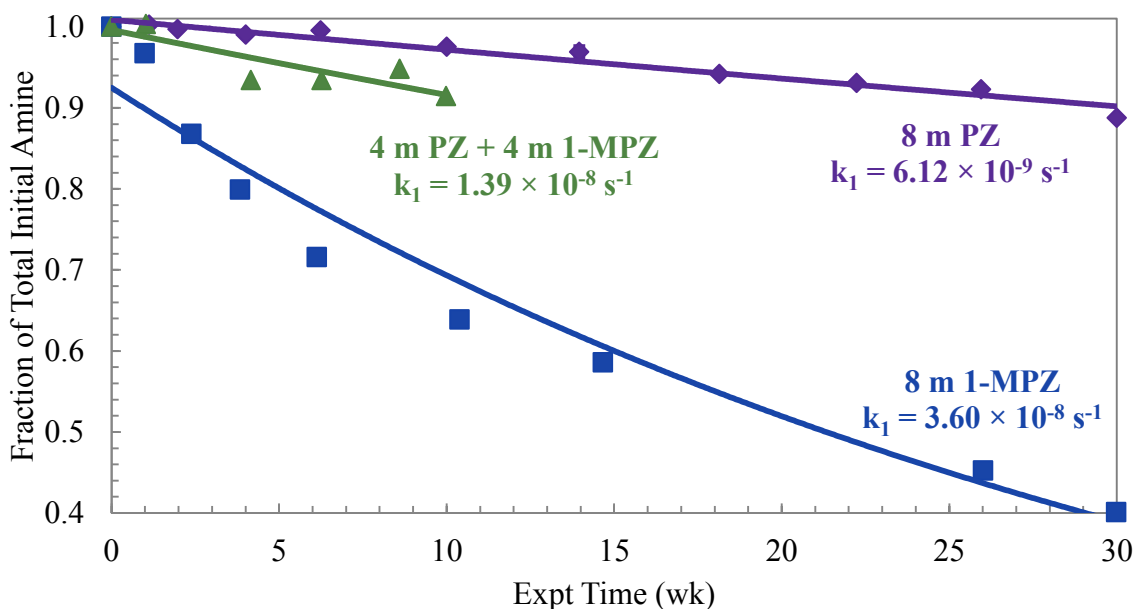


Figure 7.10: Total amine loss during degradation of 8 m PZ, 8 m 1-MPZ, and 4 m PZ + 4 m 1-MPZ blend at 150 °C

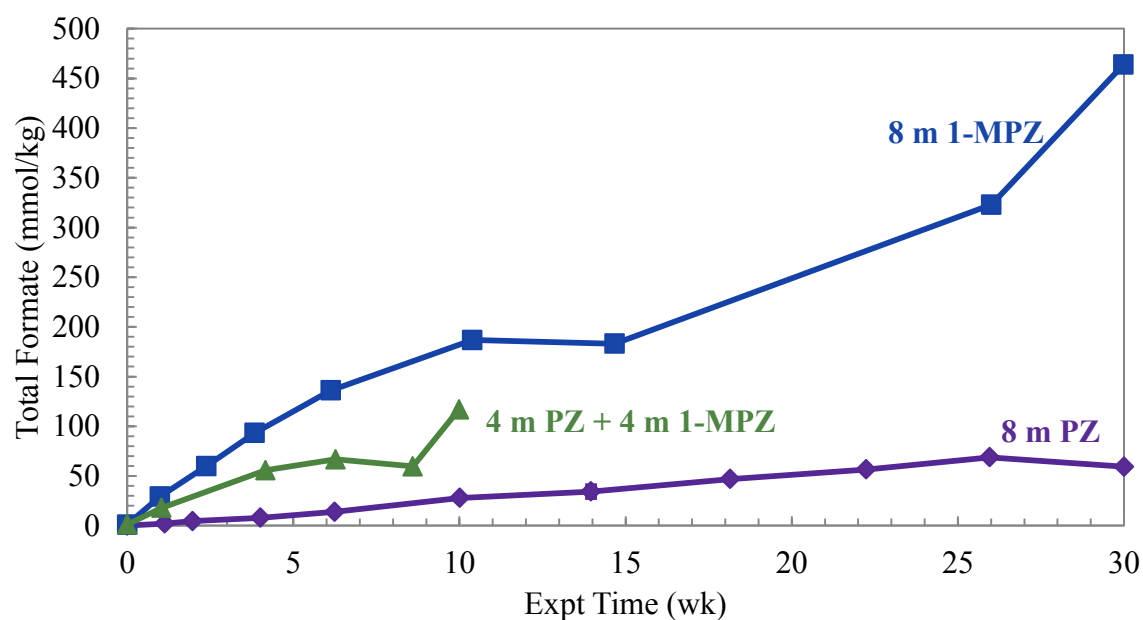


Figure 7.11: Generation of total formate in thermal degradation of 8 m PZ, 8 m 1-MPZ, and 4 m PZ + 4 m 1-MPZ blend at 150 °C

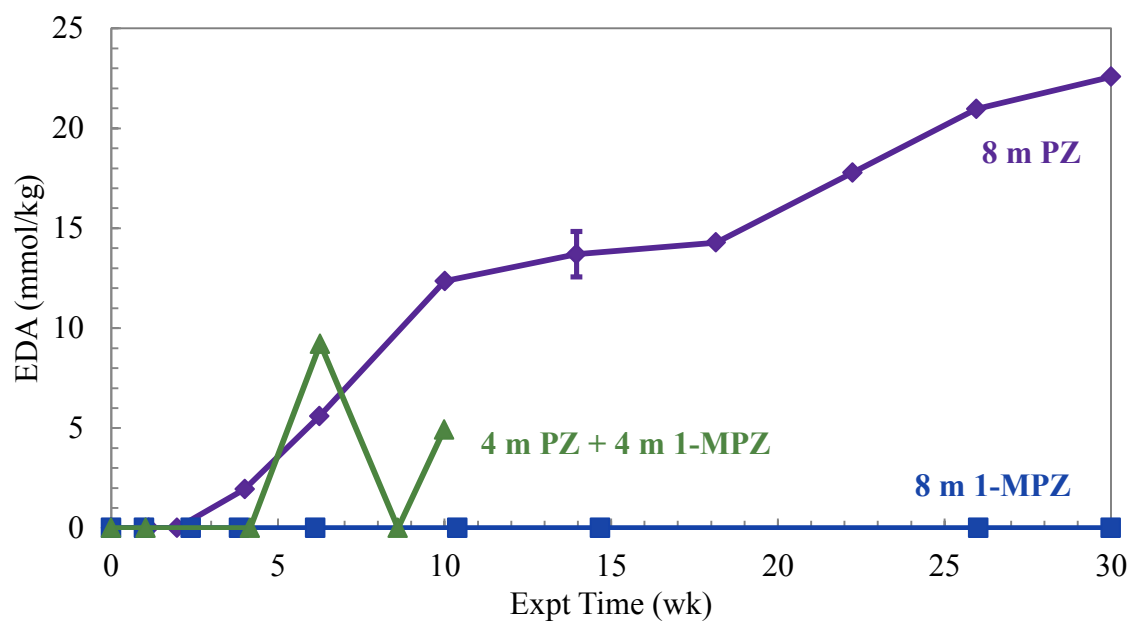


Figure 7.12: Generation of EDA in thermal degradation of 8 m PZ, 8 m 1-MPZ, and 4 m PZ + 4 m 1-MPZ blend at 150 °C

The recovery of carbon and nitrogen in the degradation of 1-MPZ was exceptionally good compared to traditional PZ degradation experiments because two major amine based degradation products were recovered and quantified (PZ and 1,4-DMPZ). The overall recovery of carbon during the experiment is shown in Figure 7.13 below. At the end of the experiment, 21% of the initial carbon as 1-MPZ was not recovered in the form of the products listed. The concentration of N-formyl PZ from the cation IC was used and no further addition to the mass balance was made from the formyl amides concentration since the specific speciation is not clear. Concentrations of oxalate, acetate, and EDA were not included in the figure. This closure of the carbon mass balance indicates the presence of a rapid equilibrium between 1-MPZ and its two major products: PZ and 1,4-DMPZ. This is a unique case of thermal degradation that has not been observed in other amines.

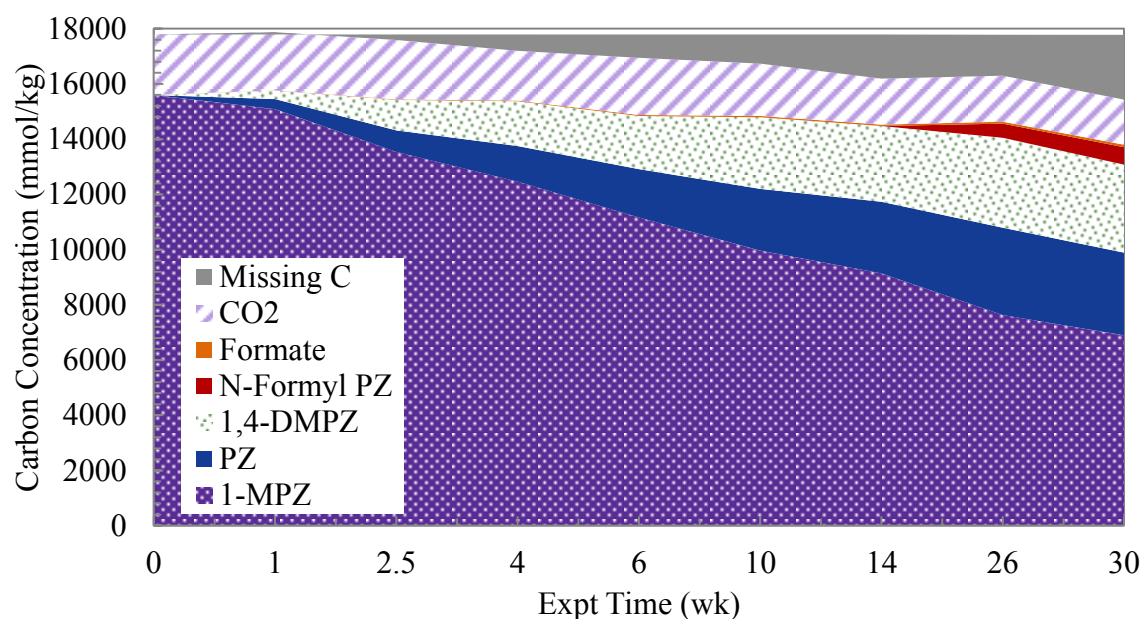


Figure 7.13: Carbon Mass Balance for 8 m 1-MPZ Degraded at 150 °C for 30 weeks

Although a unique equilibrium is being established, some conclusions can still be gleaned from the amine loss data. The fraction of amine remaining for each amine alone and in the blend is compared in Figure 7.14. The results are plotted as fraction of initial amine, despite the differences in starting concentration. The PZ results are difficult to interpret since little PZ is lost. The 1-MPZ data show that the loss of 1-MPZ is slower when blended than alone. This effect may be explained by the combination of two effects. First, the concentration is half that of when the amine is alone, 8 m versus 4 m 1-MPZ. Amine concentration is known to have a minimal effect on overall degradation rate for PZ, but the effect may be stronger in 1-MPZ systems. Secondly, the results could represent the nucleophilicity of 1-MPZ compared to other amines that have been blended with PZ. The presence of the methyl group on the amino function of 1-MPZ decreases the pKa, and therefore reactivity, of the molecule. The first and second pKa values for 1-MPZ are 9.14 and 4.63 compared to 9.73 and 5.35 for PZ (at 298K) (Khalili et al., 2009). When PZ undergoes a nucleophilic attack of 1-MPZ, this proceeds slower than when PZ is blended with MEA or AMP which it attacks readily. The decreased pKa of 1-MPZ makes it attractive for PZ to attack compared with attacking itself during thermal degradation of 8 m PZ.

7.2.2 2-Methylpiperazine (2-MPZ) and PZ + 2-MPZ

The thermal degradation of 8 m 2-MPZ and the blend of 4 m PZ + 4 m 2-MPZ were studied with 0.3 mole CO₂ per mole alkalinity at 150 °C. The loss of total initial amine in these experiments is compared with 8 m PZ in Figure 7.15. PZ and 2-MPZ were not able to be separated on the cation IC and the total area was calibrated with a PZ standard and reported as a single concentration. The k_1 values calculated with an exponential regression are included on the figure. The main degradation products of 2-

MPZ and blend degradation were EDA, formyl amides, and formate. The generation of total formate and EDA are compared for degradation of PZ, 2-MPZ, and the blend in Figure 7.16 and Figure 7.17, respectively. A standard of 2-methyl derivative of EDA, 1,2-diaminopropane, was tested on the cation IC and eluted near EDA, but was not identified as a dominant product for the thermal degradation of 2-MPZ.

The effect of blending PZ with 2-MPZ in comparison to the thermal stability of the amines by themselves can be observed directly. As with the previous comparison, the methylated PZ degrades faster than PZ alone while the blend falls in between. The generation of total formate increases with increased degradation, as expected. EDA is a contaminant in 2-MPZ solutions as it is present in initial samples containing 2-MPZ, but generation of EDA increases with further degradation.

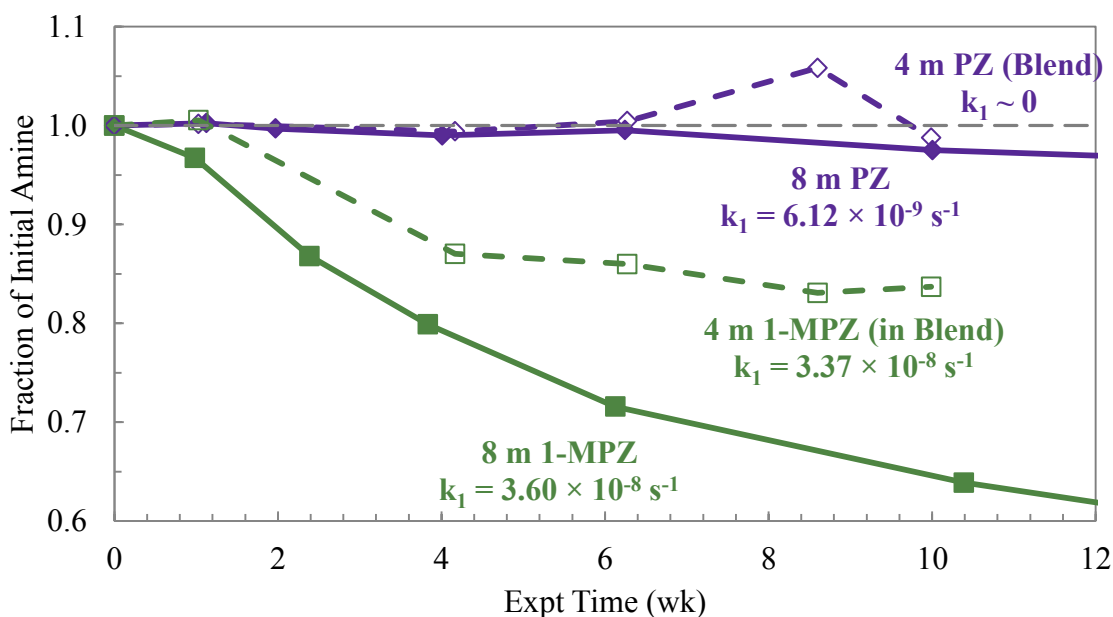


Figure 7.14: Loss of amine for degradation of PZ or 1-MPZ alone and in a 4 m PZ + 4 m 1-MPZ blend at 150 °C

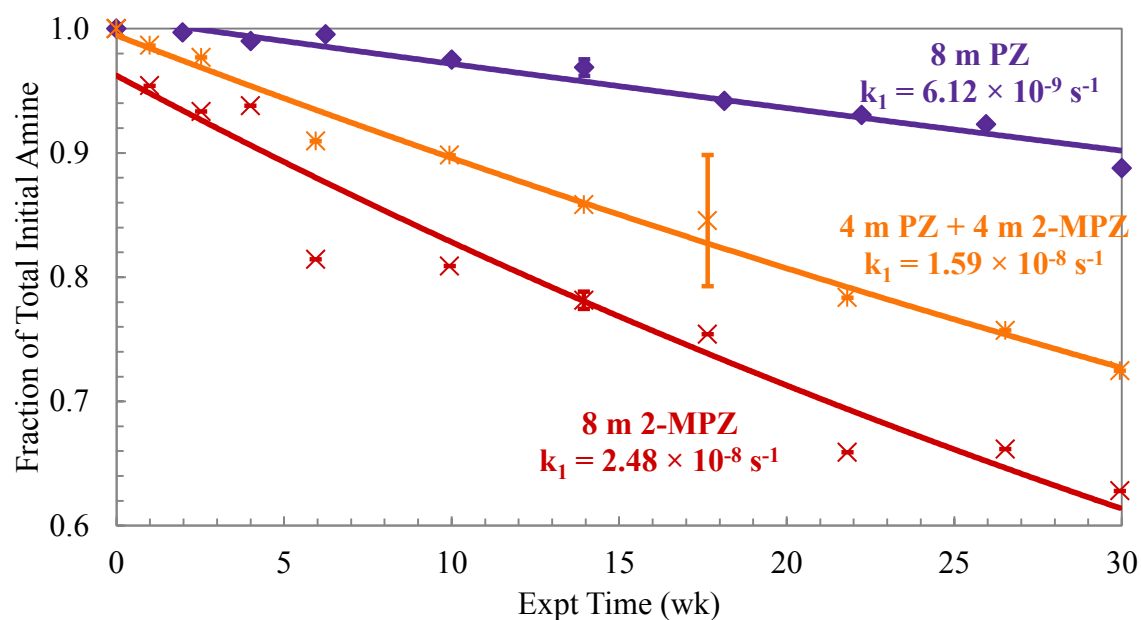


Figure 7.15: Total amine loss during degradation of 8 m PZ, 8 m 2-MPZ, and 4 m PZ + 4 m 2-MPZ blend at 150 °C

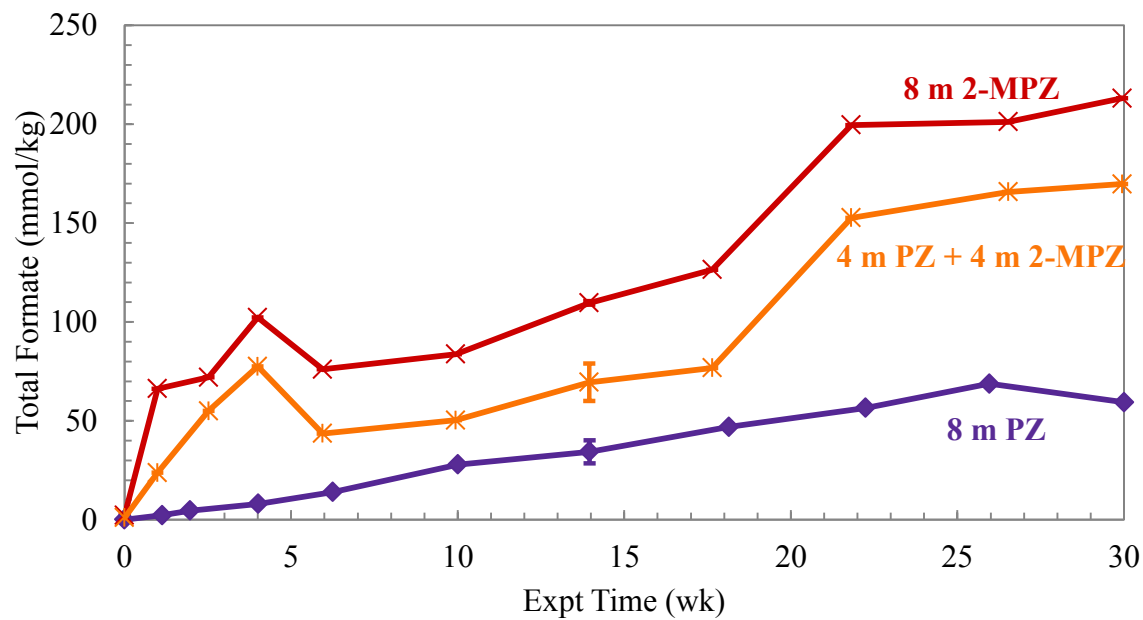


Figure 7.16: Generation of total formate in thermal degradation of 8 m PZ, 8 m 2-MPZ, and 4 m PZ + 4 m 2-MPZ blend at 150 °C

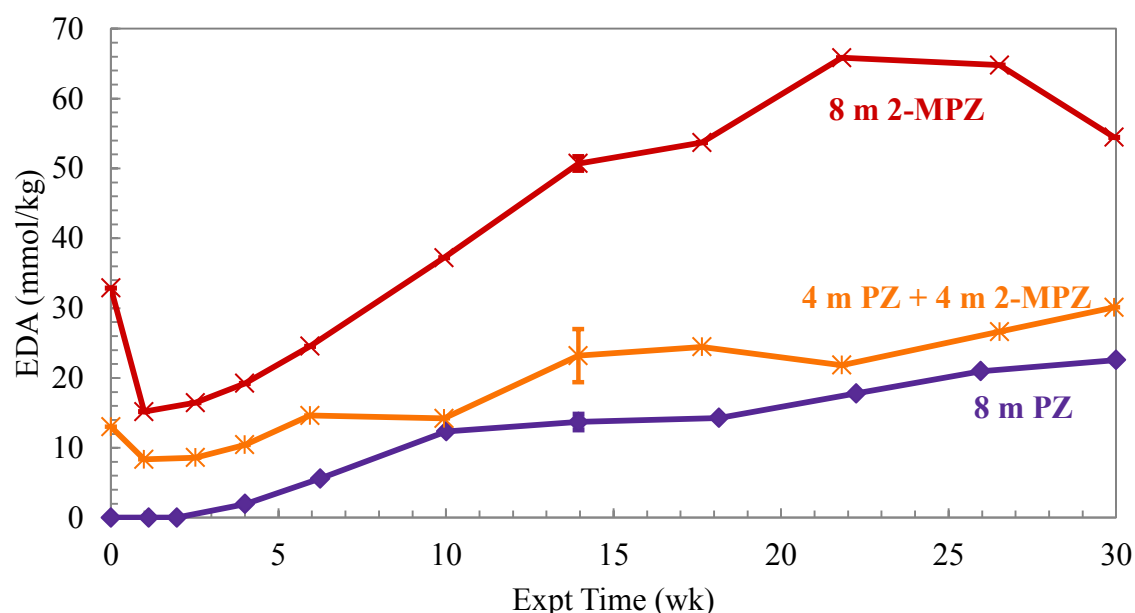


Figure 7.17: Generation of EDA in thermal degradation of 8 m PZ, 8 m 2-MPZ, and 4 m PZ + 4 m 2-MPZ blend at 150 °C

7.2.3 *trans*-2,5-Dimethylpiperazine (t2,5-DMPZ) and PZ + t2,5-DMPZ blend

The thermal degradation of 2 m t2,5-DMPZ and the blend of 4 m PZ + 4 m t2,5-DMPZ were studied with 0.3 mole CO₂ per mole alkalinity at 150 °C. The loss of total starting amine in these experiments fit with an exponential regression and compared with 8 m PZ in Figure 7.18. As with 2-MPZ, t2,5-DMPZ was not able to be separated on the cation IC from PZ and the total area was calibrated with a PZ standard and reported as a single concentration. The main degradation products of t2,5-DMPZ and blend degradation were EDA, formyl amides, and formate, as with previous methylated PZ experiments. The generation of total formate and EDA are compared for degradation of PZ, t2,5-DMPZ, and the blend in Figure 7.19 and Figure 7.20, respectively. There were additional peaks on the cation IC chromatogram that were not identified.

The k_1 data indicates that 2 m t2,5-DMPZ degrades 1.5 times faster than 8 m PZ while the blend is almost 3 times faster. This is the only comparison where the

methyated molecule was more stable than the blend, but this is likely due to the low concentration of t2,5-DMPZ. The generation of total formate and EDA behaved as expected, with higher rates of amine degradation producing higher concentrations of products. One exception was the t2,5-DMPZ case where EDA was rapidly generated, then maintained at an equilibrium concentration of 10 to 14 mmole per kg.

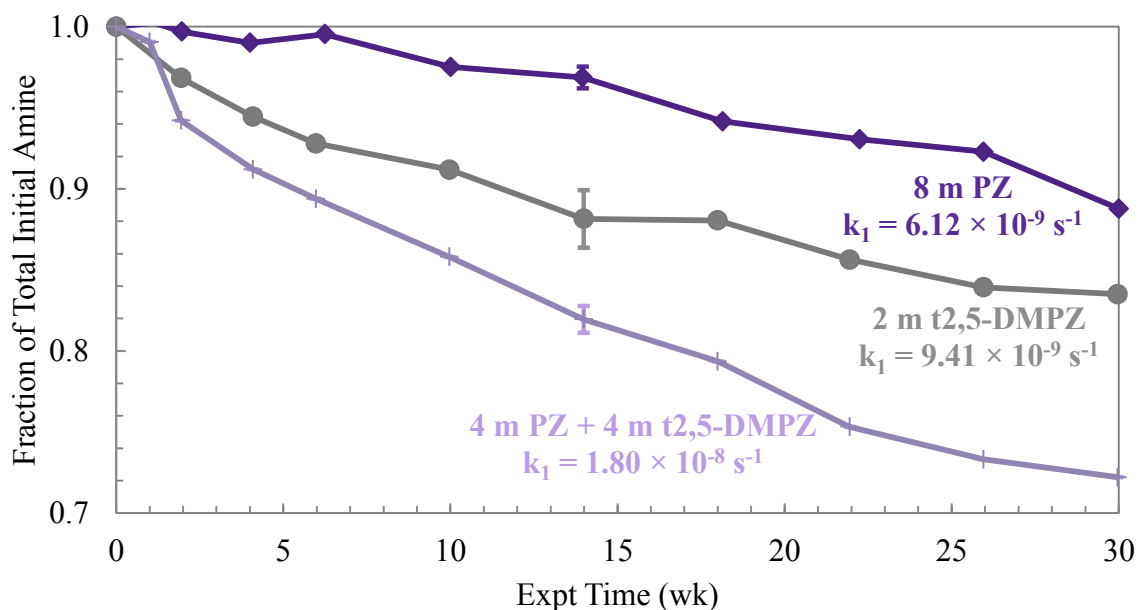


Figure 7.18: Total amine loss during degradation of 8 m PZ, 2 m t2,5-DMPZ, and 4 m PZ + 4 m t2,5-DMPZ blend at 150 °C

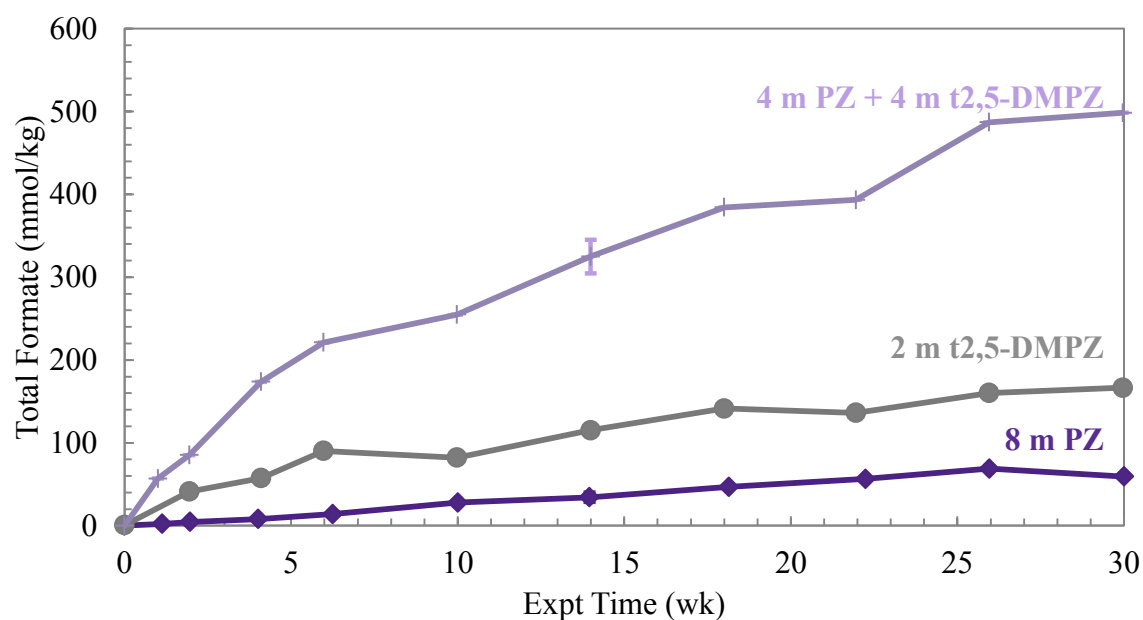


Figure 7.19: Generation of total formate in thermal degradation of 8 m PZ, 8 m t2,5-DMPZ, and 4 m PZ + 4 m t2,5-DMPZ blend at 150 °C

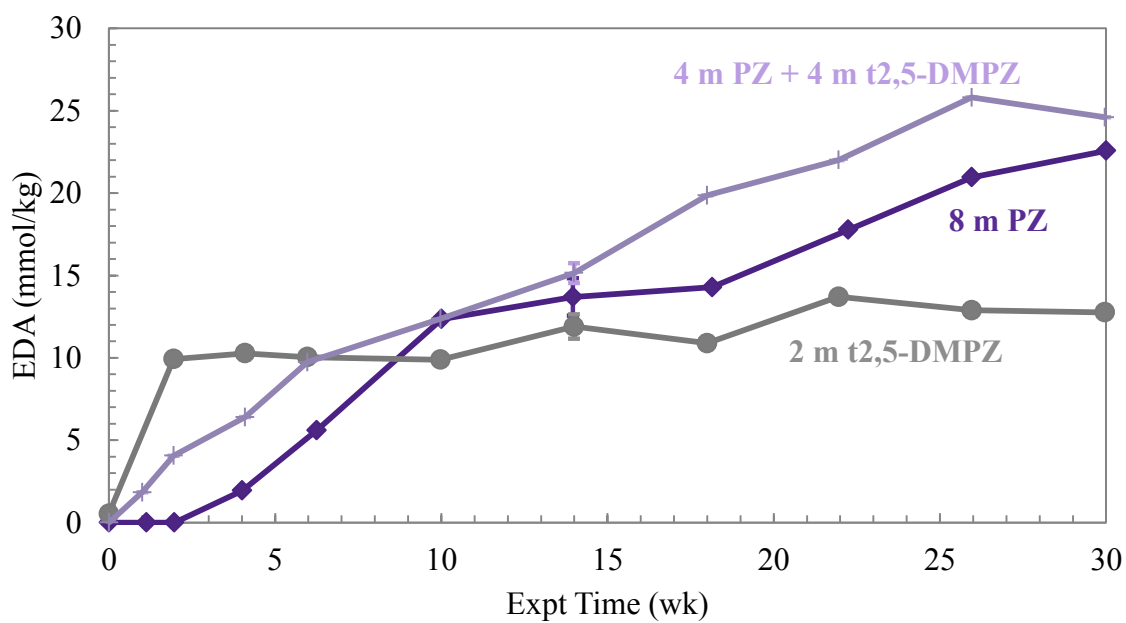


Figure 7.20: Generation of EDA in thermal degradation of 8 m PZ, 8 m t2,5-DMPZ, and 4 m PZ + 4 m t2,5-DMPZ blend at 150 °C

7.2.4 Effect of methyl substitution

The effect of methylation on PZ was assessed at 150 °C and a first order rate constant, k_1 , was regressed for all experiments. The addition of a methyl group at either the 1- or 2-position on PZ weakens the molecule to thermal degradation reactions. The data discussed in the previous section indicate that an amino methyl, rather than an α -methyl, enhances degradation, but a discussion of the 1-MPZ thermal equilibrium discussed in the following section negates this conclusion. Blending either 1-MPZ or 2-MPZ will decrease the thermal stability of PZ, although to a lesser extent than when blended with MEA, AMP, and MDEA (Closmann et al., 2009; Davis, 2009). Despite the degradation measured, the overall rate of degradation in blends of PZ with 1-MPZ and 2-MPZ is slow compared to other CO₂ capture solvents of interest and should prove to be valuable replacements for thermally instable solvents.

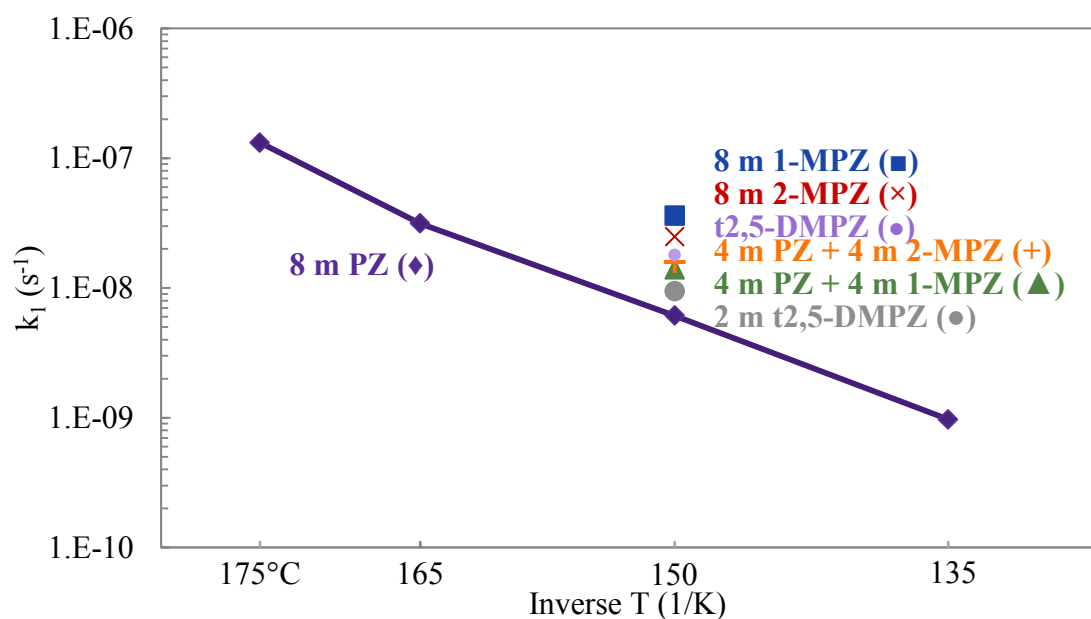


Figure 7.21: Amine loss in thermal degradation of methyl substituted PZs at 150 °C

7.3 THERMAL EQUILIBRIUM OF METHYL-SUBSTITUTED PZs

A new solvent concept in the field of post-combustion CO₂ capture is the use of amines that demonstrate noticeable levels of overall thermal degradation, but degrade to useful products that can react with CO₂ and maintain alkalinity of the solution. One example of this solvent concept is the use of a blend of PZ, 1-MPZ, and 1,4-DMPZ (Rochelle et al., 2010). As described above in section 7.2.1, 1-MPZ degrades to form nearly equimolar concentrations of PZ and 1,4-DMPZ. PZ as a degradation product is an obvious advantage of any 1-MPZ-based solvent system. If 1-MPZ is the starting solvent, appreciable concentrations of PZ and 1,4-DMPZ will eventually accumulate due to degradation. Observations indicate that systems of this nature will tend toward an equilibrium set of concentrations as they interconvert.

To demonstrate this concept, blends of PZ + 1-MPZ + 1,4-DMPZ were thermally degraded in an attempt to understand the equilibrium between the three amines. Solutions with varying amine compositions with 0.3 mole CO₂ per mole alkalinity were degraded at 150 °C for up to 15 weeks. At this temperature, some degradation will occur, but the interconversion of PZ, 1-MPZ, and 1,4-DMPZ is assumed to occur more rapidly than degradation processes based on the slow degradation rates discussed in the previous section. The concentration combinations studied, listed as the molal concentrations of PZ, 1-MPZ, and 1,4-DMPZ, were 5 m PZ + 2 m 1-MPZ + 1 m 1,4-DMPZ, or 5/2/1, 5/2.5/0.5, 5/1.5/1.5, 3.9/3.9/0.2, and 3.75/3.75/0.5 blends. In addition to these blends, information can be gleaned from previously discussed experiments performed on 8 m 1-MPZ and the blend of 4 m PZ + 4 m 1-MPZ.

It is important to note that the interconversion of PZ, 1-MPZ, and 1,4-DMPZ represents multiple arm-switching reactions between molecules. The change of substituent groups, or ‘arms’, has been observed previously for 2-hydroxyethyl and

methyl arms attached directly to a reactive amine center such as the conversion of MDEA to diethanolamine (DEA), triethanolamine (TEA), or N,N-dimethylethanolamine (DMEA) (Bedell et al., 2010; Closmann and Rochelle, 2011). Similar reactions are seen in blends of MDEA and PZ where the protonated MDEA reacts with a PZ molecule to produce DEA and 1-MPZ (Closmann et al., 2009). This reaction is commonly called ‘arm-switching’, but likely occurs as a S_N2 substitution or nucleophilic attack reaction similar to that described in section 6.1. In this reaction, a strong nucleophile, such as one of the amine functions on PZ or 1-MPZ, reacts with the α -carbon of the substituent to be transferred from another molecule. In traditional S_N2 reactions, this α -carbon must have a strong leaving group such as a halide or other weak base (McMurry, 2000). The amine functions on PZ act as good nucleophiles since strong bases are generally considered strong nucleophiles and given the first pKa of PZ and 1-MPZ, either could act as a good nucleophile. In this particular reaction, an amine function is both a leaving group and a nucleophile. The lower pKa of the tertiary amino function of 1-MPZ makes this group a willing leaving group since it is a weaker base than other secondary amine functions.

An example of this type of reaction for the solvent system under discussion is provided in Figure 7.22. In this example, a methyl group from 1,4-DMPZ is transferred to a PZ to produce two 1-MPZ molecules through a quaternary intermediate complex. The carbon that is transferred is highlighted in blue to distinguish the main reaction. The reaction is initiated when the tertiary amine attached to the arm to be transferred is protonated. Given the complex speciation of a mixture of PZ-based it is likely that the tertiary amine would be protonated to a small degree, even if not the dominant protonated molecule. A strong nucleophile at this point can attack the α -carbon and initiate the arm switch.

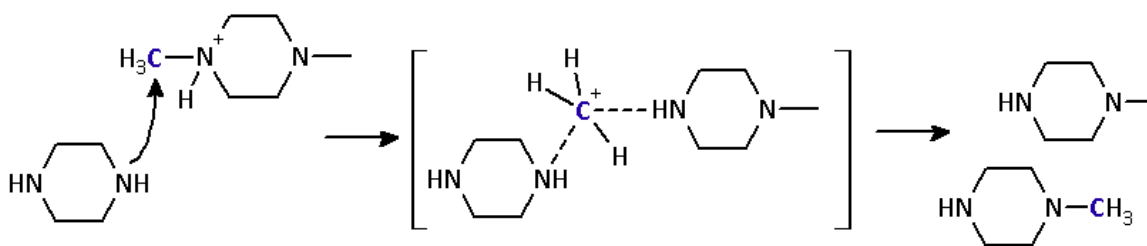


Figure 7.22: Mechanism for S_N2 nucleophilic attack to transfer a methyl group

The expected equilibrium reaction of 1-MPZ is as follows, where the brackets indicate the concentration of the given species in units of mmole per kg (Equation 7.1). The equilibrium constant, K_{EQ} , of Equation 1 can then be calculated (Equation 7.2)



$$K_{eq} = \frac{[\text{PZ}][1,4\text{-DMPZ}]}{[1\text{-MPZ}]^2} \quad (7.2)$$

The goal of this K_{EQ} analysis is to determine the concentrations of the three amine species in equilibrium at 150 °C. These concentrations would be what were expected to be stable in a system with a reboiler temperature of 150 °C. The K_{EQ} values for the thermal equilibrium of PZ, 1-MPZ, and 1,4-DMPZ are shown in Figure 7.23. In each case, the K_{eq} was calculated at each time point according to Equation 7.2 and plotted against degradation time.

All of the experiments were found to tend toward a K_{EQ} value of 0.27-0.30, indicating the equilibrium concentrations of amine expected at 150 °C. The long term blend experiments containing 3.9/3.9/0.2 and 3.75/3.75/0.5 demonstrate this tendency toward a K_{EQ} of 0.29. Even the two experiments with only limited data demonstrate the trend toward the same approximate K_{EQ} value as the other blends.

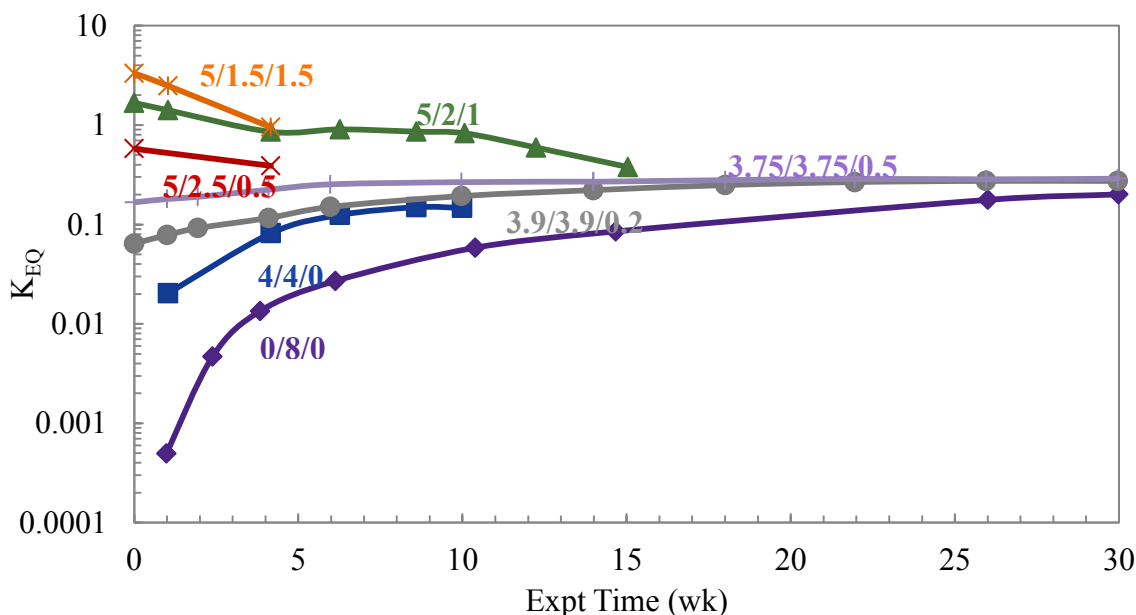


Figure 7.23: K_{eq} for PZ + 1-MPZ + 1,4-DMPZ Solutions Thermally Degraded at 150 °C ($\alpha=0.3$). Labels indicate the concentrations of PZ, 1-MPZ, and 1,4-DMPZ in solution in molal (m)

Degradation of PZ alone will not yield these results as 1-MPZ and 1,4-DMPZ are minor products. However, when a blend begins with at least some 1-methylated PZs (i.e., 1-MPZ or 1,4-DMPZ), these methyl groups can easily undergo a straightforward nucleophilic attack and disproportionation, resulting in switching of the methyl groups between molecules. Overall, the data suggest that any system starting with 1-MPZ will tend toward a K_{eq} of 0.28 to 0.30 at 150 °C.

7.3.1 Implications for other CO₂ capture solvents

The interconversion and equilibrium of methylated PZs is an important concept for blended CO₂ capture amines. The results demonstrate the advantages of starting with a blended solvent rather than a monosubstituted solvent that is likely to react to form its corresponding unsubstituted and disubstituted counterparts during degradation. This

concept can be applied to a number of solvents already being used or being suggested for industrial application.

As an example, N-(2-hydroxyethyl)piperazine (HEP) is being suggested as a novel CO₂ capture solvent. Given the structure of this molecule, it is likely that when exposed to stripping temperatures, HEP will react to form its unsubstituted form (PZ) and its disubstituted form (bis-(2-hydroxyethyl)piperazine, bHEP). In order to establish this equilibrium quickly, it could be advantageous to being with a blend of these three molecules, whose structures are shown in Figure 7.24. Depending on the route of manufacturing of the parent molecule, HEP, an additional advantage could be gained by decreasing the purification needed if the contaminants are PZ or bHEP. In that way, the cost of the amine itself can be decreased while higher levels of contamination could be tolerated if the equilibrium between the molecules were understood.

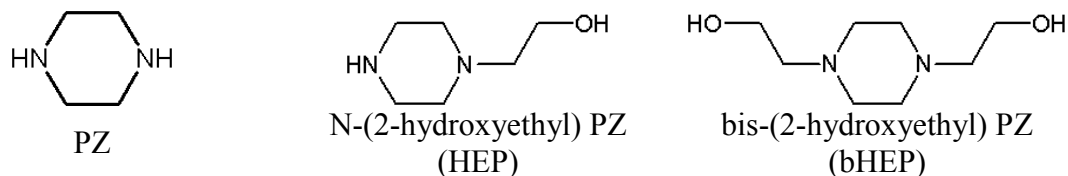


Figure 7.24: Molecules present in an equilibrium mixture of HEP

There could be numerous advantages to a solvent with equilibrium distribution of related molecules. Another system that may be of interest is that based on N-Ethyl PZ (1-EPZ) where its complementary unsubstituted and disubstituted molecules are PZ and N,N'-diethyl PZ (1,4-DEPZ) whose structures are shown in Figure 7.25. Since 1-EPZ is a common product of PZ thermal degradation, there already exists routes of reaction between the molecules. The ease of transfer of ethyl groups has not yet been observed but can be assumed to be slightly more sterically hindered than methyl arm switching.

The fact that 2-hydroxyethyl groups arm switch readily indicates that ethyl arm switching should be possible.

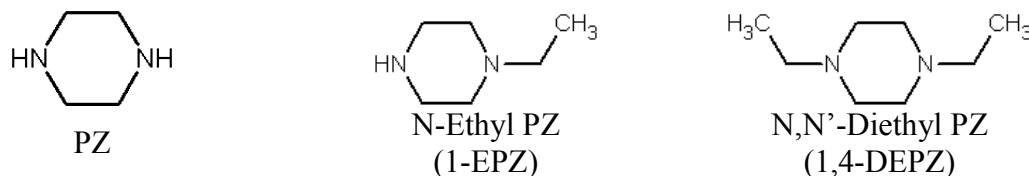


Figure 7.25: Molecules present in an equilibrium mixture of 1-EPZ

7.4 THERMAL STABILITY OF CO₂ CAPTURE AMINES

The thermal stability of a PZ, PZ structural analogs, and substituted PZs has been analyzed during the course of this work. The degradation behavior of amines is a notoriously complex issue which is complicated to compare directly because of differences in temperature, CO₂ concentration, CO₂ partial pressure, and amine concentration. The comparison presented in this section utilizes first order rate constants, k_1 , regressed from raw amine data. A second analysis based on this will be presented that calculates the maximum operating stripper temperature for a given amine solvent.

7.4.1 Comparisons of first-order rate constants for thermal amine loss

The methodology for calculating first-order rate constants, k_1 , was developed in section 5.2 of this dissertation. A k_1 was calculated for each amine studied in this thesis and those found in literature. Data for 7 m MEA, 7 m AMP, 7 m Diglycolamine[®] (DGA[®]), 3.5 m HEP, 2.33 m diethylenetriamine (DETA), 2.33 m N-(2-aminoethyl) PZ (AEP), N-(2-hydroxyethyl) EDA (HEEDA), and 7 m MEA / 2 m PZ blend were reported previously (Davis, 2009). Data for EDA and 2-piperidineethanol (2-PE) were reported previously by Zhou while data for MDEA and the blend of MDEA and PZ were reported previously by Closmann (Closmann, 2011; Closmann et al., 2009; Zhou et al., 2010).

Data for thermal degradation of 3-(methylamino)propylamine (MAPA) were obtained from unpublished work of Vevelstad (Vevelstad, 2010). Eide-Haugmo tested a variety of amines including MEA, EDA, and DETA using a CO₂ concentration of 0.5 mole CO₂ per mole amine for all amines (Eide-Haugmo et al., 2011). Lepaumier investigated numerous amines but used continuously stirred cells with constant CO₂ partial pressure in the headspace, rather than a constant CO₂ loading in the liquid phase (Lepaumier et al., 2010; Lepaumier et al., 2009a). These data are included, although difficult to compare since the initial loading is unknown and CO₂ solubility for these specialized amines is not available. Data from Chakma and Meisen are included but their data was also obtained at constant CO₂ partial pressure, rather than loading (Chakma and Meisen, 1997).

A summary of k_1 values for thermal degradation are compared in the next three tables. In Table 7.2, PZ is compared with PZ structural analogs and substituted PZs. In Table 7.3, PZ-based blends are compared with some MEA-based blends. Finally, PZ is compared with other CO₂ capture amines in Table 7.4. In all three tables, amines are listed in approximate order of decreasing resistance to thermal degradation. This order is based on the analysis presented in the next section. The data for 8 m PZ with 0.3 mole CO₂ per mole alkalinity and 7 m MEA with 0.4 mole CO₂ per mole alkalinity are highlighted with bold text in the tables. For Pyr, HMI, HomoPZ, and 20 m PZ, where amine loss is initially drastic and certainly not first order in amine, the initial rate demonstrated after 1-6 weeks of degradation was used to calculate an apparent k_1 . For some literature data with limited data, an apparent k_1 was calculated using the available data.

Table 7.2: Apparent first order rate constant (k_1) for thermal degradation of PZ, structural analogs of PZ, and substituted PZs

Amine	Conc. m	Loading mol/mol alk	$k_1 \times 10^9$ (s ⁻¹)					Ref [*]
			100 °C	120	135	150	165	175
Piperazine (PZ)	8	0				0.1	0.8	7
PZ	8	0.47						24
PZ	20	0.1						45
Morpholine	8	0.3						50
PZ	8	0.1					18	66
PZ	8	0.2						79
Piperidine	8	0.3						84
PZ	4	0.3					36	114
PZ	8	0.3			1	6	31	132
PZ	8	0.4			0.5	8	41	171
t2,5-DimethylPZ	2	0.3				9		
PZ	12	0.3					50	156
Hexamethylenediamine	8	0.3						169
PZ	10	0.3			5	9		
PZ	20	0.3				24		168
2-MethylPZ	8	0.3				25		
1-MethylPZ	8	0.3				36		
PZ	10	0.4				6		
Ethylenediamine (EDA)	8	0.2	5	5	30			Z
Pyrrolidine	8	0.3						1400
EDA	8	0.4	5	38	167			Z
Homopiperazine	8	0.3						1850
N-(2-Hydroxyethyl) PZ	3.5	0.4			58			D
Hexamethyleneimine	8	0.3						5900
EDA	3.5	0.4			247	339		D
N-(2-Aminoethyl) PZ	2.33	0.4			191			D
EDA	7.13	0.25			143			EH

* If not specified, from this work; D = (Davis, 2009); EH = (Eide-Haugmo et al., 2011); Z = (Zhou et al., 2010).

Table 7.3: Apparent first order rate constant (k_1) for thermal degradation of blended solvents CO₂ capture amines

Amine	Blend Components	Conc. m	Loading mol/mol alk	$k_1 \times 10^9$ (s ⁻¹)					Ref*
				100 °C	120	135	150	200	
PZ	PZ/1-MPZ	4/4	0.3				~0		
3.9/3.9/0.2 (TA)	PZ/1-MPZ/1,4-DMPZ	-	0.3				8		
3.75/3.75/0.5 (TA)	PZ/1-MPZ/1,4-DMPZ	-	0.3				10		
5/2/1 (TA)	PZ/1-MPZ/1,4-DMPZ	-	0.3				14		
PZ + 1-MPZ (TA)	PZ/1-MPZ	4/4	0.3				14		
5/2.5/0.5 (TA)	PZ/1-MPZ/1,4-DMPZ	-	0.3				14		
PZ + 2-MPZ (TA)	PZ/2-MPZ	4/4	0.3				16		
MDEA	MDEA/DEA	5.3/1.7	0.27					1550	RT
PZ + t2,5-DMPZ (TA)	PZ/t2,5-DMPZ	4/4	0.3				18		
MDEA + DEA (TA)	MDEA/DEA	5.3/1.7	0.27					2200	RT
1-MPZ	PZ/1-MPZ	4/4	0.3				34		
MDEA	MDEA/PZ	7/2	0			34	19		C
MDEA + PZ (TA)	MDEA/PZ	7/2	0			33	21		C
PZ	MDEA/PZ	7/2	0			32	27		C
5/1.5/1.5 (TA)	PZ/1-MPZ/1,4-DMPZ	-	0.3				75		
MDEA	MDEA/PZ	7/2	0.11			25	42		C
PZ	PZ/AMP	6/4	0.4			32	92		Z
MDEA + PZ (TA)	MDEA/PZ	7/2	0.11			49	61		C
PZ + AMP (TA)	PZ/AMP	6/4	0.4			46	144		Z
DEA	MDEA/DEA	5.3/1.7	0.27					13700	RT
AMP	MEA/AMP	7/2	0.4	5		6	85		D
AMP	PZ/AMP	6/4	0.4			67	249		Z

Table 7.3: Apparent first order rate constant (k_1) for thermal degradation of blended solvents CO₂ capture amines (continued)

Amine	Blend Components	Conc. m	Loading mol/mol alk	$k_1 \times 10^9$ (s ⁻¹)					Ref*
				100 °C	120	135	150	200	
MDEA	MDEA/PZ	7/2	0.25		11	58	284		C
MEA + AMP (TA)	MEA/AMP	7/2	0.4	2	23	123	408		D
MEA	MEA/AMP	7/2	.04	0.8	31	1890	686		D
PZ	MDEA/PZ	7/2	0.11			378	486		C
MDEA + PZ (TA)	MDEA/PZ	7/2	0.25		27	110	297		C
PZ	MDEA/PZ	7/2	0.25		118	780	2050		C
MEA + DGA® (TA)	MEA/DGA®	7/2	0.4	19	20	162	551		D
MEA	MEA/DGA®	7/2	0.4	19	26	190	716		D
DGA®	MEA/DGA®	7/2	0.4	17	3	92	289		D
Mor	MEA/Mor	7/2	0.4	14	64	248	532		D
MEA + Mor (TA)	MEA/Mor	7/2	0.4	16	62	237	592		D
MEA	MEA/Mor	7/2	0.4	16	62	234	612		D
MEA	MEA/PZ	7/2	0.4	26	56	238	683		D
MEA + PZ (TA)	MEA/PZ	7/2	0.4	27	62	251	608		D
PZ	MEA/PZ	7/2	0.4	31	84	316	1200		D

* If not specified, from this work; C = (Closmann et al., 2009); D = (Davis, 2009); RT = (Reza and Trejo, 2006); Z = (Zhou et al., 2010)

Table 7.4: Apparent first order rate constant (k_1) for thermal degradation of CO₂ capture amines

Amine	Abbreviation ^a	Conc. ^b m	Loading mol/mol alk	$k_1 \times 10^9$ (s ⁻¹) ^c								Ref. ^d
				100 °C	120	135	140	150	160/165	175	180/200	
Morpholine	Mor	8	0.3							50		
Piperidine	PD	8	0.3							84		
Piperazine	PZ	8	0.3			1		6	31	132		
Piperazine	PZ	8	0.4			0.5		8	41	171		
3.9 / 3.9 / 0.2 (TA)	PZ/MPZ/DMPZ	8	0.3					8				
Hexamethylenediamine	HMDA	8	0.3							19		
trans-2,5-Dimethylpiperazine	t2,5-DMPZ	2	0.3					9				
3.75 / 3.75 / 0.5 (TA)	PZ/MPZ/DMPZ	8	0.3					10				
5 / 2 / 1 (TA)	PZ/MPZ/DMPZ	8	0.3					14				
PZ / 1-MPZ (TA)	PZ/1-MPZ	4/4	0.3					14				
5 / 2.5 / 0.5 (TA)	PZ/MPZ/DMPZ	8	0.3					14				
PZ / 2-MPZ (TA)	PZ/2-MPZ	4/4	0.3					16				
PZ / t2,5-DMPZ (TA)	PZ/t2,5-DMPZ	4/4	0.3					18				
2-Methylpiperazine	2-MPZ	8	0.3					25				
MDEA / DEA (TA)	MDEA/DEA	5.3/1.7	0.27								2250	RT
1-Methylpiperazine	1-MPZ	8	0.3					36				
5-amino-1-pentanol	5a1p	7	0.4			13		43				D
MDEA / PZ (TA)	MDEA/PZ	7/2	0			33		21				C
Pyrrolidine	Pyr	8	0.3							1400		
Homopiperazine	HomoPZ	8	0.3							1850		
2-Amino-2-methyl-1-propanol	AMP	4.81	0.5			17						EH
1,4-Dimethylpiperazine	DMPZ	4*	2 MPa				35.5					L1
MDEA / PZ (TA)	MDEA/PZ	7/2	0.11			49		61				C
2-amino-2-methyl-1-propanol	AMP	7	0.4		8	21		86				D
PZ + AMP (TA)	PZ/AMP	6/4	0.4			46		144				Z
4-amino-1-butanol	4a1b	7	0.4		6	37		195				D

Table 7.4: Apparent first order rate constant (k_1) for thermal degradation of CO₂ capture amines (Continued)

Amine	Abbreviation ^a	Conc. ^b m	Loading mol/mol alk	$k_1 \times 10^9$ (s ⁻¹) ^c								Ref. ^d
				100 °C	120	135	140	150	160/165	175	180/200	
Diglycolamine [®]	DGA	7	0.4			39						D
Hexamethyleneimine	HMI	8	0.3							5950		
N-(2-Hydroxyethyl)piperazine	HEP	7	0.4			58						D
N-Methyldiethanolamine	MDEA	4*	2 MPa				90					L1
N,N,N',N',N''-pentamethyldipropylenetriamine	PMDPTA	2.5*	2 MPa				99					L3
Methyldiethanolamine	MDEA	7	0.1					283				C
Ethylenediamine	EDA	8	0.2	5	5	30						Z
Methyldiethanolamine	MDEA	7	0.2			42		438				C
3-amino-1-propanol	3a1p	7	0.4	2	17	47		221				D
2-Piperidineethanol	2-PE	8	0.4			80		293				Z
N,N,N',N'-Tetramethylethylenediamine	TMEDA	4*	2 MPa				125					L1
3-aminopropanol	AP	5.71	0.5			82						EH
Monoethanolamine	MEA	11	0.2		19	69						D
Ethylenediamine	EDA	3.5	0.4			247		339.4				D
Monoethanolamine	MEA	3.5	0.2	8	33	41						D
N,N,N',N'-Tetramethypropylenediamine	TMPDA	4*	2 MPa				182					L3
2-Amino-2-methyl-1-propanol	AMP	4*	2 MPa				182					L1
MEA / AMP (TA)	MEA/AMP	7/2	0.4	2	23	123		408				D
DL-1-amino-2-propanol		7	0.4	5	17	70		282				D
N,N-Dimethylethanolamine	DMMEA	4.81	0.5			118						EH
Monoethanolamine	MEA	3.5	0.4	3	22	109						D
N-(2-Aminoethyl)piperazine	AEP	2.33	0.4			191						D
Monoethanolamine	MEA	7	0.2		28	90		397				D
Monoethanolamine	MEA	7	0.4	2	29	134		828				D

Table 7.4: Apparent first order rate constant (k_1) for thermal degradation of CO₂ capture amines (Continued)

Amine	Abbreviation ^a	Conc. ^b m	Loading mol/mol alk	$k_1 \times 10^9$ (s ⁻¹) ^c								Ref. ^d
				100 °C	120	135	140	150	160/165	175	180/200	
Ethylenediamine	EDA	7.14	0.25			143						EH
MDEA / PZ (TA)	MDEA/PZ	7/2	0.25		27	110		297				C
N-Methyldiethanolamine	MDEA	3.6	0.5			153						EH
N-Methyldiethanolamine	MDEA	8.4	0.4			166						D
Diethylenetriamine	DETA	4.15	0.17			186						EH
N,N-Dimethylethanolamine	DMAE	4*	2 MPa				321					L1
Monoethanolamine	MEA	7	0.5	2	68	201		1300				D
Ethylenediamine	EDA	8	0.4	5	38	167						Z
3-(Methylamino)propylamine	MAPA	4.81	0.25			229						EH
6-amino-1-hexanol	6a1h	7	0.4	3		590		541				D
Monoethanolamine	MEA	11	0.4		61	174						D
Monoethanolamine	MEA	4*	2 MPa				420					L1
Monoethanolamine	MEA	7.01	0.5			264						EH
N,N-Dimethylethylenediamine	N,N-diMEDA	4*	2 MPa				46					L1
N-(2-Hydroxyethyl) ethylenediamine	HEEDA	4.12	0.25			303						EH
3-(Methylamino)propylamine	MAPA	9	0.4			313						V
DL-2-amino-1-propanol	MIPA	7	0.4	9		131		523				D
MEA / DGA [®] (TA)	MEA/DGA [®]	7/2	0.4	19	20	162		551				D
N,N,N'-Trimethylethylenediamine	triMEDA	4*	2 MPa				651					L1
Monoethanolamine	MEA	11	0.5		112	249						D
Monoethanolamine	MEA	3.5	0.5	13	58	137						D
2-Piperidinemethanol	2-PM	7	0.4			541						D
Diethylenetriamine	DETA	7	0.4			1150		1600				D
MEA / Mor (TA)	MEA/Mor	7/2	0.4	16	62	237		592				D
N,N,N',N'- tetramethylbutylenediamine	TMBDA	4*	2 MPa				1250					L3

Table 7.4: Apparent first order rate constant (k_1) for thermal degradation of CO₂ capture amines (Continued)

Amine	Abbreviation ^a	Conc. ^b m	Loading mol/mol alk	$k_1 \times 10^9$ (s ⁻¹) ^c								Ref. ^d
				100 °C	120	135	140	150	160/165	175	180/200	
N,N,N',N',N''-pentamethyldiethylenetriamine	PMDETA	2.5*	2 MPa				1550					L3
N-Methylethanolamine	MAE	4*	2 MPa				1650					L1
Diethanolamine	DEA	4.08	0.5			991						EH
N,N'-Dimethylethylenediamine	N,N'-diMEDA	4*	2 MPa				1700					L1
MEA / PZ (TA)	MEA/PZ	7/2	0.4	27	62	251.3		608				D
Diethanolamine	DEA	4*	2 MPa				2050					L1
N-Methyldiethanolamine	MDEA	8.39	2.59 MPa	49	83		333		611		25000	CM
2-Methylaminoethanol	MMEA	5.71	0.5			1300						EH
N-(2-Hydroxyethyl)ethylenediamine	HEEDA	3.5	0.4			1600						D
N-(2-Hydroxyethyl)ethylenediamine	HEEDA	4*	2 MPa				3550					L1

^a MPZ = 1-MPZ; DMPZ = 1,4-DMPZ^b Asterisk (*) indicates unites of moles amine per kg solution^c Data from this study was at 165 °C; Chakma and Meisen (CM) data was at 160 and 180 °C; Reza and Trejo (RT) data was at 200 °C,^d If not specified, from this work; CM = (Chakma and Meisen, 1997); C = (Closmann et al., 2009); D = (Davis, 2009); EH = (Eide-Haugmo et al., 2011); L1 = (Lepaumier et al., 2009a); L3 = (Lepaumier et al., 2010); RT = (Reza and Trejo, 2006); V = (Vevelstad, 2010); Z = (Zhou et al., 2010).

The data presented in the previous tables can be shown graphically with a plot of k_1 against T^{-1} . This comparison is made for PZ related compounds, blends, and CO₂ capture amines in Figure 7.26, Figure 7.27, and Figure 7.28, respectively. With these plots, the trends and differences in magnitude of k_1 can readily be observed.

PZ is highly resistant to thermal degradation, as evidenced by the low k_1 values associated with a variety of experimental conditions. The least stable PZ conditions were 10, 12 and 20 m PZ while unloaded and lean loaded PZ was the most stable. Mor and PD are the only amines found to be more resistant to thermal degradation than PZ. The k_1 values of Mor and PD were found to be 2.7 and 1.6 times lower than PZ at 175 °C. Mor was previously identified as highly stable to thermal degradation at 135 °C (Davis, 2009).

The k_1 analysis for the blended PZ solvents demonstrates that PZ is preferentially degraded. The PZ / 1-MPZ blend is omitted from the figure since it is in equilibrium, rather than just degrading. In blends with MDEA, PZ is preferentially degraded 12 to 15 times faster than MDEA and 4 to 8 times faster than the total amine concentration. In this case, PZ reacts faster with CO₂ and exists mostly as PZCOO⁻. PZ is a stronger nucleophile than MDEA and is degraded through S_N2 nucleophilic substitution reactions where PZ is the preferred accepting molecule when reacting with protonated MDEA. In blends with MEA, PZ degrades only 1.2 to 1.7 times faster than MEA and 1.1 to 1.9 times faster than the total amine concentration. The effect of blending is not as extreme with MEA as with MDEA.

The k_1 values for MEA and AMP were found to be 132 and 14 times higher, respectively, than 8 m PZ with 0.3 mole CO₂ per mole alkalinity. This is a significant advantage for concentrated, aqueous PZ CO₂ capture systems. All PZ structural analogs (Mor, PD, HMDA) and substituted PZs (1-MPZ, 2-MPZ) compared in Table 7.4 and Figure 7.28 are all more thermally stable than MEA, AMP, EDA, DGA, or MDEA.

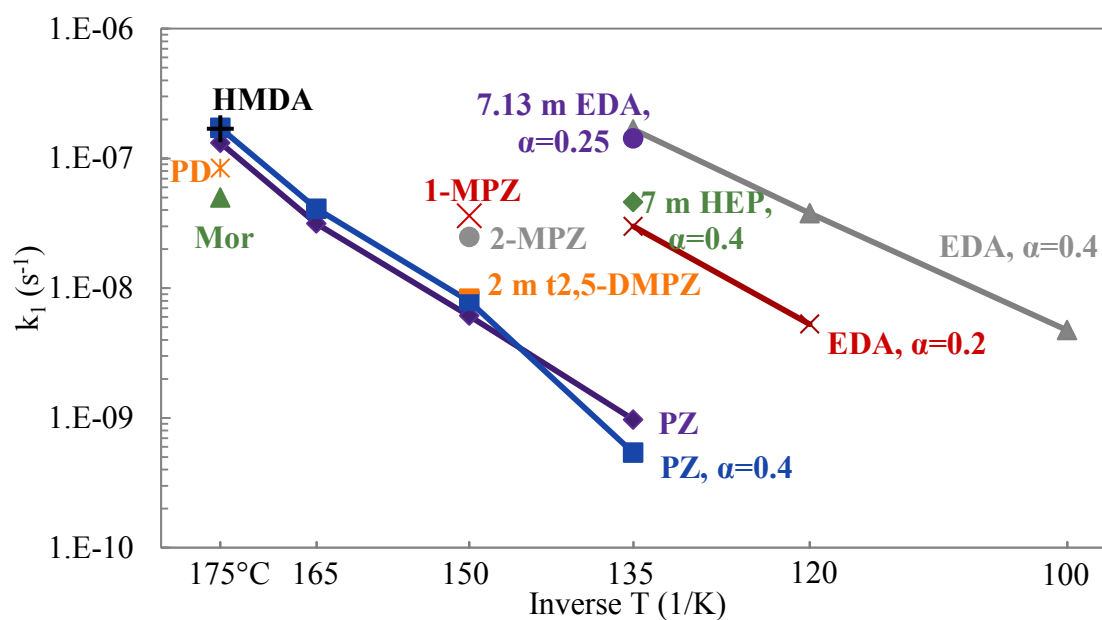


Figure 7.26: Comparison of k_1 values for PZ, PZ structural analogs, and substituted PZ; all solutions are 8 m amine with 0.3 mole CO_2 per mole alkalinity, unless noted (7.13 m EDA data from (Eide-Haugmo et al., 2011))

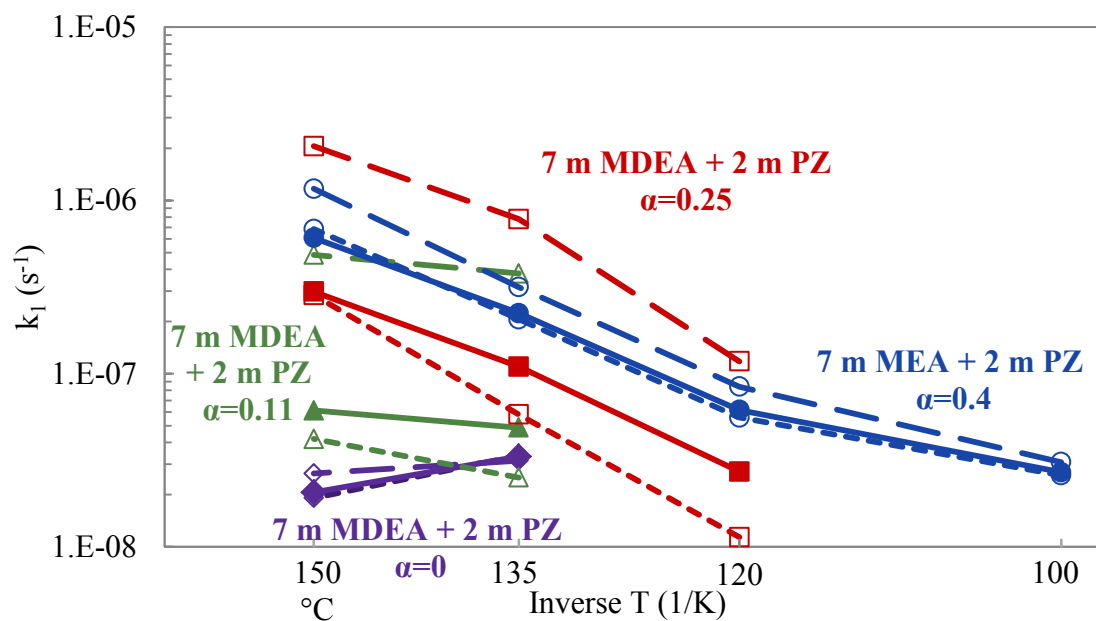


Figure 7.27: Comparison of k_1 values for 7 m MDEA + 2 m PZ (Closmann, 2011) and 7 m MEA + 2 m PZ blends (Davis, 2009). Lines: solid, total amine; short dash, MDEA or MEA; long dash, PZ

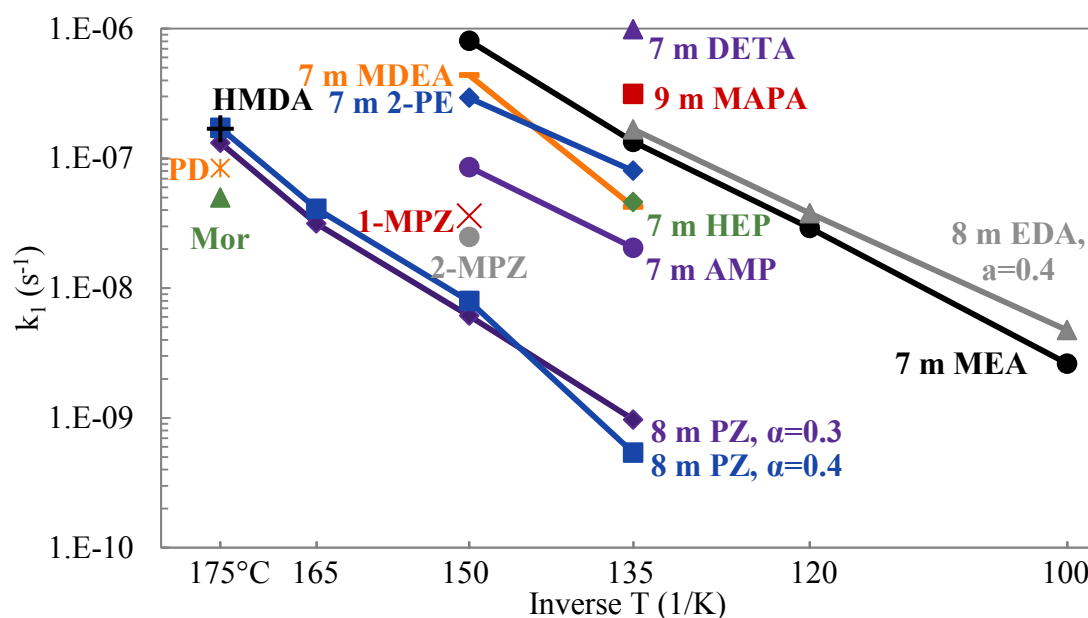


Figure 7.28: Comparison of k_1 values for CO₂ capture amines (Closmann et al., 2009; Davis, 2009; Vevelstad, 2010; Zhou et al., 2010)

7.4.2 Maximum operating stripper temperature

Although a powerful representation of thermal stability of each amine, the k_1 -analysis is limited because any figure developed for comparisons can quickly become cluttered. Additionally, extending the data to predict behavior outside the tested temperature range is not easily accomplished. A second analysis to understand and compare the thermal stability of amines used for CO₂ capture is presented that calculates the maximum allowable stripper temperature. This analysis provides a real number that can be used and understood by the reader who only has cursory knowledge of the fundamentals of thermal degradation of amines.

The work of Davis determined that the optimal or acceptable operating temperature for a 7 m MEA solution was 122 °C (Davis, 2009). This determination was based on an optimization and balance of energy savings from higher temperature operation with the cost of thermal degradation including amine replacement, reclaiming,

and disposal costs. Based on his data for 7 m MEA, this temperature corresponds to a loss of approximately 2% of the initial amine per week (Davis, 2009). This also corresponds to an apparent first order rate constant (k_1) value of $2.91 \times 10^{-8} \text{ s}^{-1}$ ($1.05 \times 10^{-4} \text{ hr}^{-1}$, $2.51 \times 10^{-3} \text{ d}^{-1}$, or $1.76 \times 10^{-2} \text{ wk}^{-1}$). The cost of this loss rate of MEA was deemed acceptable and balanced by the advantageous of high temperature and pressure operation of the stripper. This conclusion is supported by the fact that numerous MEA based absorption-stripping systems for CO_2 scrubbing have operated successfully and economically at 115 to 120 °C for extended periods of time (Arnold et al., 1982; St.Clair and Simister, 1983).

Based on the acceptable loss rate for 7 m MEA, a tolerable stripper temperature can be determined for any amine. The k_1 values for 8 m PZ with 0.3 mole CO_2 per mole alkalinity and 7 m MEA with 0.4 mole CO_2 per mole alkalinity are compared from 100 to 175 °C in Figure 7.29. A stripper temperature of 122 °C for MEA corresponds to a k_1 value of $2.91 \times 10^{-8} \text{ s}^{-1}$, as indicated by the dashed line in the figure. Using this k_1 value as a basis, the temperature at which any amine meets this value can be determined from the available k_1 data and an activation energy. For the 8 m PZ data shown in the figure, the regressed fit provided an activation energy of 183.5 kJ per mole was used to determine that at 162.8 °C the k_1 value would be $2.91 \times 10^{-8} \text{ s}^{-1}$. This procedure can be used for the amines with multiple k_1 values at a given condition such as PZ, EDA and AMP where a well behaved regression for k_1 can be created to determine the activation energy.

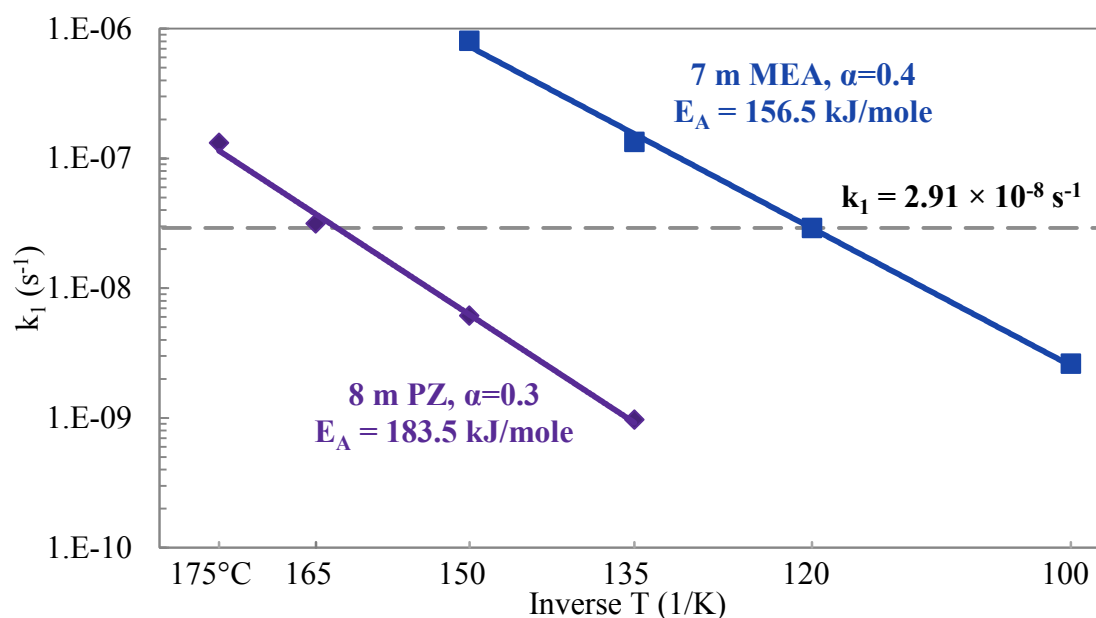


Figure 7.29: Analysis of k_1 values for 8 m PZ ($\alpha=0.3$) and 7 m MEA ($\alpha=0.4$) (Davis, 2009)

For numerous amines, only one or two data points exist so a regression for activation energy cannot be performed. The activation energy, and therefore, slope of the Arrhenius k_1 plot, does not fluctuate greatly between amine systems, as demonstrated by Figure 7.28 above. Amines shown in this figure vary greatly in structure and include primary amines, secondary amines, monoamines, diamines, hindered amines, and alkanolamines. These diverse molecules all demonstrate similar k_1 behavior so it can be safely assumed that a majority of amines would behave likewise. For amines with only one data point, the slope of the data for 7 m MEA with 0.4 mole CO_2 per mole alkalinity, and therefore the activation energy of 156.5 kJ per mole, was used for extrapolation. For amines with two data points, the prediction was done using the slope of MEA independently and then the average stripper temperature calculated from each point was averaged to provide the final temperature. For amines with at least three temperatures, an activation energy was calculated and used for that data. For PZ experiments with less

than three points, the slope of the data for 8 m PZ with 0.3 mole CO₂ per mole alkalinity was used, rather than the MEA data, in the same fashion. When the lowest temperature data of a given amine data set was too high, showing a difficulty at accurately detecting small changes in amine concentration, the lowest temperature data point was not used in the prediction of stripper temperature. A summary of the activation energies calculated and used is given in Table 7.5.

The raw material cost for the amines compared in this section is not included in this analysis and would have a great impact on the results if included. Costs can vary greatly between amines by factors as much as 10 or 50 and will impact the level of tolerable thermal degradation for an operator. For many of the amines compared in this work, reliable bulk prices are not easily obtained and laboratory or small quantity prices are not necessarily reflective of bulk pricing. This analysis could easily be amended if the amine of interest has known bulk pricing. The objective k_1 value could be adjusted by a factor representative of the relative difference between the price of MEA and the amine of interest. In that way, an estimate of the stripper temperature could still be obtained.

A summary table of the calculated stripper temperatures that correspond to a loss of 2% of the initial amine per week is shown in Table 7.6. All of the amines screened in this work and previous works are included for completeness and are listed in order of decreasing stripper temperature (Chakma and Meisen, 1997; Closmann et al., 2009; Davis, 2009; Eide-Haugmo et al., 2011; Lepaumier et al., 2010; Lepaumier et al., 2009a; Reza and Trejo, 2006; Vevelstad, 2010; Zhou et al., 2010). This analysis provides a very clear ranking of amines in terms of their thermal stability. A summary of only MEA and MEA blends is shown in Table 7.7 to demonstrate the range of values due to differences in amine concentration, CO₂ loading, and data source. Over a range of 3.5 to 11 m MEA

with 0.2 to 0.5 mole CO₂ per mole alkalinity, the estimated stripper temperature varies from 111 to 126 °C. Similar ranges are present for amines that have been degraded under varying conditions by different authors such as EDA, AMP, and HEEDA.

Table 7.5: Summary of activation energies used for the calculation of maximum stripper temperatures

Amine	Conc. m	Loading mol/mol alk	Act. Energy kJ/mol	Temperatures °C	Ref. ^a
Piperazine (PZ)	8	0.3	184	135, 150, 165, 175	
Piperazine (PZ)	8	0.4	191	150, 165, 175	
Monoethanolamine (MEA)	3.5	0.2	60	100, 120, 135	D
Monoethanolamine (MEA)	3.5	0.4	129	100, 120, 135	D
Monoethanolamine (MEA)	3.5	0.5	86	100, 120, 135	D
Monoethanolamine (MEA)	7	0.2	123	120, 135, 150	D
Monoethanolamine (MEA)	7	0.4	157	100, 120, 135, 150	D
Monoethanolamine (MEA)	7	0.5	162	100, 120, 135, 150	D
2-amino-2-methyl-1-propanol (AMP)	7	0.4	112	120, 135, 150	D
3-amino-1-propanol (3a1p)	7	0.4	117	100, 120, 135, 150	D
4-amino-1-butanol (4a1b)	7	0.4	161	120, 135, 150	D
6-amino-1-hexanol (6a1h)	7	0.4	148	100, 135, 150	D
DL-2-amino-1-propanol (MIPA)	7	0.4	105	100, 135, 150	D
DL-1-amino-2-propanol	7	0.4	106	100, 120, 135, 150	D
MEA in MEA/AMP Blend	7/2	0.4	179	100, 120, 135, 150	D
AMP in MEA/AMP Blend	7/2	0.4	623	100, 135, 150	D
Total Amine in MEA/AMP Blend	7/2	0.4	146	100, 120, 135, 150	D
MEA in MEA/Mor Blend	7/2	0.4	97	100, 120, 135, 150	D
Mor in MEA/Mor Blend	7/2	0.4	99	100, 120, 135, 150	D
Total Amine in MEA/Mor Blend	7/2	0.4	97	100, 120, 135, 150	D
MEA in MEA/PZ Blend	7/2	0.4	88	100, 120, 135, 150	D
PZ in MEA/PZ Blend	7/2	0.4	96	100, 120, 135, 150	D
Total Amine in MEA/PZ Blend	7/2	0.4	84	100, 120, 135, 150	D
MEA in MEA/DGA [®] Blend	7/2	0.4	99	100, 120, 135, 150	D
DGA [®] in MEA/DGA [®] Blend	7/2	0.4	72	100, 135, 150	D
Total Amine in MEA/DGA [®] Blend	7/2	0.4	94	100, 120, 135, 150	D
N-Methyldiethanolamine (MDEA)	8.39	2.6 MPa	100	100, 120, 140, 160, 180	CM
Ethylenediamine (EDA)	8	0.4	154	100, 120, 135	Z
MDEA in MDEA/PZ Blend	7/2	0.25	148	120, 135, 150	C
PZ in MDEA/PZ Blend	7/2	0.25	132	120, 135, 150	C
Total Amine in MDEA/PZ Blend	7/2	0.25	111	120, 135, 150	C

^a If not specified, from this work; CM =(Chakma and Meisen, 1997); C = (Closmann et al., 2009); D = (Davis, 2009); Z = (Zhou et al., 2010)

The most thermally stable amine tested to date is 8 m Mor which can tolerate a stripper temperature of 169 °C. Davis found no loss of Mor after 4 weeks at 135 °C, confirming the stability of Mor found in this project (Davis, 2009). The top rows of Table 7.6, indicating the most stability, are dominated by PZ, cyclic PZ analogs, and PZ blends. Towards the middle of the ranking, tertiary amines, sterically hindered amines and unique functionalities, such as esters, are present. The most instable, or bottom of the table, is dominated by straight-chain alkanolamine and amines. The only straight chain molecule with appreciable stability is HMDA, which draws its stability from an inability to form a stable 9-membered oxazolidone.

The most instable amines measured, MMEA, DEA, DETA, and MAPA, are longer straight-chain alkyl amines with at least one secondary amino function and either hydroxyl groups or multiple amino function. DEA, DETA, and MAPA degrade to N-(2-aminoethyl) imidazolidone (CAS 6281-41-1), tetrahydro-1-methyl-2(1H)-Pyrimidinone (CAS 10166-54-8), and 3-(2-hydroxyethyl)-2-Oxazolidone (HEOD, CAS 3356-88-5), respectively, all very stable 5 and 6-member urea structures. As with MEA, the stability of the initial cyclic urea intermediate or reaction product dictates the extent of thermal degradation.

Table 7.6: Estimated stripper temperature at $k_1 = 2.91 \times 10^{-8} \text{ s}^{-1}$

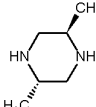
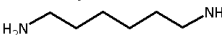
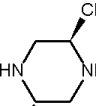
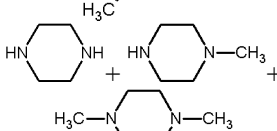
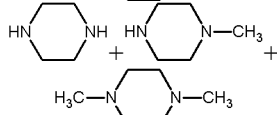
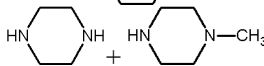
Amine	Abbreviation	Structure(s)	Conc. ^a m	Loading mol/mol alk	T Range of Data °C	Act. Energy ^b kJ/mol	Stripper Temp °C	Ref. ^c
Morpholine	Mor		8	0.3	175	PZ	170	
Piperidine	PD		8	0.3	175	PZ	166	
Piperazine	PZ		8	0.3	135-175	184	163	
Piperazine	PZ		8	0.4	135-175	191	162	
Piperazine / 1-Methylpiperazine / 1,4-Dimethylpiperazine (TA)	PZ/ 1-MPZ/ 1,4-DMPZ		3.9/ 3.9/ 0.2	0.3	150	PZ	160	
Hexamethylenediamine	HMDA		8	0.3	175	PZ	160	
trans-2,5-Dimethylpiperazine	t2,5-DMPZ		2	0.3	150	PZ	159	
Piperazine / 1-Methylpiperazine / 1,4-Dimethylpiperazine (TA)	PZ/ 1-MPZ/ 1,4-DMPZ		3.75/ 3.75/ 0.5	0.3	150	PZ	159	
Piperazine / 1-Methylpiperazine / 1,4-Dimethylpiperazine (TA)	PZ/ 1-MPZ/ 1,4-DMPZ		5/ 2/ 1	0.3	150	PZ	156	
Piperazine / 1-Methylpiperazine (TA)	PZ /1-MPZ		4 /4	0.3	150	PZ	156	

Table 7.6: Estimated stripper temperature at $k_1 = 2.91 \times 10^{-8} \text{ s}^{-1}$ (Continued)

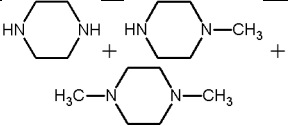
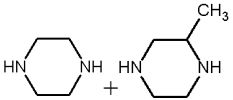
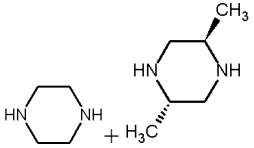
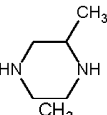
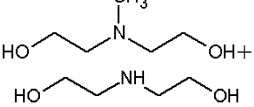
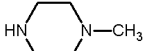
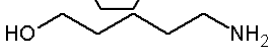
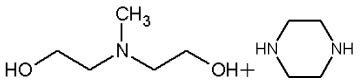
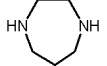
Amine	Abbreviation	Structure(s)	Conc. ^a m	Loading mol/mol alk	T Range of Data °C	Act. Energy ^b kJ/mol	Stripper Temp °C	Ref. ^c
Piperazine / 1-Methylpiperazine / 1,4-Dimethylpiperazine (TA)	PZ/ 1-MPZ/ 1,4-DMPZ		5/ 2.5/ 0.5	0.3	150	PZ	156	
Piperazine / 2-Methylpiperazine (TA)	PZ/ 2-MPZ		4/ 4	0.3	150	PZ	155	
Piperazine / <i>trans</i> -2,5- Dimethylpiperazine (TA)	PZ/ t2,5-DMPZ		4/ 4	0.3	150	PZ	154	
2-Methylpiperazine	2-MPZ		8	0.3	150	PZ	151	
N-Methyldiethanolamine / Diethanolamine (TA)	MDEA/ DEA		5.3/ 1.7	0.27	200	MEA	151	RT
1-Methylpiperazine	1-MPZ		8	0.3	150	PZ	148	
5-amino-1-pentanol	5a1p		7	0.4	135-150	MEA	145	D
N-Methyldiethanolamine / Piperazine (TA)	MDEA/ PZ		7/ 2	0	135-150	PZ	143	C
Pyrrolidine	Pyr		8	0.3	175	PZ	142	
Homopiperazine	HomoPZ		8	0.3	175	PZ	140	

Table 7.6: Estimated stripper temperature at $k_1 = 2.91 \times 10^{-8} \text{ s}^{-1}$ (Continued)

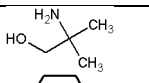
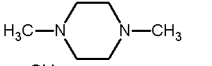
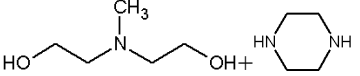
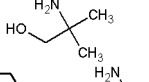
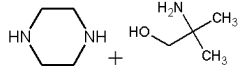
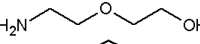
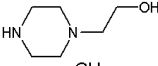
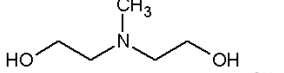
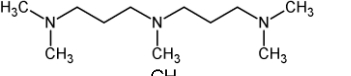
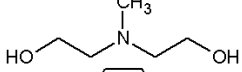
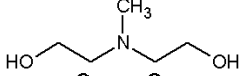
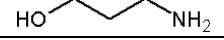
Amine	Abbreviation	Structure(s)	Conc. ^a m	Loading mol/mol alk	T Range of Data °C	Act. Energy ^b kJ/mol	Stripper Temp °C	Ref. ^c
2-Amino-2-methyl-1-propanol	AMP		4.81	0.5	135	MEA	140	EH
1,4-Dimethylpiperazine	1,4-DMPZ		4*	2 MPa	140	PZ	138	L1
N-Methyldiethanolamine / Piperazine (TA)	MDEA/ PZ		7/ 2	0.11	135-150	PZ	138	C
2-amino-2-methyl-1-propanol	AMP		7	0.4	120-150	112	137	D
Piperazine / 2-amino-2-methyl-1- propanol (TA)	PZ/ AMP		6/ 4	0.4	135-150	PZ	134	Z
4-amino-1-butanol	4a1b		7	0.4	120-150	161	133	D
Diglycolamine®	DGA		7	0.4	135	MEA	132	D
Hexamethyleneimine	HMI		8	0.3	175	PZ	131	
N-(2-Hydroxyethyl)piperazine	HEP		7	0.4	135	PZ	130	D
N-Methyldiethanolamine	MDEA		4*	2 MPa	140	MEA	129	L1
N,N,N',N',N''- pentamethyldipropylenetriamine	PMDPTA		2.5*	2 MPa	140	MEA	129	L3
Methyldiethanolamine	MDEA		7	0.1	150	MEA	128	C
Ethylenediamine	EDA		8	0.2	100-135	MEA	128	Z
Methyldiethanolamine	MDEA		7	0.2	135-150	MEA	128	C
3-amino-1-propanol	3a1p		7	0.4	100-150	117	127	D

Table 7.6: Estimated stripper temperature at $k_1 = 2.91 \times 10^{-8} \text{ s}^{-1}$ (Continued)

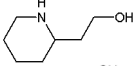
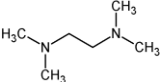
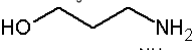
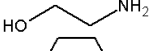
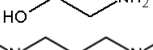
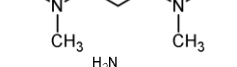
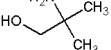
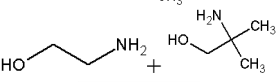
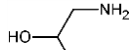
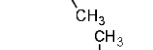
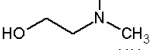
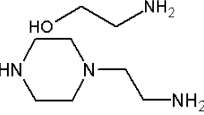
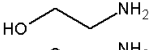
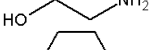
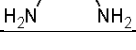
Amine	Abbreviation	Structure(s)	Conc. ^a m	Loading mol/mol alk	T Range of Data °C	Act. Energy ^b kJ/mol	Stripper Temp °C	Ref. ^c
2-Piperidineethanol	2-PE		8	0.4	135-150	MEA	127	Z
N,N,N',N'- Tetramethylethylenediamine	TMEDA		4*	2 MPa	140	MEA	127	L1
3-aminopropanol	AP		5.71	0.5	135	MEA	126	EH
Monoethanolamine	MEA		11	0.2	120-135	MEA	125	D
Ethylenediamine	EDA		3.5	0.4	135-150	PZ	125	D
Monoethanolamine	MEA		3.5	0.2	100-135	60	123	D
N,N,N',N'- Tetramethylpropylenediamine	TMPDA		4*	2 MPa	140	MEA	123	L3
2-Amino-2-methyl-1-propanol	AMP			2 MPa	140	MEA	123	L1
Monoethanolamine / 2-Amino-2- methyl-1-propanol (TA)	MEA/ AMP		7/ 2	0.4	100-150	146	123	D
DL-1-amino-2-propanol			7	0.4	100-150	106	123	D
N,N-Dimethylethanolamine	DMMEA		4.81	0.5	135	MEA	122	EH
Monoethanolamine	MEA		3.5	0.4	100-135	129	122	D
N-(2-Aminoethyl)piperazine	AEP		2.33	0.4	135	PZ	121	D
Monoethanolamine	MEA		7	0.2	120-150	123	121	D
Monoethanolamine	MEA		7	0.4	100-150	157	121	D
Ethylenediamine	EDA		7.14	0.25	135	MEA	121	EH

Table 7.6: Estimated stripper temperature at $k_1 = 2.91 \times 10^{-8} \text{ s}^{-1}$ (Continued)

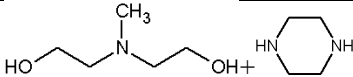
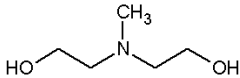
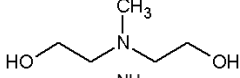
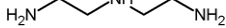
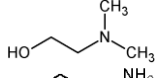
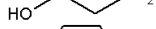
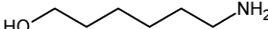
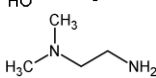
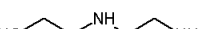
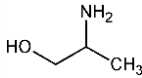
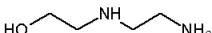
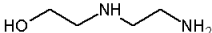
Amine	Abbreviation	Structure(s)	Conc. ^a m	Loading mol/mol alk	T Range of Data °C	Act. Energy ^b kJ/mol	Stripper Temp °C	Ref. ^c
N-Methyldiethanolamine / Piperazine (TA)	MDEA/ PZ		7/ 2	0.25	120-150	111	120	C
N-Methyldiethanolamine	MDEA		3.60	0.5	135	MEA	120	EH
N-Methyldiethanolamine	MDEA		8.4	0.4	135	MEA	119	D
Diethylenetriamine	DETA		4.15	0.17	135	MEA	118	EH
N,N-Dimethylethanolamine	DMAE		4*	2 MPa	140	MEA	118	L1
Monoethanolamine	MEA		7	0.5	100-150	162	117	D
Ethylenediamine	EDA		8	0.4	100-135	154	117	Z
3-(Methylamino)propylamine	MAPA		4.81	0.25	135	MEA	117	EH
6-amino-1-hexanol	6a1h		7	0.4	100-150	148	117	D
Monoethanolamine	MEA		11	0.4	120-135	MEA	116	D
Monoethanolamine	MEA		4*	2 MPa	140	MEA	116	L1
Monoethanolamine	MEA		7.01	0.5	135	MEA	115	EH
N,N-Dimethylethylenediamine	N,N- diMEDA		4*	2 MPa	140	MEA	115	L1
N-(2-Hydroxyethyl)ethylenediamine	HEEDA		4.12	0.25	135	MEA	114	EH
3-(Methylamino)propylamine	MAPA		9	0.4	135	MEA	114	V
DL-2-amino-1-propanol (MIPA)	MIPA		7	0.4	100-150	105	114	D

Table 7.6: Estimated stripper temperature at $k_1 = 2.91 \times 10^{-8} \text{ s}^{-1}$ (Continued)

Amine	Abbreviation	Structure(s)	Conc. ^a m	Loading mol/mol alk	T Range of Data °C	Act. Energy ^b kJ/mol	Stripper Temp °C	Ref. ^c
Monoethanolamine / Diglycolamine [®] (TA)	MEA/ DGA [®]		7/ 2	0.4	100-150	94	112	D
N,N,N'-Trimethylethylenediamine	triMEDA		4*	2 MPa	140	MEA	112	L1
Monoethanolamine	MEA		11	0.5	120-135	MEA	112	D
Monoethanolamine	MEA		3.5	0.5	100-135	86	111	D
2-Piperidinemethanol	2-PM		7	0.4	135	MEA	109	D
Diethylenetriamine	DETA		7	0.4	135-150	MEA	108	D
Monoethanolamine / Morpholine (TA)	MEA/ Mor		7/ 2	0.4	100-150	97	108	D
N,N,N',N'- tetramethylbutylenediamine	TMBDA		4*	2 MPa	140	MEA	107	L3
N,N,N',N',N''- pentamethyldiethylenetriamine	PMDETA		2.5*	2 MPa	140	MEA	105	L3
N-Methylethanolamine	MAE		4*	2 MPa	140	MEA	105	L1
Diethanolamine	DEA		4.08	0.5	135	MEA	105	EH
N,N'-Dimethylethylenediamine	N,N'- diMEDA		4*	2 MPa	140	MEA	104	L1
Monoethanolamine / Piperazine (TA)	MEA/ PZ		7/ 2	0.4	100-150	84	104	D
Diethanolamine	DEA		4*	2 MPa	140	MEA	103	L1
N-Methyldiethanolamine	MDEA		8.39	2.6 MPa	100-180	100	103	CM
2-Methylaminoethanol	MMEA		5.71	0.5	135	MEA	102	EH

Table 7.6: Estimated stripper temperature at $k_1 = 2.91 \times 10^{-8} \text{ s}^{-1}$ (Continued)

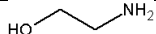
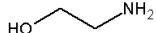
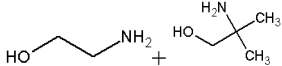
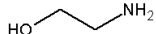
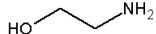
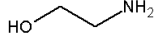
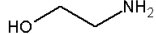
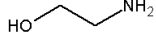
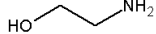
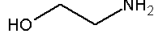
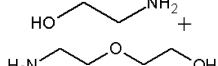
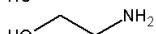
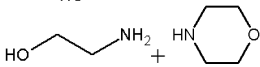
Amine	Abbreviation	Structure(s)	Conc. ^a m	Loading mol/mol alk	T Range of Data °C	Act. Energy ^b kJ/mol	Stripper Temp °C	Ref. ^c
N-(2-Hydroxyethyl) ethylenediamine	HEEDA		3.5	0.4	135	MEA	101	D
N-(2-Hydroxyethyl) ethylenediamine	HEEDA		4*	2 MPa	140	MEA	99	L1

^a Concentrations indicated with asterisks (*) are in units of mole amine per kg solution, not molal (m)

^b Activation Energy used to estimate stripper temperature is noted; PZ indicates that the activation energy of 184 kJ/mole was used based on data at 8 m PZ, $\alpha=0.3$; MEA indicates that the activation energy of 157 kJ/mole was used based on data at 7 m MEA, $\alpha=0.4$.

^c Reference: If blank, data is from this work, otherwise: CM = (Chakma and Meisen, 1997); C = (Closmann et al., 2009); D = (Davis, 2009); EH = (Eide-Haugmo et al., 2011); L1 = (Lepaumier et al., 2009a); L3 = (Lepaumier et al., 2010); RT = (Reza and Trejo, 2006); V = (Vevelstad, 2010); Z = (Zhou et al., 2010).

Table 7.7: Comparison of estimated stripper temperature at $k_1 = 2.91 \times 10^{-8} \text{ s}^{-1}$ for a variety of MEA conditions

Amine	Abbreviation	Structure(s)	Conc. ^a m	Loading mol/mol alk	T Range of Data °C	Act. Energy ^b kJ/mol	Stripper Temp. °C	Ref. ^c
Monoethanolamine	MEA		11	0.2	120-135	MEA	126	D
Monoethanolamine	MEA		3.5	0.2	100-135	60	123	D
Monoethanolamine / 2-Amino-2-methyl-1-propanol (TA)	MEA/ AMP		7/	0.4	100-150	146	123	D
			2					
Monoethanolamine	MEA		3.5	0.4	100-135	129	122	D
Monoethanolamine	MEA		7	0.2	120-150	123	121	D
Monoethanolamine	MEA		7	0.4	100-150	157	121	D
Monoethanolamine	MEA		7	0.5	100-150	162	117	D
Monoethanolamine	MEA		11	0.4	120-135	MEA	117	D
Monoethanolamine	MEA		4*	2 MPa	140	MEA	116	L1
Monoethanolamine	MEA		7.01	0.5	135	MEA	115	EH
Monoethanolamine / Diglycolamine® (TA)	MEA/ DGA®		7/	0.4	100-150	94	112	D
			2					
Monoethanolamine	MEA		11	0.5	120-135	MEA	112	D
Monoethanolamine	MEA		3.5	0.5	100-135	86	111	D
Monoethanolamine / Morpholine (TA)	MEA/ Mor		7/	0.4	100-150	97	108	D
			2					

^a Concentrations indicated with asterisks (*) are in units of mole amine per kg solution, not molal (m)

^b Activation Energy used to estimate stripper temperature is noted; MEA indicates that the activation energy of 156.5 kJ/mole was used based on data at 7 m MEA, $\alpha=0.4$.

^c Reference: D = (Davis, 2009); EH = (Eide-Haugmo et al., 2011); L1 = (Lepaumier et al., 2009a).

7.5 CONCLUSIONS

The calculated k_1 values for thermal degradation were successfully translated into predicted stripper temperatures that represent a maximum acceptable degradation rate. Morpholine (Mor) was determined to be the most stable amine tested to date with a predicted stripper temperature of 170 °C. Piperidine (PD) and piperazine (PZ) and with 0.3 mole CO₂ per mole alkalinity were the next most stable amines with estimated stripper temperatures of 166 and 163 °C, respectively. Cyclic, 6-membered amines such as PZ, Mor, and PD were determined to be exceptionally resistant to thermal degradation.

Substituted PZs such as 1-methylpiperazine (1-MPZ), 2-methylpiperazine (2-MPZ) and PZ analogs such as hexamethylenediamine (HMDA) were shown to be stable, tolerating temperatures between 148 and 160 °C. PZ structural analogs with 5- or 7-membered rings such as pyrrolidine (Pyr), hexamethyleneimine (HMI), and homopiperazine (HomoPZ), were found to have diminished stability. Methylation of the PZ structure at the 1- or 2-position also decreased stability of the PZ molecule to thermal degradation.

The most instable amines measured, such as N-(2-hydroxyethyl)ethylenediamine (HEEDA), 2-methylaminoethanol (MMEA), diethanolamine (DEA), N-methylethanolamine (MAE), diethanoltriamine (DETA), and 3-(methylamino)propylamine (MAPA), which will all degrade significantly at temperatures above 120 °C, are longer straight-chain alkyl amines with at least one secondary amino function and either hydroxyl groups, methyl groups, or multiple amino function. The estimated stripper temperature for 3.5 to 11 m MEA solutions with 0.2 to 0.5 mole CO₂ per mole alkalinity ranged from 111 to 126 °C.

A thermal equilibrium between PZ, 1-MPZ, and 1,4-DMPZ was discovered that offers the opportunity for a blended solvent that is resistant to overall thermal degradation. At 150 °C, the equilibrium constant for the disproportionation of 1-MPZ into PZ and 1,4-DMPZ with 0.3 mole CO₂ per mole alkalinity was found to be 0.28. A tertiary blend designed around this constant, 3.9 m PZ / 3.9 m 1-MPZ / 0.2 m 1,4-DMPZ degraded with a k_1 value of $8.44 \times 10^{-9} \text{ s}^{-1}$, only 37% higher than the k_1 for 8 m PZ with 0.3 mole CO₂ per mole alkalinity.

PZ was not found to preferentially degrade in a blend of 4 m PZ + 4 m 1-MPZ since an equilibrium is being established that occurs more rapidly than thermal degradation. PZ is preferentially degraded in blends with MDEA and MEA. In the presence of MDEA, PZ degrades up to 15 times faster than MDEA. The stability of PZ when blended with another amine depends heavily on the pK_a or nucleophilic strength of the amine. Blending PZ has been previously stated as inadvisable, but could be advantageous when matched with a similarly stable molecule, such as 1-MPZ or 2-MPZ.

Chapter 8 – Oxidation of Concentrated, Aqueous PZ

The oxidation of concentrated PZ was investigated over a variety of conditions to understand oxidative degradation expected in absorption-stripping CO₂ capture systems. Previous work on concentrated PZ demonstrated a resistance to oxidation that was identified as an advantageous characteristic of the solvent (Sexton, 2008). This chapter details the experiments performed that analyzed the effect of oxygen (O₂), temperature, CO₂, and PZ. The effect of CO₂ was not fully analyzed due to the compounding effect of changing both CO₂ and O₂ at the same time. The reactor used to perform the oxidation experiments is analyzed in detail for possible sources of error. All of the oxidation products that have been identified are described in detail along with carbon and nitrogen balances typically achieved in concentrated PZ oxidation experiments.

8.1 SUMMARY OF OXIDATION EXPERIMENTS PERFORMED

A summary of the experiments performed investigating the oxidation of concentrated PZ is shown in Table 8.1. All experiments were performed with 8 molal (m) PZ, except for the first two. After the first 16 experiments, the reactor was redesigned as described in Section 3.2.3, and the remaining experiments were carried out in the new reactor. The temperature of the reactor was varied between 55 and 70 °C through the addition of an oil bath as a way to further accelerate oxidation. O₂ content was varied between 40 and 98 kPa in the headspace with CO₂ loadings varying from 0.2 to 0.4 mole CO₂ per mole alkalinity. A variety of metal catalysts including iron (II) (Fe²⁺), chromium (III) (Cr³⁺), nickel (II) (Ni²⁺), copper (II) (Cu²⁺), and vanadium (V) (V⁵⁺) were used to induce oxidation. Three inhibitors, Inhibitor A, Inhibitor B, and Inhibitor C, were also tested for their efficacy at inhibiting metal-catalyzed PZ oxidation. The effects of metal catalysts and inhibitors are discussed in detail in Chapter 9. The tabulated results of each experiment can be found in Appendix E of this dissertation.

8.2 MECHANICAL LIMITATIONS OF EXPERIMENTAL APPARATUS

Oxidation of concentrated PZ was first attempted by Sexton when 2.5 and 5 m PZ were oxidized using a low gas flow reactor (Sexton, 2008). Sexton found that oxidation occurred, but at significantly slower rates than MEA under similar conditions. The slow oxidation was difficult to quantify accurately with the analytical equipment utilized at the time. Experiments performed in this project matched the work of Sexton and confirmed his observations on the resistance of PZ to oxidation.

Table 8.1: Summary of PZ oxidation experiments performed

Expt.	Rxtr.	PZ m	T °C	P _{CO2} kPa	CO ₂ Ldg mol/mol alk	P _{O2} kPa	Additives* mM
OE1	OOR	10	55	2	0.3	98	Fe (0.23), Cr (1.6), Ni (0.2)
OE2	OOR	10	55	2	0.3	98	Cu (4)
OE3	OOR	8	55	2	0.3	98	Fe (0.1), V (0.1)
OE4	OOR	8	55	2	0.3	98	Fe (0.1), Cu (5), A (100)
OE5	OOR	8	55	2	0.3	98	Fe (1)
OE6	OOR	8	55	2	0.3	98	Fe (1), A (100)
OE7	OOR	8	55	2	0.3	98	Fe (1), B (20)
OE8	OOR	8	55	2	0.3	98	Fe (1), C (30)
OE9	OOR	8	55	2	0.3	0	-
OE10	OOR	8	55	2	0.3	0	-
OE11	OOR	8	55	2	0.3	98	-
OE12	OOR	8	55	2	0.3	98	-
OE13	OOR	8	55	2	0.3	98	Fe (1)
OE14	OOR	8	55	2	0.3	98	Fe (1), A (100)
OE15	OOR	8	55	2	0.3	98	SSM
OE16	OOR	8	55	2	0.3	98	SSM, A (10)
OE17	TOR	8	55	2	0.3	98	Fe (1)
OE18	TOR	8	55	2	0.3	98	SSM
OE19	TOR	8	70	2	0.2	98	SSM
OE20	TOR	8	70	2	0.2	98	SSM, Formate (500)
OE21	TOR	8	70	2	0.2	98	SSM, Formaldehyde (500)
OE22	TOR	8	70	60	0.4	40	SSM
OE23	TOR	8	70	6	0.3	40	Cu (4)
OE24	TOR	8	70	6	0.3	40	Cu (4), A (100)
OE25	TOR	8	70	6	0.3	94	Cu (4)
OE26	TOR	8	70	6	0.3	94	SSM
OE27	TOR	8	55	2	0.3	40	Cu (4)
OE28	TOR	8	55	2	0.3	40	SSM

* Abbreviations are as follows: Fe is Fe²⁺ added as FeSO₄·7H₂O; Cr is Cr³⁺ added as CrK(SO₄)₂·12H₂O; Ni is Ni²⁺ added as NiSO₄·6H₂O; Cu is Cu²⁺ added as CuSO₄·5H₂O; V is V⁵⁺ added as NaVO₃; A is Inhibitor A; B is Inhibitor B; C is Inhibitor C; SSM indicates the standard stainless steel metals mixture (0.4 mM Fe²⁺ + 0.1 mM Cr³⁺ + 0.05 mM Ni²⁺)

There were mechanical limitations of both low gas flow reactors used to oxidize PZ in this project. The Original Oxidation Reactor (OOR), which was used previously and had a rubber stopper as a lid, and the Teflon® Oxidation Reactor (TOR), which was

designed for this work from a jacketed glass reactor with flange and Teflon[®] lid, were subject to similar limitations. The primary difficulty encountered in both was in maintaining the water balance during the experiment. Water and amine are primarily lost during experiments through the annular space surrounding the agitator. In order to maintain the water balance, the assumption was made that liquid loss between sampling was all water, which agrees with an analysis of the relative volatility of water and PZ (see section 8.2.4 for more details). The water balance is also influenced by the pre-saturator and the amount of water that enters the reactor system in the gas phase.

Another operational concern is the mechanical stability of the agitator, which vibrates due to the fast agitation rate (1400 rpm). The agitator shaft can catch on the lid, causing catastrophic failure of the reactor which is a serious safety concern due the presence of glass and hot liquid amine.

The quality of data obtained from either reactor (OOR or TOR) is subjective and depends heavily on the individual conditions of each experiment. The goal during each experiment was to minimize the error in an effort to make the data as smooth and understandable as possible. There are many times, however, when data is scattered and does not behave as expected. It is assumed that there were influences from the reactor and water balance on these occasions. For instance, if a sampling port was left uncovered overnight or the flange was not fully tightened, extra liquid can evaporate due to this opening and cause a drastic shift in the water balance. A small operational change or error can greatly influence the data obtained from these types of reactors.

All of these operational concerns are only of critical importance for amine systems that do not degrade readily, like PZ. The same conditions were present for the work of Sexton but were not as influential because MEA, AMP, and other amines tested easily degraded with short experiments. Errors due to the water balance were likely

overshadowed in most cases by the loss of amine due to rapid oxidation. PZ presents a unique problem of attempting to measure oxidation that occurs very slowly and requires longer experiments. Small fluctuations in the operation of the reactor impacted the data immensely causing more scatter and difficulty in quantifying only small changes in concentration of either PZ or the degradation products.

An issue discussed throughout this chapter is the fact that oxidation experiments show PZ losses in the range of 2 to 10% of the initial PZ while producing few quantified degradation products, usually accounting for less than 1% of the lost PZ. The most likely explanation is that the products to which PZ is degrading are not able to be detected, identified, or quantified with the analytical techniques employed for PZ oxidation thus far. The techniques regularly employed for PZ thermal degradation (i.e. anion IC and cation IC) may not capture the most important oxidation products. In a similar vein, it is possible that one or more major degradation products are volatile and escape the reactor without retaining a significant concentration in the liquid phase for analysis. The impact of this possibility was not assessed because the current reactor design does not support gas phase analysis. There may also be additional mechanical issues relating to the reactor itself, which does not exclude the presence of unidentified volatile or non-volatile degradation products. All of these options for explaining the mass balance disparity are discussed in detail in the next sections.

8.2.1 Baseline oxidation experiments

A series of baseline oxidation experiments were performed in an attempt to assess both the repeatability of the entire experimental procedure and the impact of the reactor itself of PZ losses in the absence of catalyst. The first two baseline experiments (OE9 and OE10) were performed at 55 °C with agitation at 1400 rpm and with a gas stream of

100 mL per minute of 98% N₂/2% CO₂ in the absence of any metal catalyst or inhibitors. These conditions were meant to measure the loss of PZ that was due to mechanical losses from volatility at 55 °C, entrainment, or water balance inconsistencies due to the air stream exiting the reactor around the agitator opening. The second two baseline experiments (OE11 and OE12) were performed at the same conditions, except for a change in the gas phase composition to 98% O₂/2% CO₂. These conditions were intended to provide a baseline level of degradation due to O₂ alone, in the absence of metal catalysts. The agitator shaft is constructed of stainless steel, however, so the solutions may have been exposed to a small amount of leached metal. Each of these conditions was duplicated to observe the repeatability in oxidation experiments.

The raw and sulfate adjusted data for PZ loss in the presence of N₂/CO₂ is compared in Figure 8.1. Sulfate adjustment of the data is used in to take into account the water balance of the reactor at any given time through the use of a tracer compound (Sexton, 2008). Sulfate added as potassium sulfate (K₂SO₄) was used as a tracer and all concentrations are adjusted based on the ratio of sulfate in the current sample to that of the initial sample. Since the analysis of the baseline experiments deals with how well the water balance is maintained, both the raw and sulfate adjusted data are shown.

The repeatability in these oxidation experiments was poor. For either the raw or adjusted data, the PZ loss for OE9 and OE10 were substantially different over the course of the experiment. After 150 hours, OE9 has lost 5% of the initial PZ while OE10 has lost only 0.5%. The data were more similar at 240 hours where they have lost 4 and 2%, respectively. The sulfate adjusted data show even stronger disagreement in both the values and the trends of each experiment. The overall range of values is not large and both experiments lose 3 to 7% of the initial PZ during the experiment in the absence of O₂ due to mechanical losses. From these results, it was determined that the sulfate

adjusted data were not providing any insight into the water balance of the reactor. The trends of the raw data are more regular and proceed as expected without rapid changes.

The generation of formate, total formate, and EDA are compared between the two experiments in Figure 8.2. It was not expected that detectable and increasing levels of degradation products would be produced in the absence of O₂, but small concentrations were quantified. The concentration profiles for each species do not track closely between the two experiments, but the overall quantity of formate and total formate are approximately the same at the end of the experiments. The concentrations themselves are small, all being less than 6 mmole per kg at the most.

The raw and sulfate adjusted PZ loss data in the O₂/CO₂ baseline experiments are compared in Figure 8.3. Unlike the previous set of experiments, it was expected that a small amount of oxidation would occur in these experiments due to the presence of O₂ and trace amount of metals from the agitator. The repeatability between the two experiments is similar to the previous set, but the sulfate adjustment appears to skew the data into unexpected trends and added scatter. The raw data is well behaved and produced the expected trend of a small rate of oxidation. After about 300 hours, each experiment has lost between 3.5 and 6.5% of the initial PZ. The repeatability of the two experiments is approximately the same as that between OE9 and OE10.

The degradation products generated during the O₂/CO₂ baseline experiments are compared in Figure 8.4. Detectable and increasing levels of formate and formyl amides were found in both experiments while EDA was only detected in OE11. The concentration profiles for formate track closely to each other while there is appreciable deviation in the EDA and total formate concentrations. As with the N₂/CO₂ baseline experiments, the maximum concentrations of all degradation products are small, all being less than 6 mmole per kg at their maximum.

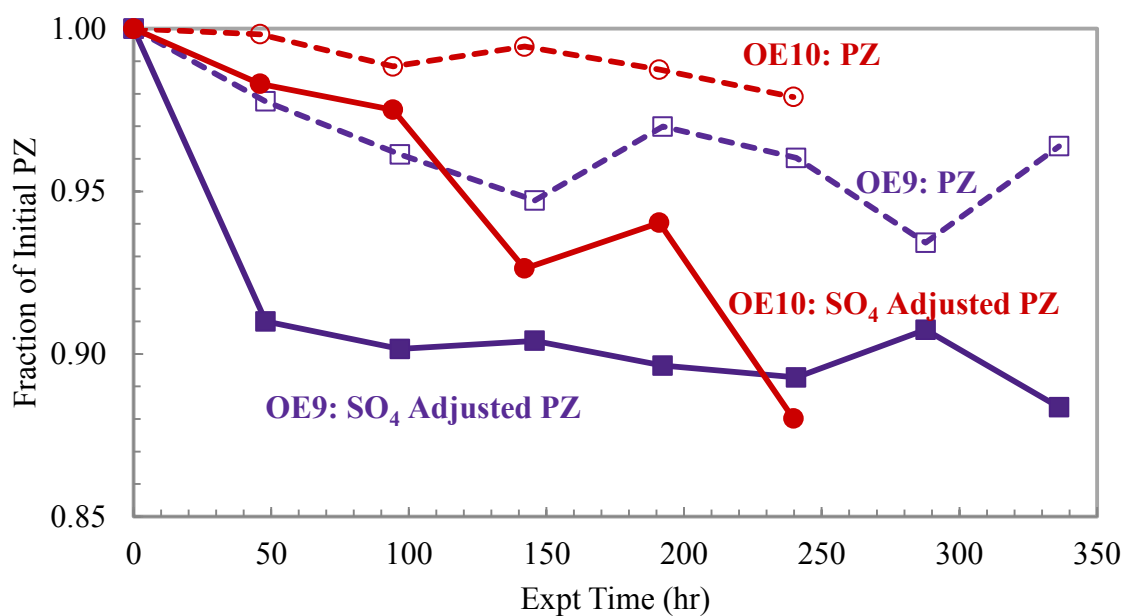


Figure 8.1: Comparison of PZ loss in N₂/CO₂ baseline experiments with original (dashed) and sulfate adjusted (solid) data (8 m PZ, 55 °C, 1400 rpm, 100 mL per minute of 98% N₂/2% CO₂, no catalyst)

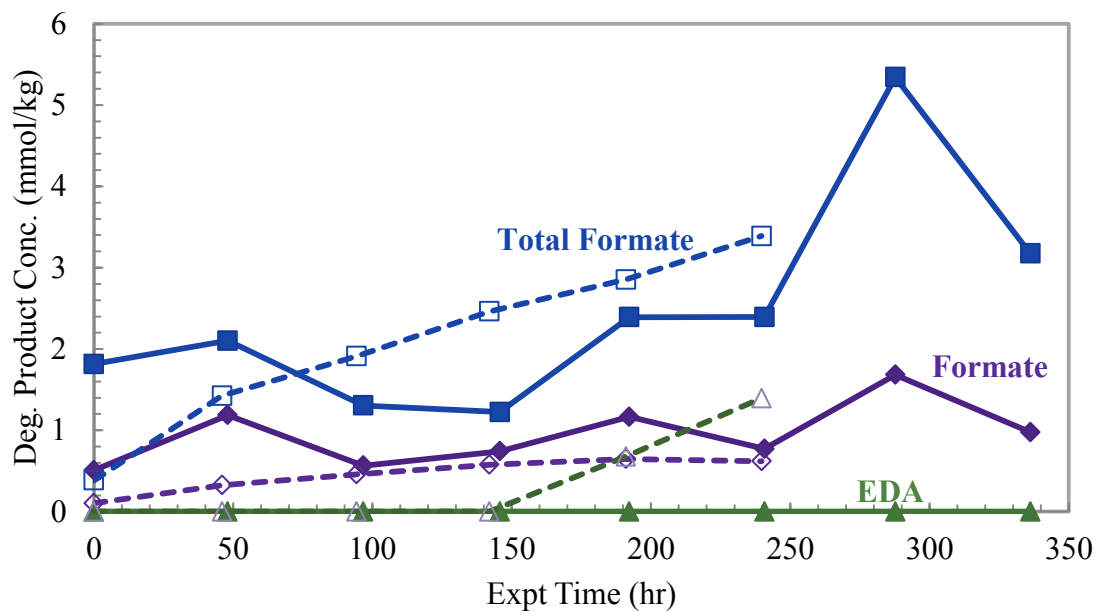


Figure 8.2: Generation of formate (◆), total formate (■), and EDA (▲) in N₂/CO₂ baseline experiments for OE9 (filled points) and OE10 (open points) (8 m PZ, 55 °C, 1400 rpm, 100 mL per minute of 98% N₂/2% CO₂, no catalyst)

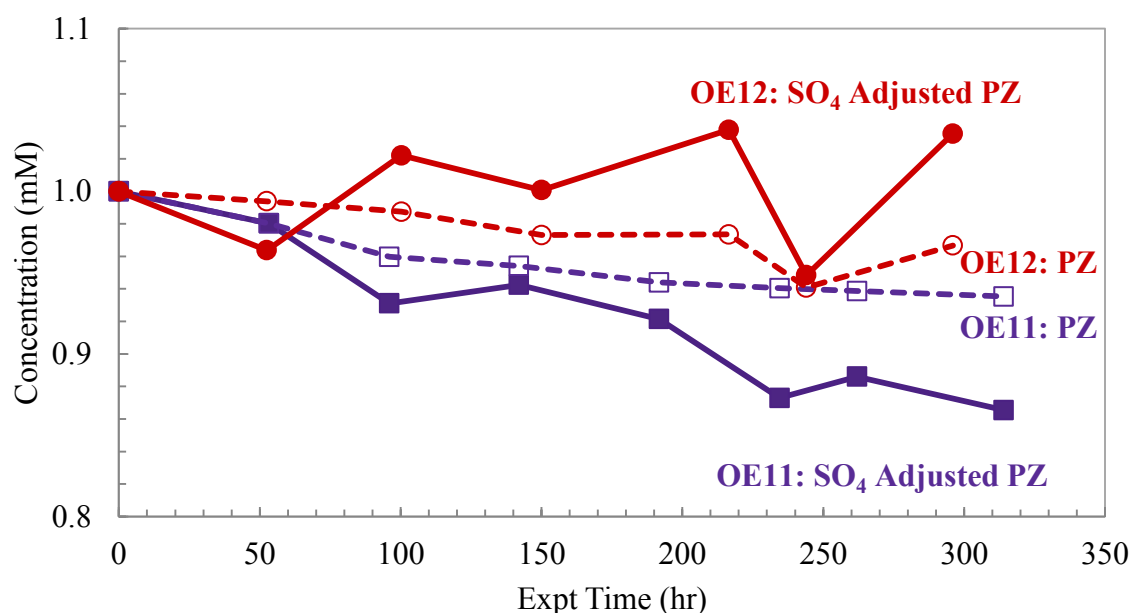


Figure 8.3: Comparison of PZ loss in O₂/CO₂ baseline experiments with original (dashed) and sulfate adjusted (solid) data (8 m PZ, 55 °C, 1400 rpm, 100 mL per minute of 98% O₂/2% CO₂, no catalyst)

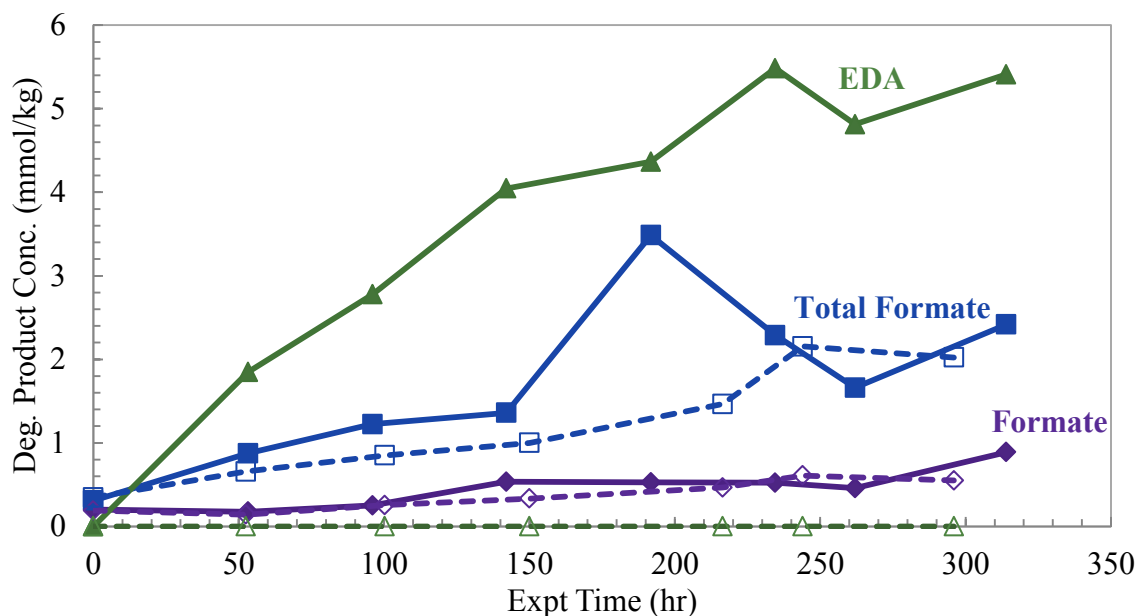


Figure 8.4: Comparison of formate (◆), total formate (■), and EDA (▲) in O₂/CO₂ baseline experiments for OE11 (filled points) and OE12 (open points) (8 m PZ, 55 °C, 1400 rpm, 100 mL per minute of 98% O₂/2% CO₂, no catalyst)

8.2.2 Repeatability and error

These baseline experiments quantify repeatability and show a systematic loss of PZ without corresponding concentrations of oxidation products. The repeatability of the oxidation experiments is not as high as preferred and is assumed to be primarily to the low level of oxidation occurring and, to a lesser extent, due to limitations in the analytical equipment. The quantification of PZ and EDA is performed on cation IC with a 10000X dilution prepared from a set of serial 100X dilutions. Since serial dilutions are used, there is more opportunity for error and inconsistency. EDA and PZ have nearly identical response factors on the cation IC, so the small expected concentration of EDA is problematic with this high dilution. Also, there is a bump in the baseline due to a change in the eluent gradient in the cation IC method where EDA elutes, adding to the difficulty. The concentration of degradation products are expected to be within the detection limit of the analytical equipment, generally understood to be near 1-2 mmole per kg, but the disparity in concentration creates additional error.

Comparing PZ loss in all four baseline experiments demonstrates a loss of 2 to 7% of the initial PZ due to all of sources of error discussed (Figure 8.5). This includes PZ losses due to oxidation, volatility, entrainment, dilution or concentration of PZ due to water balance issues, the addition of water or loss of water through the pre-saturator, losses experienced during start-up, sampling, and the clean-up of the reactor, and analytical error. All oxidation experiments discussed in this chapter and the next should be examined in light of this conclusion. PZ losses of less than or close to 7% over a two week standard experiment length should be cautiously described as oxidation. Oxidation above and beyond 7% in two weeks is needed to positively identify PZ oxidation versus the losses due to experimental considerations. A majority of figures showing PZ loss presented in these two chapters include these baseline curves in light gray. These data

are included to allow more accurate interpretation of data in light of the conclusions from the baseline experiments. The data for the generation of degradation products during the baseline experiments are also included on figures when data is difficult to interpret due to low oxidation rates.

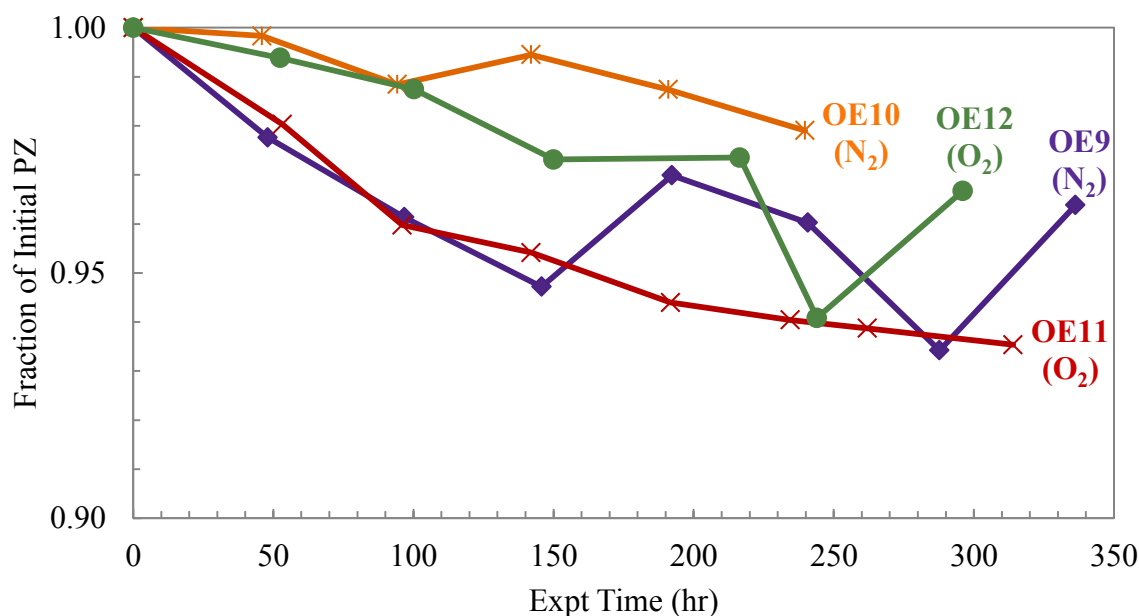


Figure 8.5: Comparison of PZ loss for all baseline experiments (8 m PZ, 55 °C, 1400 rpm, 100 mL per minute of 98% N₂ or O₂/2% CO₂, no catalyst)

8.2.3 Comparison of OOR and TOR

Once the Teflon[®] Oxidation Reactor (TOR) was built to replace the Original Oxidation Reactor (OOR), a baseline Fe²⁺-catalyzed experiment was performed in the new reactor. Solutions of 8 m PZ were oxidized in each reactor at 55 °C with 100 mL per minute of 98% O₂/2% CO₂, agitation at 1400 rpm, and 1 mM Fe²⁺. The PZ loss and generation of dominant degradation products is compared between the OOR (OE13) and TOR (OE17) experiments in Figure 8.6 and Figure 8.7, respectively. The results, unfortunately, do not demonstrate strong agreement in PZ loss (Figure 8.6). The trend in

the OE17 data, however, shows a clear dip in the initial sample and then a leveling off of the data to a subtle downward slope. This behavior is typical of a period of time where the reactor was open to the environment in some way and experienced a high rate of water loss. Since this was the first experiment in the TOR, the flange clamp holding the top of the reactor to the Teflon[®] lid was not fully tightened, allowing water loss. The clamp was not tightened fully because the appropriate tightness to obtain a secure connection without damaging the flange was not yet known. An accumulation of water between the lid and the glass flange was observed during the first sample and the clamp was then tightened, the slope in the PZ data after this point, excluding the initial point, likely demonstrate the expected loss of PZ under these conditions. The slope of the data in this region agrees with that of the OOR experiment which shows about 8% loss of the initial PZ after 450 hours.

The generation of degradation products mostly agrees between the two experiments (Figure 8.7). Formate and total formate generation rates agree, but with some scatter in the data. EDA, on the other hand, was not detected in the earlier experiment in the OOR. This may be similar error as was seen with EDA detection in the baseline experiments, or analysis done later in OE17 was more advanced. In both cases, oxidation was slow and degradation products did not accumulate to significant concentrations during the course of the 450 hour experiment.

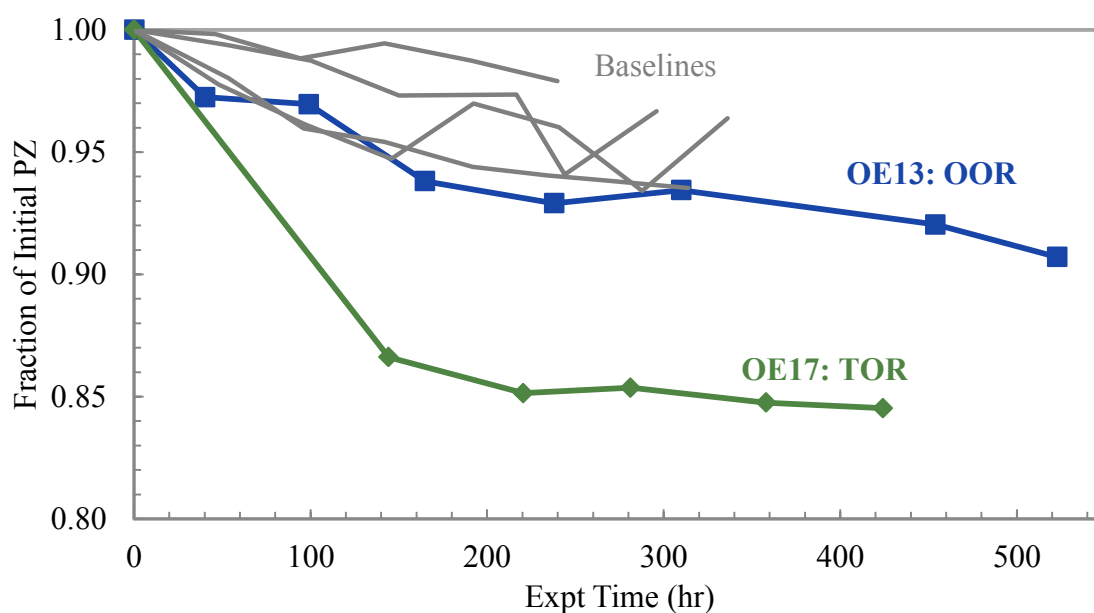


Figure 8.6: Comparison of PZ loss during oxidation in the OOR and TOR (8 m PZ, 55 °C, 1400 rpm, 100 mL per minute of 98% O₂/2% CO₂, 1 mM Fe²⁺)

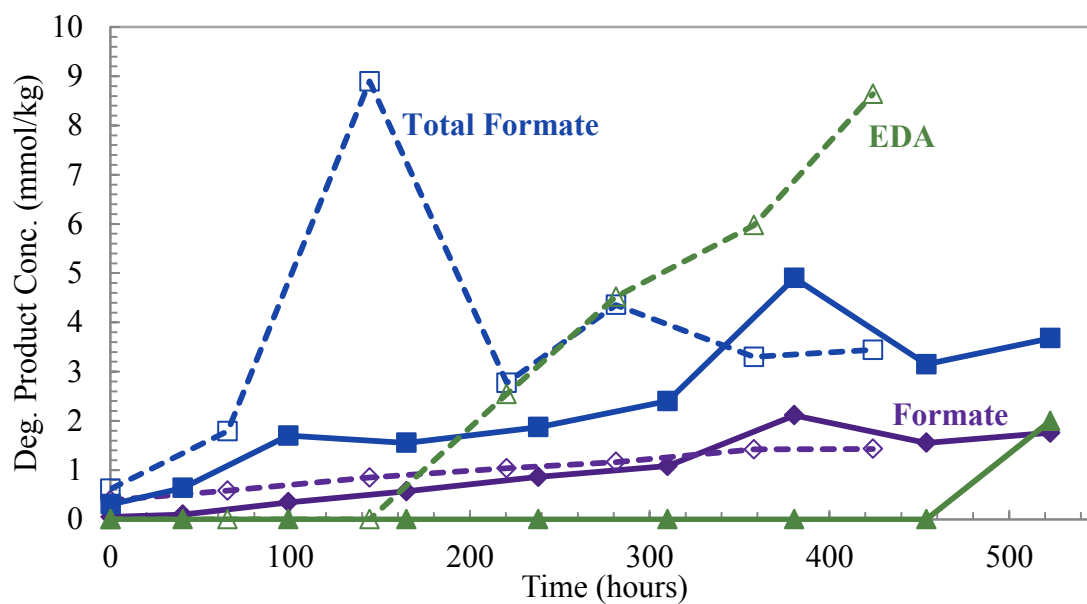


Figure 8.7: Generation of formate (◆), total formate (■), and EDA (▲) during PZ oxidation in the OOR (filled points, OE13) and TOR (open points, OE17) (8 m PZ, 55 °C, 1400 rpm, 100 mL per minute of 98% O₂/2% CO₂, 1 mM Fe²⁺)

8.2.4 Volatility of PZ in oxidation experiments

The volatility of PZ is a concern for all oxidation experiments because the reactors are open to the atmosphere around the agitator and have with 100 mL per minute of gas flowing in and out of the headspace of the reactor. The volatility of PZ and water in loaded 8 m PZ has been accurately measured by Nguyen using a multi-component FTIR, as discussed in section 2.3.5 (Nguyen et al., 2010). Using this information, an estimation of the PZ and water loss due to volatility during operation of the TOR reactors was made to determine the effect of volatility to the PZ mass balance. The partial pressure of PZ in 8 m PZ with a loading of 0.29 moles CO₂ per mole alkalinity is shown at 40 and 60 °C in Figure 8.8. The two data points were regressed with a linear trendline and the partial pressure of PZ was extrapolated to 55 and 70 °C. The partial pressure of PZ in a lean loaded (0.3 mole CO₂ per mole alkalinity) solution was estimated to be 0.00438 and 0.00798 kPa at 55 and 70 °C, respectively. This value was then converted to parts per million (ppm) using atmospheric pressure of 1 atm.

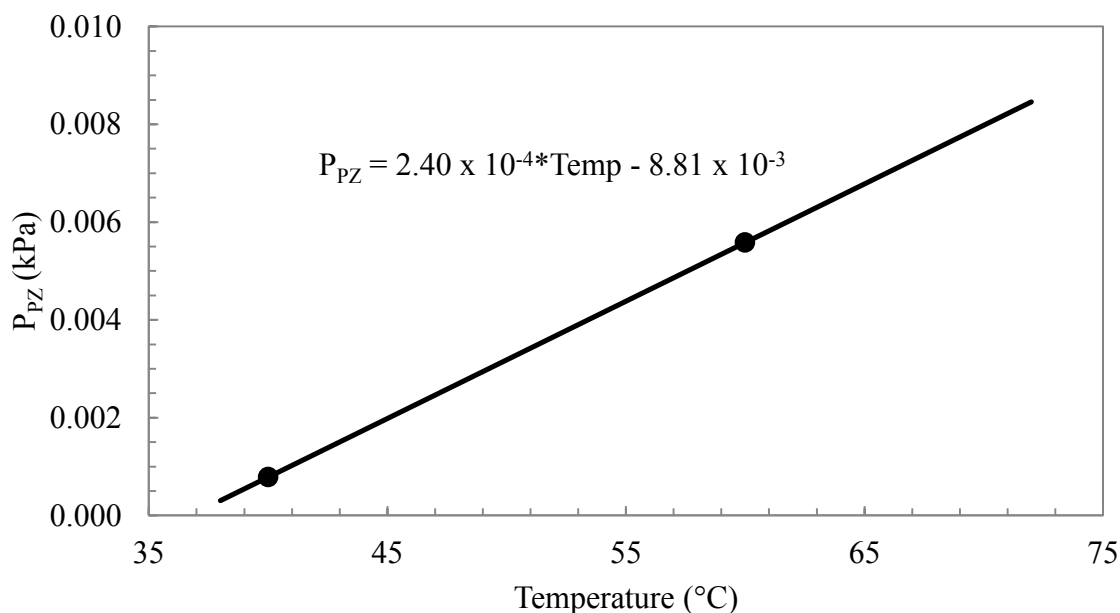


Figure 8.8: Volatility of 8 m PZ with 0.29 mole CO₂ per mole alkalinity

The concentration in ppm estimated for each temperature was then converted to a volumetric flow rate using the total gas flow rate. First, the molar volume of an ideal gas (V_M), was calculated using the ideal gas law (Equation 8.1) for each temperature using the ideal gas constant, R , system temperature, T , and system pressure, P .

$$PV = nRT \quad (8.1)$$

$$\frac{V}{n} = \frac{RT}{P} = V_M \quad (8.2)$$

The molar volume of an ideal gas at 55 and 70 °C are calculated in Equation 8.3 and Equation 8.4, respectively.

$$V_{M, 55^\circ \text{C}} = \frac{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) \times (55^\circ \text{C} + 273.15)\text{K}}{(1 \text{ atm})} = 26.93 \frac{\text{L}}{\text{mol}} \quad (8.3)$$

$$V_{M, 70^\circ \text{C}} = \frac{\left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) \times (70^\circ \text{C} + 273.15)\text{K}}{(1 \text{ atm})} = 28.16 \frac{\text{L}}{\text{mol}} \quad (8.4)$$

Using the calculated values for the molar volume at each temperature, the concentration in ppm can be converted to a volumetric concentration, C_V , in each case using the following equation (Equation 8.5).

$$C_V = \frac{\text{ppm} \times \text{MW}}{V_M} \quad (8.5)$$

The estimated volumetric concentration of PZ exiting the reactor at 55 and 70 °C are calculated in Equation 8.6 and Equation 8.7, respectively.

$$C_{V,55^{\circ}\text{C}} = \frac{\left(\frac{43.24 \mu\text{g}}{\text{g}}\right) \times \left(\frac{1 \text{ g}}{10^6 \mu\text{g}}\right)}{\left(26.93 \frac{\text{L}}{\text{mole}}\right) \times \left(\frac{1 \text{ mole}}{1000 \text{ mmole}}\right) \times \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right)} = 1.61 \times 10^{-6} \frac{\text{mmole}}{\text{mL}} \quad (8.6)$$

$$C_{V,70^{\circ}\text{C}} = \frac{\left(\frac{78.74 \mu\text{g}}{\text{g}}\right) \times \left(\frac{1 \text{ g}}{10^6 \mu\text{g}}\right)}{\left(28.16 \frac{\text{L}}{\text{mole}}\right) \times \left(\frac{1 \text{ mole}}{1000 \text{ mmole}}\right) \times \left(\frac{1000 \text{ mL}}{1 \text{ L}}\right)} = 2.80 \times 10^{-6} \frac{\text{mmole}}{\text{mL}} \quad (8.7)$$

Using the total flow rate of gas entering and exiting the reactor, the loss of PZ can be calculated per unit time. The loss of PZ per hour of operation has been estimated for operation at 55 °C in units of mmole and mg per hour in Equation 8.8 and Equation 8.9, respectively. The same has been calculated for operation at 70 °C in Equation 8.10 and Equation 8.11, respectively.

$$\text{Loss}(55^{\circ}\text{C}) = \left(\frac{1.61 \times 10^{-6} \text{ mmole}}{\text{mL}}\right) \times \left(\frac{100 \text{ mL}}{\text{min}}\right) \times \left(\frac{60 \text{ min}}{\text{hr}}\right) = 0.00963 \frac{\text{mmole}}{\text{hr}} \quad (8.8)$$

$$\text{Loss}(55^{\circ}\text{C}) = \left(\frac{1.38 \times 10^{-4} \text{ mg}}{\text{mL}}\right) \times \left(\frac{100 \text{ mL}}{\text{min}}\right) \times \left(\frac{60 \text{ min}}{\text{hr}}\right) = 0.83 \frac{\text{mg}}{\text{hr}} \quad (8.9)$$

$$\text{Loss}(70^{\circ}\text{C}) = \left(\frac{2.80 \times 10^{-6} \text{ mmole}}{\text{mL}}\right) \times \left(\frac{100 \text{ mL}}{\text{min}}\right) \times \left(\frac{60 \text{ min}}{\text{hr}}\right) = 0.0168 \frac{\text{mmole}}{\text{hr}} \quad (8.10)$$

$$\text{Loss}(70^{\circ}\text{C}) = \left(\frac{2.41 \times 10^{-4} \text{ mg}}{\text{mL}}\right) \times \left(\frac{100 \text{ mL}}{\text{min}}\right) \times \left(\frac{60 \text{ min}}{\text{hr}}\right) = 1.45 \frac{\text{mg}}{\text{hr}} \quad (8.11)$$

These loss rates lead to daily losses of only 0.23 and 0.40 mmole PZ per day, or 0.020 and 0.035 gram of PZ at 55 and 70 °C. At 55 °C, this loss rate could account for the experiments with minimum or even negligible loss rates of PZ, such as OE6, OE15,

or OE18. At 70 °C, this volatility accounts for only 11.6% of the minimum loss rate of PZ observed (OE19). At worst, volatility accounts for only 0.3 and 0.2%, respectively, of the PZ loss rate in heavily oxidized experiments at 55 and 70 °C (OE2 and OE25, for example). This indicates that PZ losses due to volatility are not an important portion of the PZ loss seen over the course of an experiment. Volatility is on the same order as PZ loss only in experiments with difficult to detect levels of oxidation due to weak catalysts. In the reactor, PZ may also leave the reactor through entrainment, or the effect of liquid drops leaving the reactor through splashing of the liquid or aerosolization, which is not included in this calculation. This phenomenon is not well understood and would be dictated by the temperature of the reactor, gas flow in the headspace, agitation rate, and agitator shaft position relative to the liquid surface. Entrainment and aerosolization could cause more PZ to leave than by simple volatility, but the effect is not definitively known.

This same analysis was performed for water using water volatility measurements obtained during the same experiments used to determine PZ volatility. Water volatility is strictly dependent on temperature, not CO₂ loading as with PZ volatility. The partial pressure measurements for water at 40 and 60 °C were extrapolated to determine those at 55 and 70 °C. The estimated values are partial pressures of 13.17 and 20.46 kPa water, or 130002 and 201875 ppm water, at each temperature respectively. Using the same analysis presented above for PZ, the loss of water at each temperature was determined to be 12.51 and 18.58 gram water per day at 55 and 70 °C. These high loss rates are comparable with the water replacement rates quantitatively observed with experiments at each temperature.

For seven experiments performed at 70 °C in the TOR, an average of 11.51 g of water (range of 8.1 to 18.9 grams) was added per day to the reactor and the saturator in total (OE19 through OE25). This represents the total amount of replacement water that

was needed in the system to maintain system levels. The actual water additions are of a similar magnitude to the theoretical volatility of water that indicates that 18.58 grams of water should volatilize per day. During operation of the TOR at 55 °C, an average of 5.36 grams of water (range of 4.3 to 6.4 grams) was added to the reactor per day (OE17 and OE18) compared to the theoretical value of 12.51 grams, but this did not include additions to the saturator (which was not recorded). In the high temperature experiments, the water added to the saturator is nearly identical to that added to the reactor itself (average of 5.63 grams to saturator compared to 5.89 grams to the reactor). If the same ratio held for the low temperature experiments, the total water added to the low temperature experiments may have been closer to 10.7 grams of water, closely matching the theoretical water volatility calculations.

Another issue related to PZ volatility is the volatility of oxidation products that will be produced during the reactions. The volatility of some degradation products, such as EDA, is well understood (Zhou et al., 2010). On the other hand, the volatility of other degradation products are either not well understood in this particular solvent system, as is the case of ammonia volatility, or not understood at all, as in the case of PZ-based amides. The use of the low gas flow reactor, either the OOR or TOR, assumes that the solvent under investigation produces dominantly liquid phase degradation products since it is not equipped with gas phase analysis. The dominant oxidation pathways for PZ are not fully understood, but volatile products are certainly expected, such as $\text{NH}_3/\text{NH}_4^+$, NO_x , and formaldehyde, and will not be captured with this experimental procedure.

8.2.5 Total Nitrogen (TN) and Total Organic Carbon (TOC) analysis

The final explanation for mass balance issues during oxidation experiments is the inability to identify and quantify all of the degradation products generated from PZ

oxidation. One universal method to determine if the liquid phase contains additional degradation products is a total organic carbon (TOC) and total nitrogen (TN) analysis. The total organic carbon assay measures the concentration of C contained in all organic liquid phase components. This excludes inorganic C such as in carbonate or bicarbonate. Inorganic C is quantified by a separate total inorganic carbon (TIC) assay. The TN analysis quantifies all N in the liquid phase in a similar fashion. TOC and TN were not performed on all experiments, but a select few to highlight the role of unidentified degradation products. Error bars shown represent the standard deviation in five replicates of either a TOC or TN measurement. The expected overall error of both analyses is at least 5%.

OE11, one of the baseline experiments performed in the presence of O₂/CO₂ but without metal catalysts, was analyzed for TOC and TN. The TOC and TN during the course of the experiment are shown as a fraction of the initial concentration in Figure 8.9. The data show that while the concentration of organic C is maintained during the experiment, there is a statistically significant loss of N. In OE11, 6.5% of the initial PZ was lost during the experiment. Since the error in the TOC and TN analysis is expected to be around 5%, a loss of 6.5% in either assay would be observable. The error bars on the last TN data points suggest up to 8.5% of the N is lost after 350 hours of oxidation. This suggests that there are N-based products lost in the gas phase during the experiment. On the other hand, the TOC concentration is relatively constant, suggesting C-containing degradation products in solution that have yet to be identified. The TOC results indicate that the PZ loss is primarily due to the production of unidentified degradation products that remain in solution, as hypothesized.

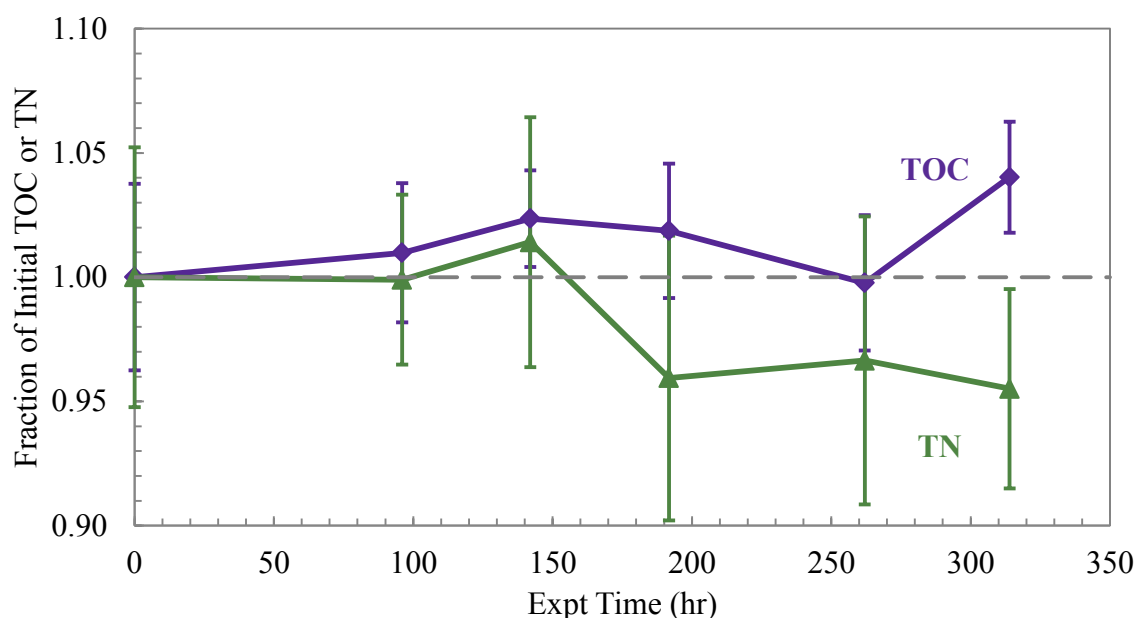


Figure 8.9: TOC and TN in the liquid phase during OE11 (8 m PZ, 55 °C, 1400 rpm, 100 mL per minute of 98% O₂/2% CO₂, no catalyst)

OE25, an oxidation experiment with a very high rate of oxidation due to the presence of Cu²⁺ catalyst and high temperature, was also analyzed for TOC and TN. The TOC and TN are presented as a fraction of the initial value in Figure 8.10. Although the reaction conditions were very different, both OE11 and OE25 had similar results for the TOC data with no appreciable loss or change of the TOC data after 350 hours. This confirms the presence of unidentified C-based degradation products at both low and high rates of oxidation. The TN data for this experiment is striking in that 27% of the initial N is lost after 350 hours. This loss of N, 2650 mmole per kg after 350 hours, is significant and well outside the analytical error. This loss of N while maintaining overall the C concentration suggests, as with OE11 discussed previously, volatile N-based compounds without attached C.

The concentrations of PZ, total alkalinity, and total N for OE25 are compared in Figure 8.11. There is a decrease in all three measurements and the extent of PZ oxidation

is clearly demonstrated. PZ is lost rapidly and degradation products are generated that retain alkalinity in solution, indicated by the higher concentration in total alkalinity. Of these products, some retain N functions and keep the TN concentration higher than either PZ or total alkalinity in the liquid phase. This comparison confirms the detection of products such as ammonium and EDA in the liquid phase that retain alkalinity. The difference between the alkalinity and TN curves represent products that retain N but would not alkalinity, like ureas or amides. The TN results clearly suggest volatile, non-C products which must be ammonia (NH_3), nitrogen oxides (NO_x ; NO or NO_2), or molecular nitrogen (N_2). Ammonia is known to be volatile and the presence of small concentrations of ammonium in the liquid suggests lost ammonia in the gas phase. Ammonia was found as an oxidation product of PZ previously in a high-gas flow reactor using multi-component FT-IR while NO_x was not mentioned as a gaseous product (Sexton, 2008).

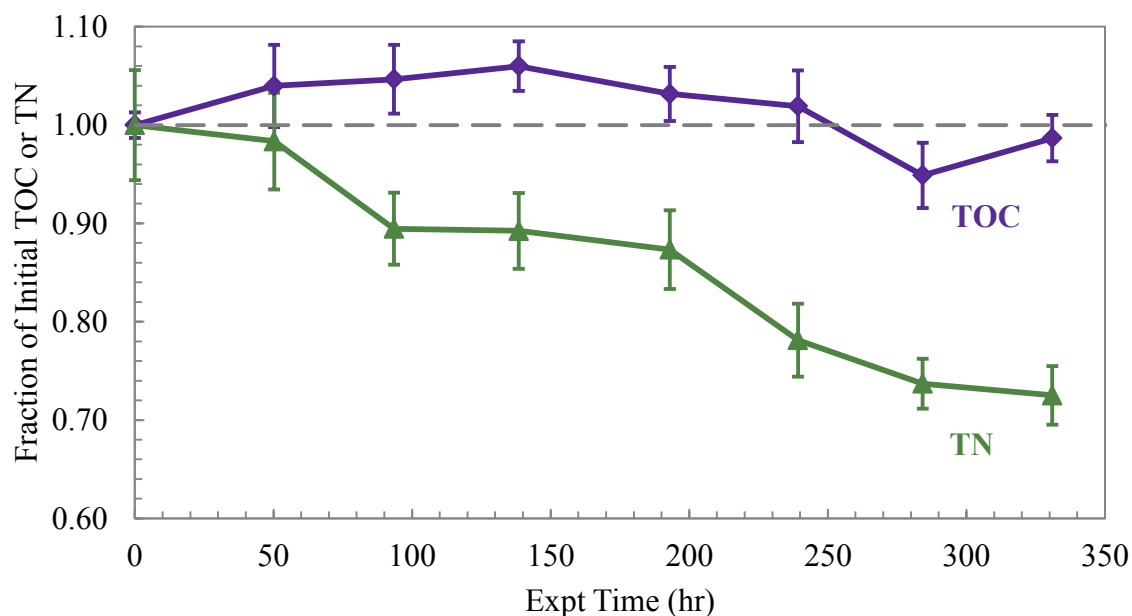


Figure 8.10: TOC and TN in the liquid phase during OE25 (8 m PZ, 70 °C, 1400 rpm, 100 mL per minute of 94% O_2 /2% CO_2 , 4 mM Cu^{2+})

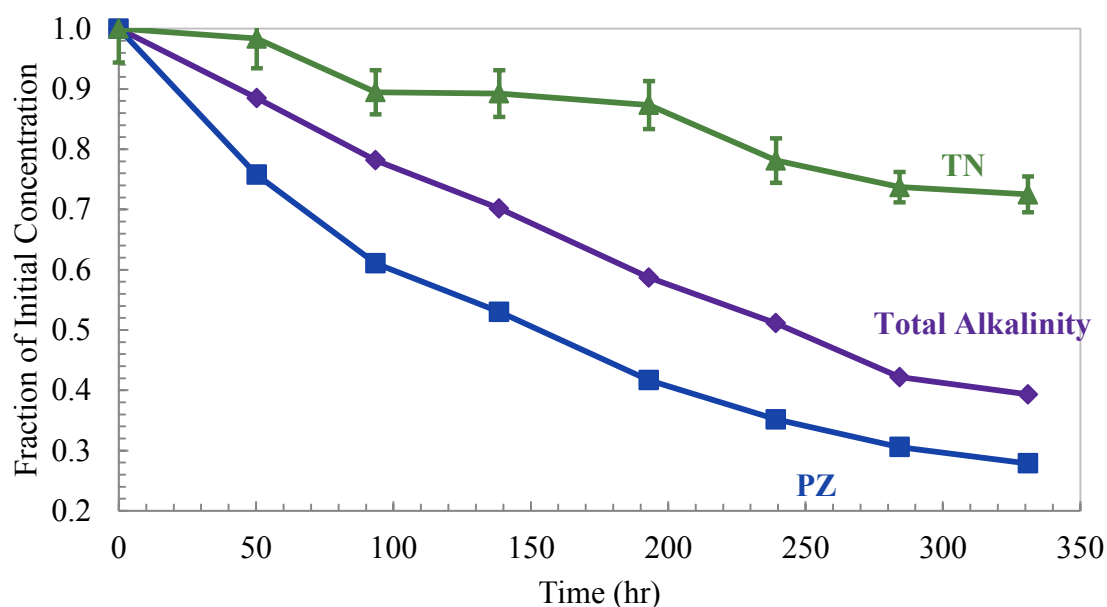


Figure 8.11: Comparison of PZ, total alkalinity, and total N for OE25 (8 m PZ, 70 °C, 1400 rpm, 100 mL per minute of 94% O₂/2% CO₂, 4 mM Cu²⁺)

The TOC results suggest the need for more sophisticated analytical techniques to effectively identify and quantify liquid-phase oxidation products of PZ. In the next section, the degradation products that have been identified and quantified are discussed along with unknown products that have been observed, but not yet identified. There are clearly many products remaining to identify, and some are observable on the current analytical tools including anion IC, cation IC, and amino acid detection.

8.2.5.1 Estimated volatility of ammonia during oxidation

The volatility of ammonia during PZ oxidation can be estimated to determine the impact of this species on the TN analysis. To estimate volatility, a Henry's constant is first estimated based on NH₃ solubility data in water (Perry and Green, 1997). An assumption will be made that NH₃ solubility in 8 m PZ is similar to that of water since data in PZ is not available. Solubility data for a solution of 2.91 mass percent NH₃ were

available at 50 and 60 °C and those points were used to estimate values for 55 and 70 °C (Table 8.2). With this data, the Henry's constant can be estimated at the two temperatures of interest using Henry's Law shown in Equation 8.12. Henry's Law relates the partial pressure of a species such as ammonia, P_{NH_3} , to its liquid phase concentration, C_{NH_3} , at a constant temperature using Henry's constant, H_{NH_3} . The mass percent concentration of the data is converted to the more useful units of mmole NH_3 per kg solution in Equation 8.13. The Henry's constant for is then calculated for 55 and 70 °C in Equation 8.14 and 8.15.

Table 8.2: Partial pressure of NH_3 over 2.91 mass percent NH_3 in water (Perry and Green, 1997)

Temp °C	P_{NH_3} mmHg
50	67.1
55	80.7
60	94.3
70	121.5

$$P_{\text{NH}_3} = H_{\text{T},\text{NH}_3} \cdot C_{\text{NH}_3} \quad (8.12)$$

$$\frac{2.91 \text{ g NH}_3}{\text{g soln}} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mole}}{17 \text{ g NH}_3} \times \frac{1000 \text{ mmole}}{1 \text{ mole}} = 1713.3 \frac{\text{mmole NH}_3}{\text{kg soln}} \quad (8.13)$$

$$H_{55^\circ\text{C},\text{NH}_3} = \frac{80.7 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}}}{\frac{1713.3 \text{ mmole}}{\text{kg soln}}} = 6.20 \times 10^{-5} \frac{\text{atm} \cdot \text{kg}}{\text{mmole}} \quad (8.14)$$

$$H_{70^\circ\text{C},\text{NH}_3} = \frac{121.5 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}}}{\frac{1713.3 \text{ mmole}}{\text{kg soln}}} = 9.33 \times 10^{-5} \frac{\text{atm} \cdot \text{kg}}{\text{mmole}} \quad (8.15)$$

At the end of OE25, which was performed at 70 °C, nearly 4 mmole free NH_4^+ per kg and 131 mmole total NH_4^+ per kg was quantified. In order to address the issues in the TN results and the overall N balance, the potential quantity of NH_3 that volatilized during the experiment will be estimated and reported as the concentration if it had all remained in solution. This estimation will be done in order to bracket the two extremes, with both the minimum and maximum possible volatile NH_3 loss estimated. The minimum amount of volatile NH_3 lost would be a calculation based on the 4 mmole NH_4^+ per kg. The maximum loss would be calculated based on the concentration of total NH_4^+ and assuming that it is not all bound as amide, but represents other NH_3 containing species. Another quantity, an intermediate value, will also be calculated based on the total NH_4^+ data which reach a plateau around 70 mmole per kg.

An interesting observation is the behavior of the free NH_4^+ compared to the total NH_4^+ after alkaline treatment. Free NH_4^+ is only detected in the last few samples of OE25, which may indicated a sample stability issue. This experiment was highly oxidized and even at room temperature, active species such as aldehydes, peroxides, if present, and even ureas may have reacted with the free NH_4^+ before analysis in the cation IC. The NH_4^+ released during alkaline treatment would be analyzed directly, without time for additional reactions and may reflect a more representative level of NH_4^+ in the solution than the free NH_4^+ .

For any of the liquid phase concentrations, the amount of NH_3 in the gas phase can be calculated using the Henry's constant for that condition. This calculation does not take into account the change of liquid phase NH_3 production with time and assumes a constant rate of NH_3 production. If NH_3 were being generated a constant rate, which is believed to be occurring, it would like accumulate in the liquid phase before it was then

stripped into the gas phase as concentration increases and eventually an equilibrium is reached where the generation rate and volatilization rate are equal.

For each liquid phase concentration, the gas phase partial pressure can be calculated using Equation 8.12 and the Henry's constant calculated in Equation 8.14, as demonstrated in Equation 8.16.

$$P_{\text{NH}_3} = \frac{9.33 \times 10^{-5} \text{ atm} \cdot \text{kg}}{\text{mmole}} \times \frac{4 \text{ mmole}}{\text{kg}} = 3.73 \times 10^{-4} \text{ atm} \quad (8.16)$$

For the low NH_4^+ concentration case, the partial pressure of NH_3 was calculated to be 3.73×10^{-4} atm, or 373 ppm. Based on 2 weeks of operation and a gas flow rate of 100 mL per min, the overall loss of NH_3 can be estimated using the ideal gas law (Equation 8.17).

$$n_{\text{NH}_3} = \frac{(3.73 \times 10^{-4} \text{ atm}) \times \left(2 \text{ wk} \times \frac{10080 \text{ min}}{\text{wk}} \times \frac{0.1 \text{ mL}}{\text{min}} \right)}{(70^\circ \text{C} + 273.15) \text{K} \times \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mole} \cdot \text{K}} \right)} = 0.027 \text{ mole NH}_3 \quad (8.17)$$

This amount of moles can then be converted to the liquid phase concentration if all of this volatile NH_3 had remained in solution based on the overall solution mass in the reactor (Equation 8.18).

$$C_{\text{NH}_3} = \frac{0.027 \text{ mole NH}_3 \times \frac{1000 \text{ mmole}}{1 \text{ mole}}}{390 \text{ g soln} \times \frac{1 \text{ kg}}{1000 \text{ g soln}}} = 68.5 \frac{\text{mmole}}{\text{kg}} \quad (8.18)$$

This calculation estimates that if all of the volatilized NH_3 were retained in solution, the concentration of NH_3 would be 68.5 mmole per kg higher. If the same

calculation is done for the measured liquid phase concentrations of 70 and 131 mmole NH_4^+ per kg, the volatile NH_3 would have added 1200 and 2244 mmole NH_3 per kg, respectively, to the solution if no volatilization occurred.

The TN measurements discussed earlier in this section suggested a N loss of 2650 mmole per kg throughout the course of the experiment. Volatile NH_3 is a strong candidate to explain a significant portion of this N loss, but even a calculation expected to predict the maximum amount of NH_3 lost cannot account for the entire N loss. It is not expected that NO_x species are made in significant quantities based on previous FT-IR experiments (Sexton, 2008).

8.3 DEGRADATION PRODUCTS OF CONCENTRATED PZ OXIDATION

The generation of degradation products was monitored with the best available techniques for all oxidation experiments. Anion and cation IC were performed on all experimental samples while amino acid detection, a newer technique, was only performed on select experiments. IC-MS and GC-MS techniques were also performed on some samples in an effort to find missing degradation products with limited success. A summary of degradation products successfully identified and quantified as well as suspected new products are summarized in Table A.3 (Appendix A).

In all experiments regarding the oxidation of concentrated PZ, the quantified degradation products accounted for very little of the loss PZ, with only a few exceptions. The inability to detect the most prominent degradation products, as highlighted by the TOC and TN results in the preceding section, is the most important issue regarding the study of PZ oxidation. The unidentified products are not being quantified because they are either volatile, non-ionic (i.e., not detectable on anion or cation IC), polymeric (not seen with current cation IC method), or undetectable with IC due to their molecular

structure or stability issues (e.g., aldehydes, ureas, and others). The volatility of degradation products is only a minor issue based on the TOC and TN results. It is likely that all of the abovementioned concerns are cumulatively producing poor overall mass balance results.

Despite an unsatisfactory mass balance, the products that were consistently detected can be discussed. The most prominent degradation products of oxidation were formate, oxalate, formyl amides, oxalyl amides, and EDA. Smaller concentrations of acetate and glycolate were found inconsistently while NH_4^+ , nitrite, and nitrate were found only in heavily oxidized solutions. The volatility analysis presented in the previous section suggests that volatile NH_3 and instable NH_4^+ in solution may be more important than the liquid analysis has shown. In order to demonstrate the typical, expected generation of degradation products during oxidation, two experiments will be analyzed in detail. The first experiment represents a low oxidation condition that should be similar to an absorber system which is run at moderate temperatures, without a Cu^{2+} -based corrosion inhibitor and with appropriate pre-treatment to remove a majority of SO_x and NO_x in a coal fired flue gas stream. The second experiment will examine the degradation profile of a heavily oxidized PZ solution at the absorber temperature bulge (70 °C) with a Cu^{2+} -based corrosion inhibitor and without an oxidation inhibitor.

As a representative experiment for the low oxidation condition, 8 m PZ was oxidized at 55 °C with a lean loading (0.3 moles CO_2 per mole alkalinity) with agitation at 1400 rpm in the presence of the typical SSM mixture (0.4 mM Fe^{2+} , 0.1 mM Cr^{3+} , and 0.05 mM Ni^{2+}) with 100 mL per minute of inlet gas with 98% O_2 (OE18). For the highly oxidized solution, 8 m PZ was oxidized at 70 °C with a lean loading (0.3 moles CO_2 per mole alkalinity) with agitation at 1400 rpm in the presence of 4 mM Cu^{2+} with 100 mL per minute of inlet gas with 94% O_2 (OE25). These two cases will be examined in terms

of the types of products generated, the unknowns observed in solution, and the overall mass balance at the end of the experiment.

8.3.1 Types of oxidation products

8.3.1.1 Degradation products found in experiments with low PZ oxidation rates

In OE18, 8 m PZ was oxidized at 55 °C with a lean loading (0.3 moles CO₂ per mole alkalinity) with agitation at 1400 rpm in the presence of the typical SSM mixture (0.4 mM Fe²⁺, 0.1 mM Cr³⁺, and 0.05 mM Ni²⁺) with 100 mL per minute of inlet gas with 98% O₂. Very low rates of PZ loss and product generation were observed, as shown in Figure 8.12. Essentially no PZ loss was observed in this experiment as the amine concentration changed by 135 mmole per kg compared to the initial sample. Degradation products were primarily formate and total formate. No EDA or oxalyl amides were detected in this experiment.

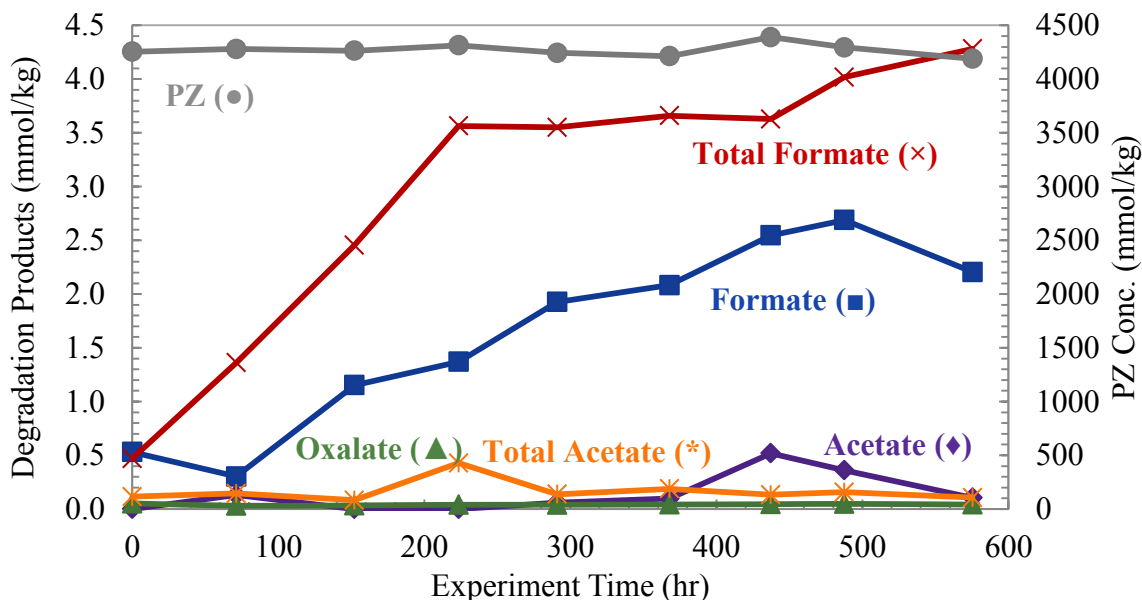


Figure 8.12: Profiles for PZ and degradation products for typical low oxidation experiment (OE18) (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O₂, SSM)

The cation and anion IC chromatograms from the initial and final samples are compared in Figure 8.13 and Figure 8.14, respectively. The lack of degradation is demonstrated by the similarity of the two chromatograms after 24 days of oxidation. The cation IC chromatogram only contains a strong peak for PZ (retention time of 13.9 minutes) outside of the background peaks for K^+ , Na^+ , and either Ca^{2+} or Mg^{2+} that also appear. The PZ peak does not appreciably decrease during the course of the experiment, indicating a very low level of oxidation occurred. The anion IC chromatogram contains only one strong product peak for formate (20.9 minutes), outside of background peaks for CO_3^- and SO_4^{2-} . Oxalate, acetate and glycolate were also detected in this sample at very low levels. There are no significant unknown peaks present on either chromatogram that would indicate an important, unidentified degradation product.

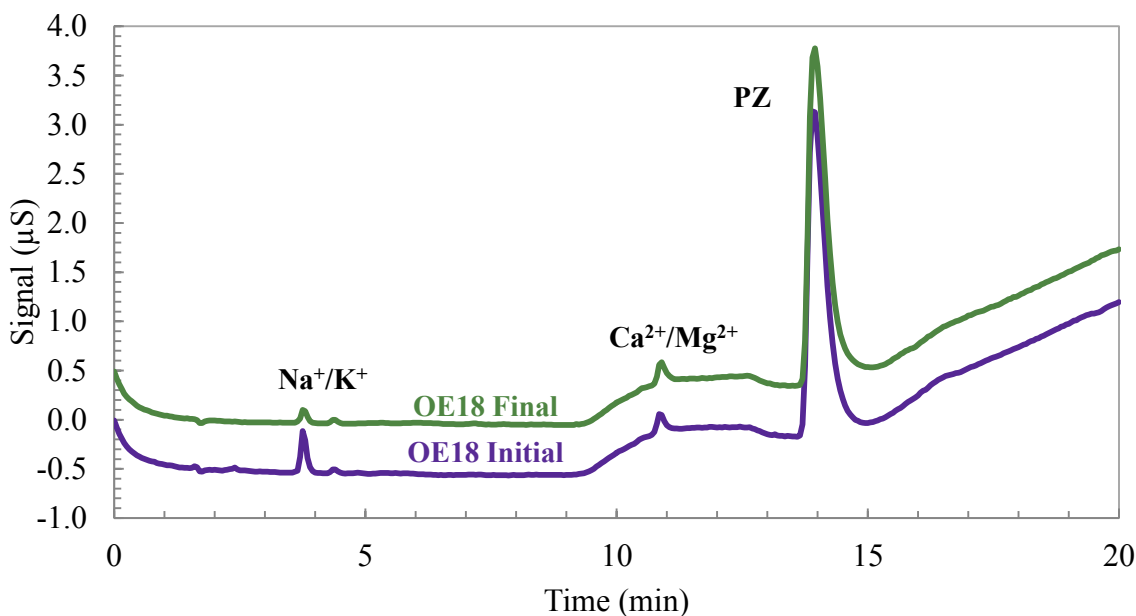


Figure 8.13: Comparison of cation IC chromatograms at the start and end of OE18 demonstrating low oxidation (signals are offset 0.5 μ S for clarity) (8 m PZ, 55 $^{\circ}$ C, 1400 rpm, 100 mL/min 98% O_2 , SSM, 24 days)

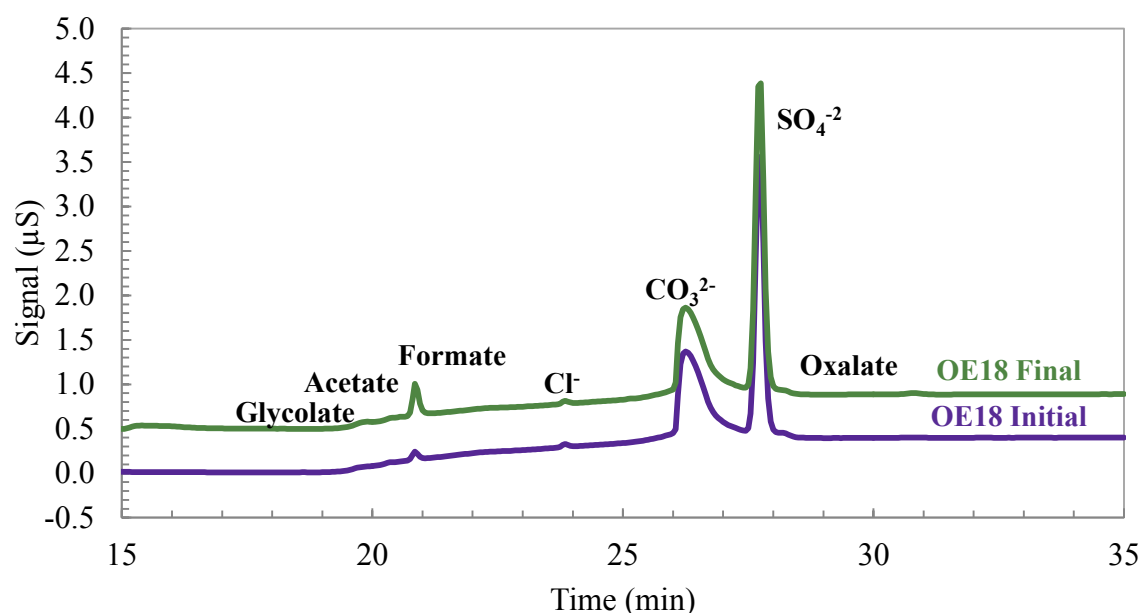


Figure 8.14: Comparison of anion IC chromatograms at the start and end of OE18 demonstrating low oxidation (signals are offset 0.5 μ S for clarity) (8 m PZ, 55 $^{\circ}$ C, 1400 rpm, 100 mL/min 98% O₂, SSM, 24 days)

Analysis of OE18 provides a representative view of the types of degradation products seen in experiments with low rates of PZ oxidation. In this project, only three Cu²⁺-catalyzed experiments showed high rates of oxidation, so a majority of oxidation data is of this nature. Despite the seeming lack of data, some conclusions can still be drawn from low PZ oxidation rates by examining production rates of formate, total formate, and EDA. Throughout this chapter and the following chapter (Chapter 9), comparisons of PZ loss and the generation of formate, total formate, and EDA will be used in order to draw conclusions on overall PZ oxidation rate. For the degradation products, an assumption is made that these three products represent the total mix of degradation products produced, either identified or unidentified. This assumption could be incorrect or an oversimplification, but appears to hold true given the data gathered in this project, especially for low oxidation experiments where there is little other data. This

type of analysis leads to inconclusive evidence in some experiments, especially in the case of EDA data. EDA is difficult to accurately detect at low levels due to the dilution required for cation IC. In cases of low oxidation, only low levels of EDA would be expected and were quantified. Formate and formyl amides are more accurately measured in the anion IC method and are considered the best overall indicators of oxidation of the degradation products quantified.

A second assumption made throughout this project is that catalysis by one metal generates the same product mix as catalysis by another metal. That is to say, that Cu^{2+} -catalyzed oxidation of PZ will lead to generation of the same degradation products as stainless steel metal-catalyzed oxidation, but at different overall rates. This assumption is supported by the fact that the same dominant products, formate, total formate, and EDA, are found across the board in both types of experiments. This assumption could be disproven when additional degradation products are identified in the various metal catalyzed systems. In the meantime, those three degradation products will be used to quantify and compare overall oxidation between experiments catalyzed in varying ways.

8.3.1.2 Degradation products found in experiments with high PZ oxidation rates

In OE25, 8 m PZ was oxidized at 70 °C with a lean loading (0.3 moles CO_2 per mole alkalinity), agitation at 1400 rpm with 4 mM Cu^{2+} and 100 mL per minute 94% O_2 . This experiment had the highest rate of PZ oxidation of all oxidation experiments. The loss of PZ and generation of carboxylate ions and their corresponding amides are shown in Figure 8.15. The loss of PZ is compared with the generation of the dominant amine-based products in Figure 8.16. The two sets of products are separated to more clearly see trends. Formyl amides are included in both figures in order to demonstrate the congruity between the concentration of formyl amides and N-formyl PZ (FPZ).

The loss of PZ is severe in this experiment, with 72% of the initial PZ lost after 350 hours of oxidation. In accordance with the high level of PZ oxidation, high concentrations of degradation products were quantified. High concentrations of formate and formyl amides were generated, reaching up to 168 and 386 mmole per kg, respectively. These are significantly higher than those concentrations found in low oxidation experiments where formyl amides, also the most dominant product, usually reached only 10 to 20 mmole per kg. Oxalate, oxalyl amides, and acetyl amides were also generated at significant quantities compared to low oxidation experiments. There was no acetate quantified in the original samples while small concentrations were detected in the NaOH treated samples indicating the presence of acetyl amides.

For amine-based products, EDA and FPZ were quantified with the highest concentration. The agreement between the formyl amides quantified on the anion IC through alkaline reversal and N-formyl PZ quantified directly on cation IC indicates that N-formyl PZ is likely the only formyl amide in solution, within experiment error of the two instruments. Total NH_4^+ concentration quantified after alkaline treatment is produced at a level similar to that of formate.

This is the only experiment where EDA concentration increased, reached a maximum and then decreased. In other oxidation experiments with appreciable degradation (e.g., OE2), the EDA concentration grew and reached a plateau, but did not decrease. The behavior of EDA clearly indicates it is a reaction intermediate. Analyzing the alkaline treated sample indicates that EDA is reacting to form amides. The total EDA concentration (Figure 8.16) grows and maintains a relatively level concentration. This shows that EDA is produced and form amides in the initial phases of PZ oxidation. Then, the generation of EDA slows due to the lower concentration of PZ, while the EDA in solution continues to form amides due to the presence of reactive carboxylate ions.

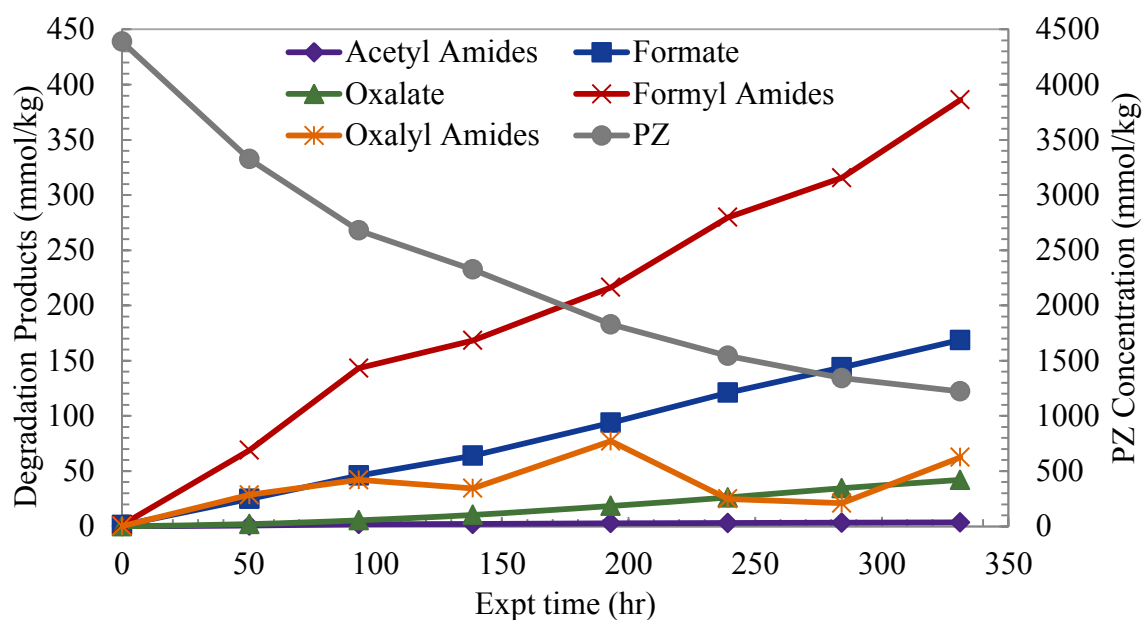


Figure 8.15: Profiles for PZ and heat stable salt products for experiment with high oxidation rates (OE25) (8 m PZ, 70 °C, 1400 rpm, 100 mL/min 94% O₂, 4 mM Cu²⁺)

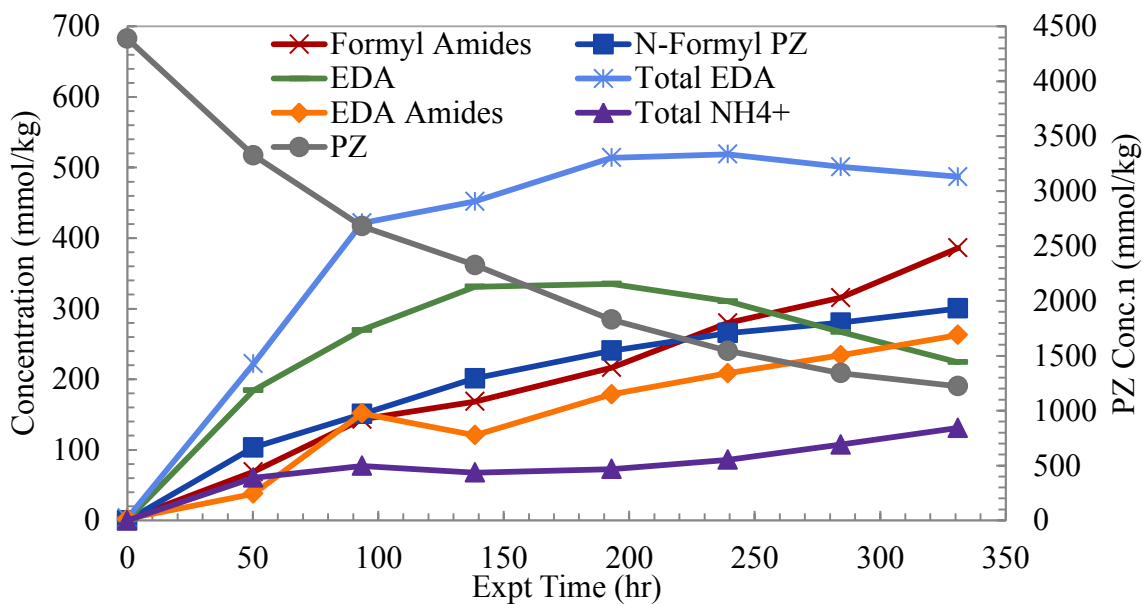


Figure 8.16: Profiles for PZ and amine products for experiment with high oxidation rates (OE25) (8 m PZ, 70 °C, 1400 rpm, 100 mL/min 94% O₂, 4 mM Cu²⁺)

The cation and anion IC chromatograms from the initial and final sample are compared in Figure 8.17 and Figure 8.20, respectively, while an enlarged view of the cation IC chromatogram is shown in Figure 8.18 to show detail. Cation and anion IC chromatograms for the final sample before and after alkaline treatment for amide reversal are shown in Figure 8.19 and Figure 8.21, respectively, to examine the impact of amide degradation products. This set of chromatograms is by far the most interesting achieved for oxidized PZ, showing numerous unidentified peaks on both anion and cation IC.

In the cation IC chromatograms, there are clear peaks for PZ, EDA, FPZ, and NH_4^+ that are visible in the expanded view (Figure 8.17). A significant decrease in the PZ peak is also visible, showing the 72% loss of PZ found in this experiment. Upon closer inspection (Figure 8.18), there are also numerous, smaller unidentified peaks that are detected on the cation IC after oxidation. There are five peaks that are likely monoamines (labeled as unidentified monoamines (UM)), and 5 peaks that are likely di-, tri-, or quadamines (labeled as unidentified polyamines (UP)). Although the peaks are small in comparison with EDA and PZ, they represent new oxidation products that were not found in previous experiments with lower oxidation rates. IC-MS work was attempted to identify the peaks, but did not prove conclusive to render identification.

Observing the changes to the cation IC chromatogram after treatment with NaOH also provides insight into the possible structure of the unidentified peaks (Figure 8.19). After treatment, which is intended to convert amides back to their respective amine and carboxylate ion portions, the peaks of two of the unidentified monoamines and the two dominant unidentified polyamines are decreased significantly. This indicates that these peaks, like the peak for FPZ, represent amides that are eliminated after alkaline treatment. These peaks are labeled as unidentified amides (UA) in the figure. Three monoamines peaks and smaller concentration polyamine peaks remain after alkaline treatment. This

sample is highly oxidized and numerous types of amides involving PZ, EDA, NH_3 , formate, acetate, or oxalate, could hypothetically be formed and mono-amides of PZ and EDA should respond on the cation IC because of the second amino function

The anion IC chromatograms from this experiment are also interesting due to the appearance of new degradation product peaks. Comparing the initial and final sample in Figure 8.20, it is clear that several degradation products were generated. The only peaks in the initial sample represent CO_3^{-2} and SO_4^{-2} . It should be noted that the position and shape of the CO_3^{-2} peak shifted in the degraded sample, as has been observed previously with significant changes in speciation or pH. After oxidation, there are still peaks for these two background compounds, but they have been swamped by the peaks representing degradation products. Formate and oxalate are the two largest peaks at retention times of approximately 20 and 27 minutes, respectively. There is not a peak for acetate, since acetate was not found in the original samples. Small concentrations of nitrite (NO_2^-) and nitrate (NO_3^-) were detected in this experiment and those peaks are labeled accordingly. This is the only experiment where appreciable quantities of either of these N-based ions were detected.

The peak eluting at approximately 20.5 minutes, right after formate, has been tentatively identified as the mono-oxalyl amide of PZ, also known as N-oxalyl PZ. Since N-oxalyl PZ has an exposed anionic functionality on the oxalate, it should be detected by anion IC. Chromatograms from the original and NaOH treated final samples from OE25 are compared in Figure 8.21. The peak thought to be N-oxalyl PZ and the third unidentified peak (labeled UA) disappear when treated with NaOH, indicating they are both amides. This confirms the possible identity of the N-oxalyl peak, although either peak could represent this molecule since a standard is not available to analyze. Mono-amides have been seen in previous work on other amines where the NaOH treatment

requires more time to fully reverse the dioxalyl amide of certain amines (Voice, 2010). The slower recovery of oxalate was also explored in the analysis of the NaOH treatment procedure discussed in section 3.1.6. The amide reaction of PZ with oxalate is especially complex given that PZ has two functional amino groups and oxalate has two carbonyl functional groups that can form a double amide. The same is true for EDA, the dominant amine degradation product for PZ oxidation, which complicates the amide generation and analysis process. The three possible amide structures of the reaction of PZ or EDA with oxalate are shown in Figure 8.22. This adds a third possible amide compared to formate and acetyl-based amides which cannot form an amide that is observable through anion IC. The identity of the last unknown anion peak (labeled U) is not known at this time.

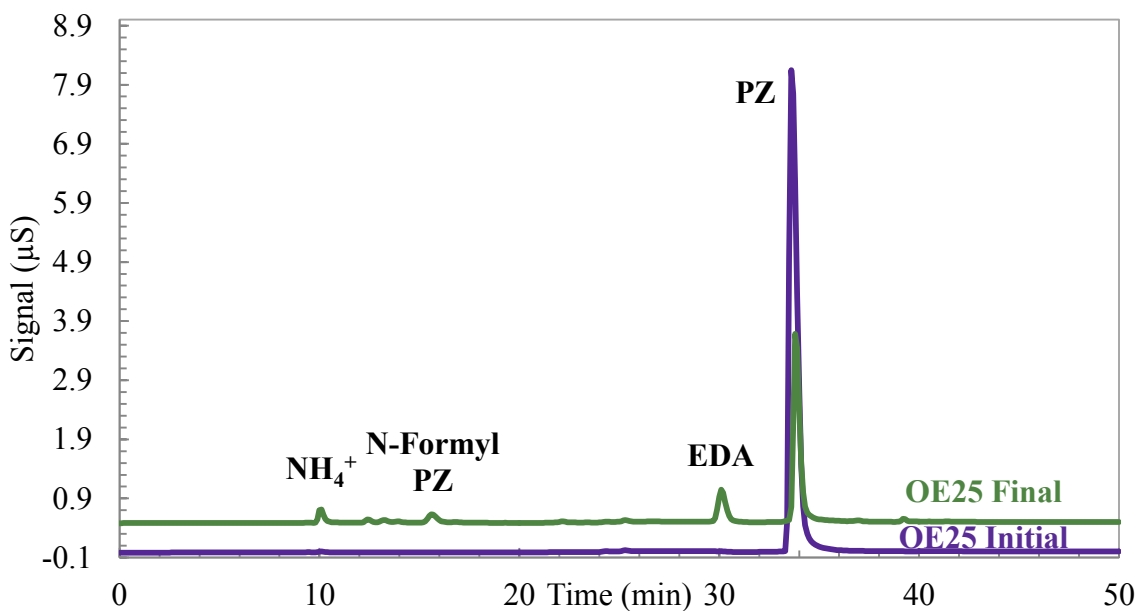


Figure 8.17: Comparison of cation IC chromatograms at the start and end of OE25 demonstrating high oxidation rates (signals are offset 0.5 μ S for clarity) (8 m PZ, 70 °C, 1400 rpm, 100 mL/min 94% O₂, 4 mM Cu²⁺, 14 days)

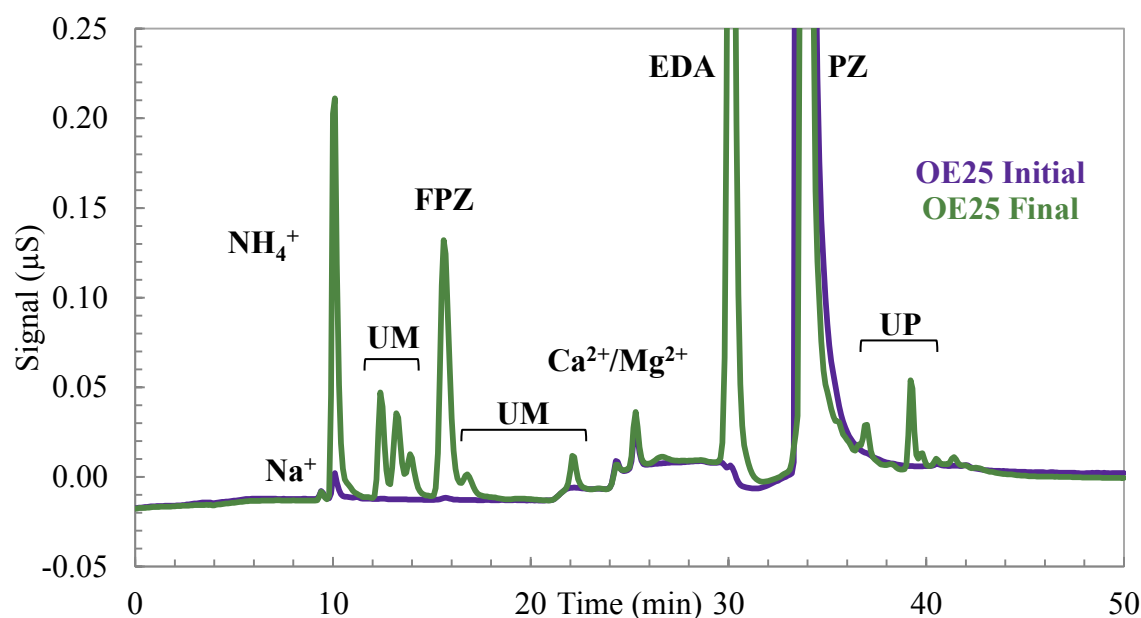


Figure 8.18: Comparison of cation IC chromatograms at the start and end of OE25 demonstrating high oxidation rates (enlarged); abbreviations: UM, unidentified monoamines; UP, unidentified polyamines (8 m PZ, 70 °C, 1400 rpm, 100 mL/min 94% O₂, 4 mM Cu²⁺, 14 days)

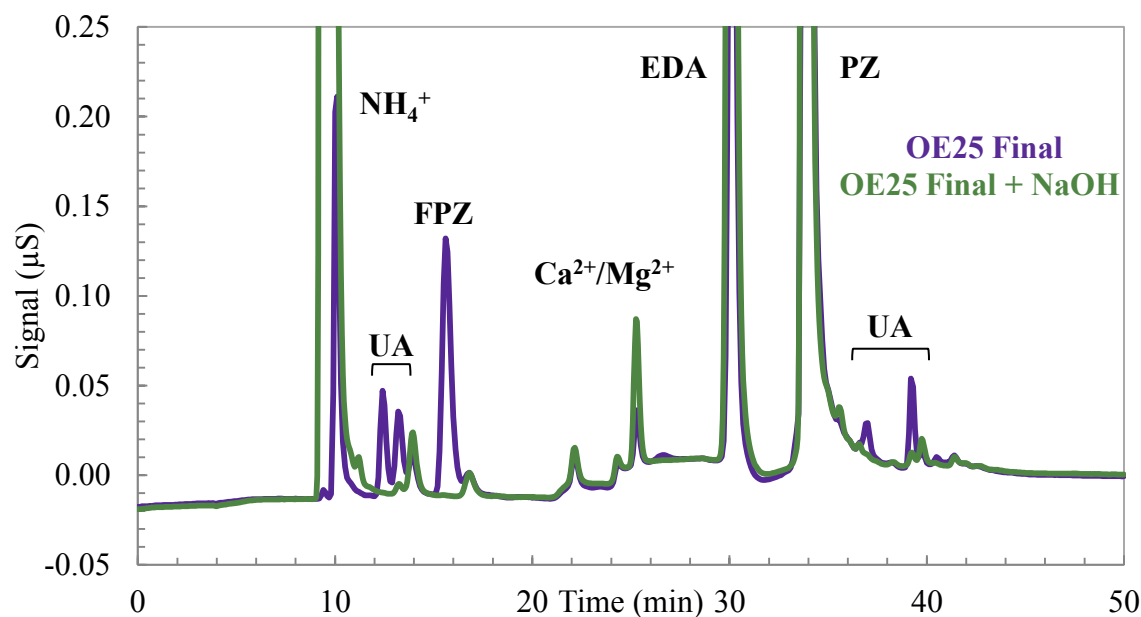


Figure 8.19: Comparison of cation IC chromatograms for the final sample of OE25 before and after NaOH treatment (enlarged); UA indicates unidentified amides (8 m PZ, 70 °C, 1400 rpm, 100 mL/min 94% O₂, 4 mM Cu²⁺, 14 days)

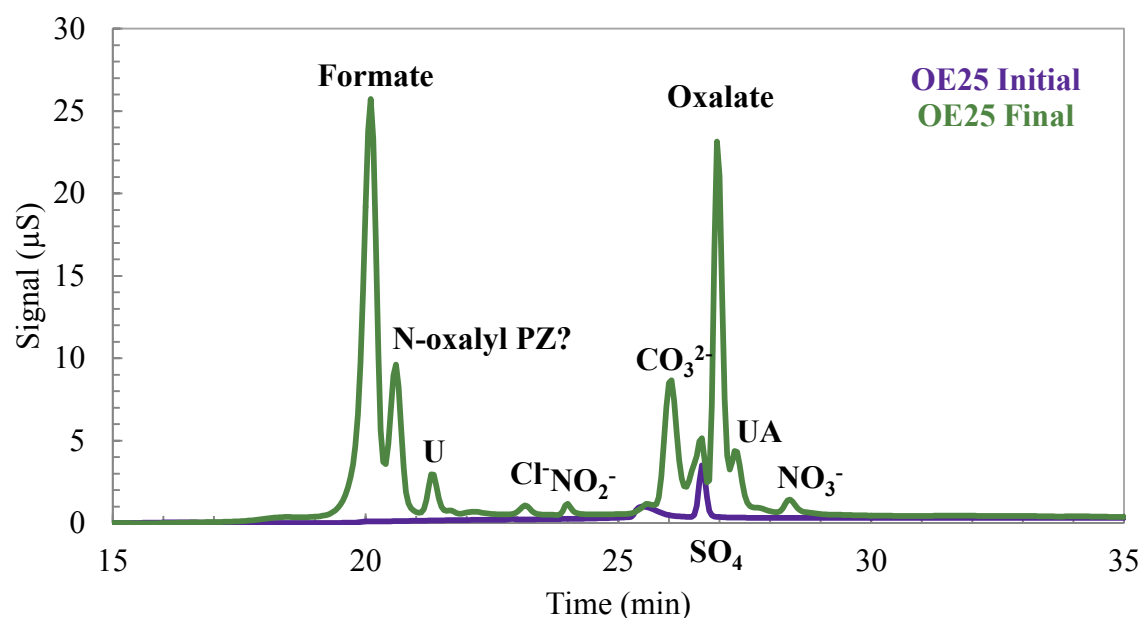


Figure 8.20: Comparison of anion IC chromatograms at the start and end of OE25 demonstrating high oxidation rates; abbreviations: U, unidentified; UA, unidentified amide (8 m PZ, 70 °C, 1400 rpm, 100 mL/min 94% O₂, 4 mM Cu²⁺, 14 days)

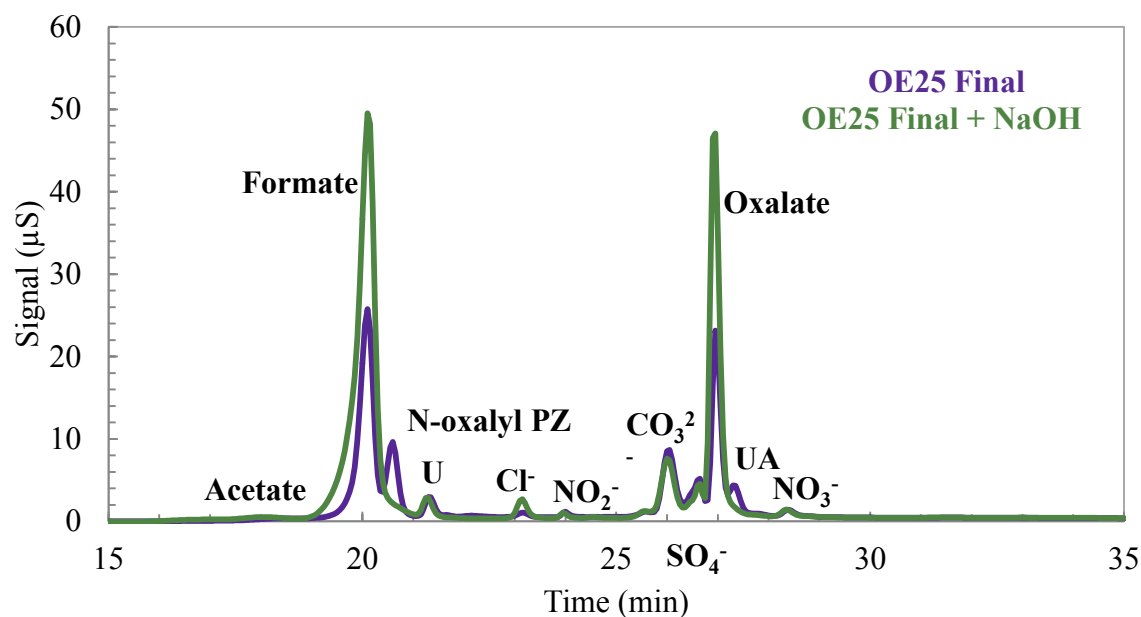


Figure 8.21: Comparison of anion IC chromatograms for the final sample of OE25 before and after NaOH treatment; abbreviations: U, unidentified; UA, unidentified amide (8 m PZ, 70 °C, 1400 rpm, 100 mL/min 94% O₂, 4 mM Cu²⁺, 14 days)

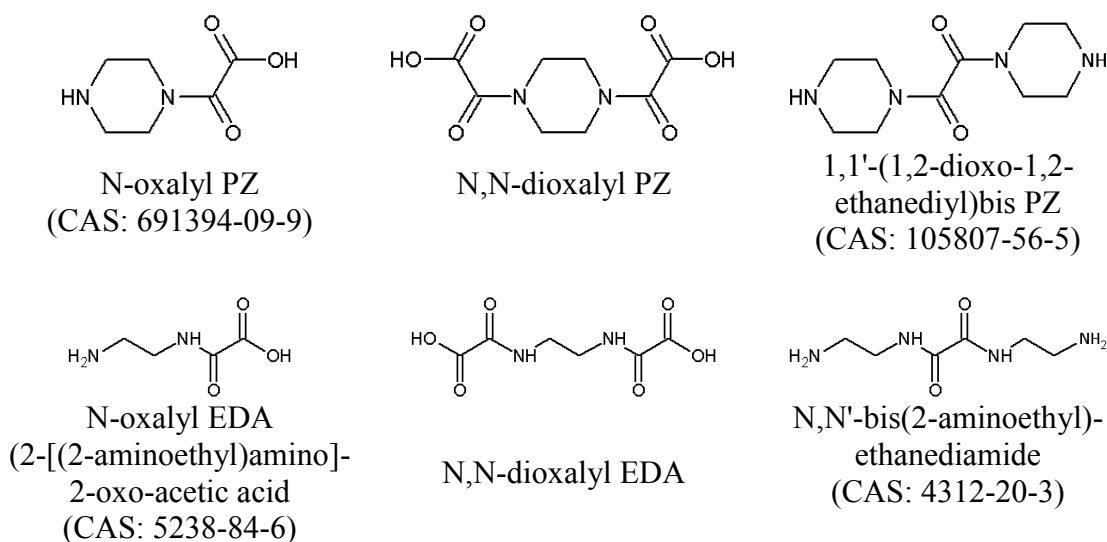


Figure 8.22: Chemical structures of products of reaction of oxalate with PZ or EDA

This experiment represents a new area of PZ study where highly oxidized PZ solutions can be analyzed in a sophisticated way to identify more degradation products than just carboxylate ions, EDA, and N-formyl PZ. Identification of these peaks could lead to new understanding of the PZ oxidation pathways that are not well understood at this point due to the lack of overall PZ oxidation usually observed under conditions that are representative of anticipated absorber conditions. On the other hand, this type of study may not be useful since PZ solutions in service would not be expected to reach this level of oxidation, even in the presence of a Cu^{2+} -based corrosion inhibitor.

8.3.2 Mass balances achieved in PZ oxidation

The oxidation experiments described in this project all suffer from a common failure to close the overall mass balance. The PZ loss observed through cation IC is not balanced with the generation of degradation products. This was true of both the nitrogen (N) and carbon (C) balance and was observed in every experiment, without fail. Three example mass balances are discussed in this section to provide an example of the mass

balanced closure usually achieved. The two experiments representing the low (OE18) and high (OE25) level of oxidation are each discussed, as well as one of the baseline experiments (OE11). The range of mass balance closure observed in all 28 oxidation experiments can be represented by these three experiments.

In the following three tables (Table 8.3 to Table 8.5) the amount of N and C in PZ lost during each oxidation experiment is shown along with the final concentrations of the quantified degradation products. For the degradation products, the percentage that each represents in terms of the amount of PZ lost is also shown as a percentage. This represents the percent of PZ lost that was recovered in each of the products in terms of either N or C. The last row of the table shows the total N or C recovered in degradation products as a percent of the overall PZ loss. If all of the lost PZ was recovered in degradation products, as in the ideal scenario, this last row would be 100. Degradation products not containing either N or C are indicated as not applicable (NA) in each case. When a listed product was tested for but not found, a concentration and percentage of zero are shown in the table.

The N and C mass balanced achieved in the experiment showing low levels of oxidation, OE18, is shown in Table 8.3. During the experiment, only 65.9 mmole per kg of PZ was lost or 131.7 mmole N from PZ per kg and 263.4 mmole C from PZ per kg. Small concentrations of formate (2.1 mmole per kg) and formyl amides (2.2 mmole per kg) were produced while no EDA was detected. Based on observations in previous oxidation experiments, this concentration of formyl amides was assumed to all be N-formyl PZ and the appropriate N and C concentrations, 4.4 and 11.1 mmole per kg, respectively, were included in the mass balance. No other N containing degradation products were detected. Very low levels of glycolate, acetate, and oxalate were also

found that accounted for a total of only 0.5 mmole per kg. Overall, only 3.4% and 5.2 % of the lost PZ N and C were recovered, respectively, in detectable degradation products.

Table 8.3: Nitrogen and Carbon Mass Balance in OE18 (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O₂, SSM, 24 days)

	Conc. mmol/kg	Nitrogen Balance		Carbon Balance	
		N Conc. mmol/kg	PZ N Loss %	C Conc. mmol/kg	PZ C Loss %
PZ Lost	65.9	131.7	-	263.4	-
DEGRADATION PRODUCTS:					
N-Formyl PZ	2.2	4.4	3.4	11.1	4.2
Formate	2.1	NA	-	2.1	0.8
Oxalate, Acetate, and Glycolate	0.2	NA	-	0.5	0.2
Total PZ Mass Recovered in Products		4.4	3.4	13.6	5.2

This experiment exhibited a very low level of PZ loss during oxidation, even lower than all four baseline experiments. In order to put this experiment in perspective, the baseline experiment with the most PZ loss, OE11, is also analyzed for its mass balance closure. Numerous PZ oxidation experiments suffered from PZ loss rates that fell between OE18 and OE11, so the analysis of these two mass balances should give a representative picture of what would be expected in experiments with low or even negligible PZ loss rates. The experiments with these low rates of oxidation are essentially all experiments performed in the absence of Cu²⁺ and at low temperature (55 °C), as is discussed in this chapter and the subsequent chapter.

The N and C mass balances achieved in this baseline experiment, OE11, are shown in Table 8.4. In this experiment, 292.9 mmole PZ per kg was lost, accounting for 585.7 and 1171.5 mmole N and C per kg, respectively. The generation of degradation products was similar to the previously example as formate (1.0 mmole per kg) and formyl amides (1.44 mmole per kg) were detected along with a low concentration of EDA (11.7

mmole per kg). As with the previous example, all of the formyl amides were assumed to be N-formyl PZ for the mass balance. Glycolate, acetate, and oxalate were not detected. Based on the TOC and TN results discussed above, the concentration of volatile N from that analysis, 426.4 mmole N per kg, was included in the mass balance. With this inclusion, the N mass balance improves significantly from 2.5 to 75.3% of the lost PZ recovered as products. On the other hand, only 1.7 % of the loss PZ C was recovered in products. The generation of degradation products was of a similar magnitude in this experiment compared with OE18, while the overall PZ loss was higher, leading to worse mass balance closure. The TOC analysis discussed in section 8.2.5 demonstrated that there are unidentified C-based degradation products that have not been quantified that could help with the overall mass balance closure. Missing degradation products will also contain N functionality based on the 24.7% of N that is yet to be recovered.

Table 8.4: Nitrogen and carbon mass balance in OE11 (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O₂, no catalyst, 13 days)

	Conc.	Nitrogen Balance		Carbon Balance	
		N Conc.	PZ N Loss	C Conc.	PZ C Loss
	mmol/kg	mmol/kg	%	mmol/kg	%
PZ Lost	292.9	585.7	-	1171.5	-
DEGRADATION PRODUCTS:					
N-Formyl PZ	1.4	2.9	0.5	7.2	0.6
EDA	5.8	11.7	2.0	11.7	1.0
Formate	1.0	NA	-	1.0	0.1
Oxalate, acetate, and glycolate	0	NA	-	0	-
Volatile N	426.4	426.4	72.8	NA	-
Total PZ Mass Recovered in Products		441.0	75.3	19.8	1.7

On the opposite extreme, the mass balance in an experiment where a high rate of oxidation was achieved (OE25) can be examined. As discussed previously in this section, the conditions of OE25 represent the maximum acceleration of oxidation through

the addition of Cu^{2+} , the most potent catalyst for PZ degradation (discussed in further detail in section 9.1.3), high temperature, and high O_2 content. This experiment had the highest concentrations of degradation products detected in any experiment and represent the best chance for mass balance closure in this study.

The N and C balances for OE25 are shown in Table 8.5. In this experiment, 3166.6 mmole PZ per kg was lost or 6333.3 mmole N from PZ per kg and 12666.5 mmole C from PZ per kg. EDA and FPZ were the most dominant products with 974.0 and 300.3 mmole per kg at the end of the experiment, respectively. Ammonium (NH_4^+), nitrite (NO_2^-), and nitrate (NO_3^-) were also found in small quantities. It should be noted that for cationic molecules, such as EDA and NH_4^+ , the total concentrations quantified after alkaline treatment were used in the mass balance to include the portion as the free molecule and the portion that was tied up as an unidentified amide. Concentrations of oxalate and acetate after alkaline treatment, representing both free carboxylate ions and carboxylate as amides, were included in the mass balance. For formate, free formate from the original sample was included in the mass balance. The concentration of formyl amides determined from alkaline treatment was adjusted to remove the concentration of FPZ quantified directly from cation IC to leave non-PZ formyl amides. Based on the results of the TOC and TN analysis for this experiment, the volatile N is also included in the mass balance although the specific species are not known. The inclusion of volatile N determined from the TN analysis improved the N balance from only 27% of the lost PZ N recovered to nearly 69%. Only 23.3% of the loss PZ C was recovered in detectable degradation products. There is still unidentified degradation products that contain both C and N based on the lack of mass balance closure in either cases.

The amide data for this experiment is especially interesting and represents how anion and cation pairs that form amides can distribute themselves in solution. The

concentrations of the anion and cation portions of potential amides are shown in Table 8.6 for the final sample of OE25. All values are the increase in concentration between the alkaline treated and original samples. All six species shown, formate, acetate, oxalate, PZ, EDA, and NH_4^+ , were all present in the oxidized solution as some form of an amide since their concentration increased after alkaline treatment. FPZ can be quantified directly and had a concentration of 300.3 mmole per kg at the conclusion of the experiment. Unfortunately, the PZ concentration was not increased by this value during the reversal, indicating some disparity in the data. This is not surprising given that PZ is the most dominant species in solution and the error in measuring a small increase in a large peak on the cation IC is high based on many analytical factors.

Table 8.5: Nitrogen and Carbon Mass Balance in OE25 (8 m PZ, 70 °C, 1400 rpm, 100 mL/min 94% O₂, 4 mM Cu²⁺, 14 days)

	Conc. mmol/kg	Nitrogen Balance		Carbon Balance	
		N Conc. mmol/kg	PZ N Loss %	C Conc. mmol/kg	PZ C Loss %
PZ Lost	3167	6333	-	12667	-
DEGRADATION PRODUCTS:					
EDA	487.0	974.0	15.4	974	7.7
N-Formyl PZ	300.3	600.6	9.5	1501.6	11.9
Formate	168.7	NA	-	168.7	1.3
NH_4^+	130.9	130.9	2.1	NA	-
Oxalate and oxalyl amides	104.6	NA	-	209.1	1.7
Formyl amides (non-PZ)	85.8	NA	-	85.8	0.7
NO_2^- and NO_3^-	4.7	4.7	0.1	NA	-
Acetate and acetyl amides	3.6	NA	-	7.2	0.1
Volatile N (unknown species)	2649	2649	41.8	NA	-
Total PZ Mass Recovered in Products		4359	68.8	2947	23.3

Assuming that FPZ was the only PZ-based amide, this leaves only 85.8 mmole formate per kg that exists in another amide form. This form could be either formamide (the amide of formate and NH_3) or N-formyl EDA, based on the cation data. The

quantified increase of EDA and NH_4^+ is much higher in concentration than the recovered anions and indicates additional unidentified anion portions of amines. One explanation could be unidentified peaks on the anion IC chromatogram or anion amide pairs that would not be detected on the anion IC. The oxalyl amides of EDA or NH_4^+ with two amines forming two amide functions on one oxalyl group are also possibilities. The oxalyl amides of PZ and EDA were discussed in the preceding section, and the mono-oxalyl EDA (N-oxalyl EDA) could also exist and account for one of the unidentified peaks on the anion IC chromatogram for this sample. Although the amide mass balance also does not close for this experiment, the detected molecules indicate a complicated reaction scheme and distribution of amide reactants that could see amides representing every combination of the detected anion and cation portions of amides present in a highly oxidized solution.

Table 8.6: Amide balance in final sample of OE25 (8 m PZ, 70 °C, 1400 rpm, 100 mL/min 94% O_2 , 4 mM Cu^{2+} , 14 days)

Anion	Concentration mmol/kg	Cation	Concentration mmol/kg
Formyl	386.1	PZ	230.7
Acetyl	3.6	EDA	262.7
Oxalyl	62.5	NH_3	127.8
TOTAL	452.2	TOTAL	621.2

This highly oxidized sample represents the best mass balance closure of any oxidized PZ experiment. This represents where PZ oxidation research lies in terms of degradation rates and the production of degradation products. Although high concentrations of products were quantified, there is still work to be done to identify the additional products. A vast majority of experiments in this project were performed on solutions that were very slow to oxidize, complicating the problem of closing a mass balance due to very low concentrations of detectable degradation products.

8.3.3 Amino Acid (AA-LC) analysis of oxidized PZ

One additional advanced chromatographic technique was employed in an effort to find degradation products. Amino acid LC (AA-LC) was used to analyze oxidized PZ samples in an effort to identify and quantify new oxidation products that would satisfy the mass balance. An experiment with a very low level of oxidation (OE26) and one highly oxidized experiment (OE25) were analyzed using AA-LC. The initial and final chromatograms for the low level of oxidation experiment are shown in Figure 8.23. Chromatograms from the highly oxidized experiment at the start, after 4 days, and at the end of the experiment are compared Figure 8.24. The large peak between retention times of 5 and 13 minutes is the initial PZ charge in each figure. The bump between 25 and 29 minutes is part of the eluent ramp and is seen in each initial sample.

As with other techniques, the low level of oxidation seen in OE26 did not produce peaks on the AA-LC chromatogram. There are few changes in the chromatogram after 14 days of degradation and there were not significant amino acids produced during oxidation. On the other hand, the highly oxidized OE25 experiment shows the generation of numerous peaks on the AA-LC chromatogram, along with a significant decrease in the PZ peak. The shape of the chromatogram changes significantly over 14 days and multiple peaks are seen to grow with time, indicating the presence of amino acid-based degradation products. Unfortunately, none of the peaks matched standards of glycine, bicine, 2-piperazinone, 2,5-pipearzinone (glycine anhydride), or N-(2-aminoethyl) glycine. None of the peaks on the AA-LC chromatogram have been identified.

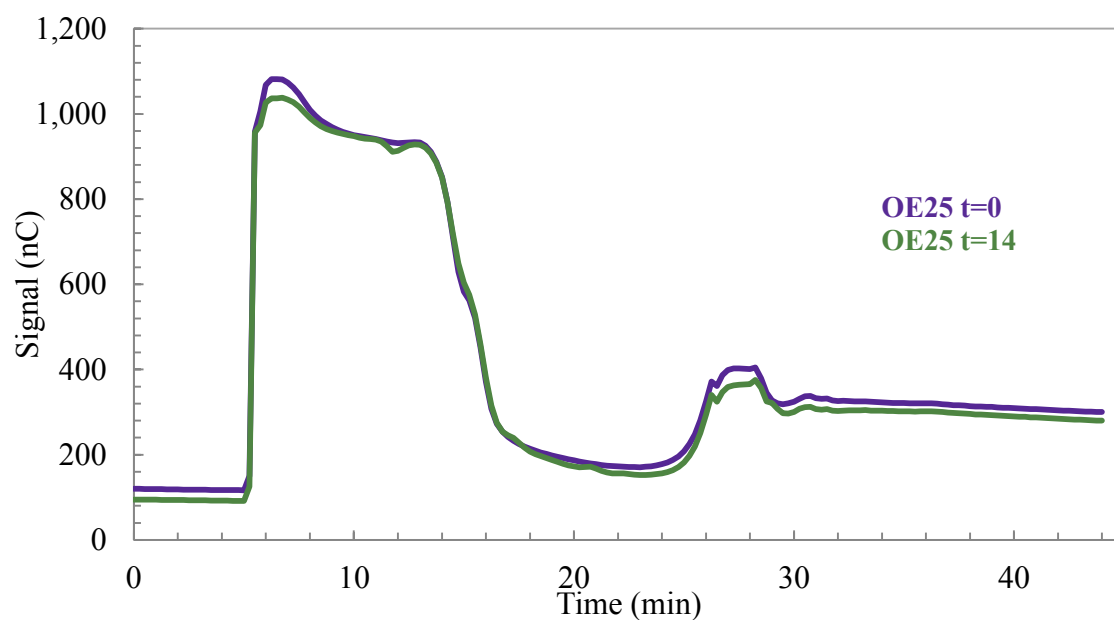


Figure 8.23: Amino acid (AA-LC) analysis of low level oxidation of PZ (OE26) showing little evidence of oxidation (8 m PZ, 70 °C, 1400 rpm, 100 mL/min 94% O₂, SSM, 14 days)

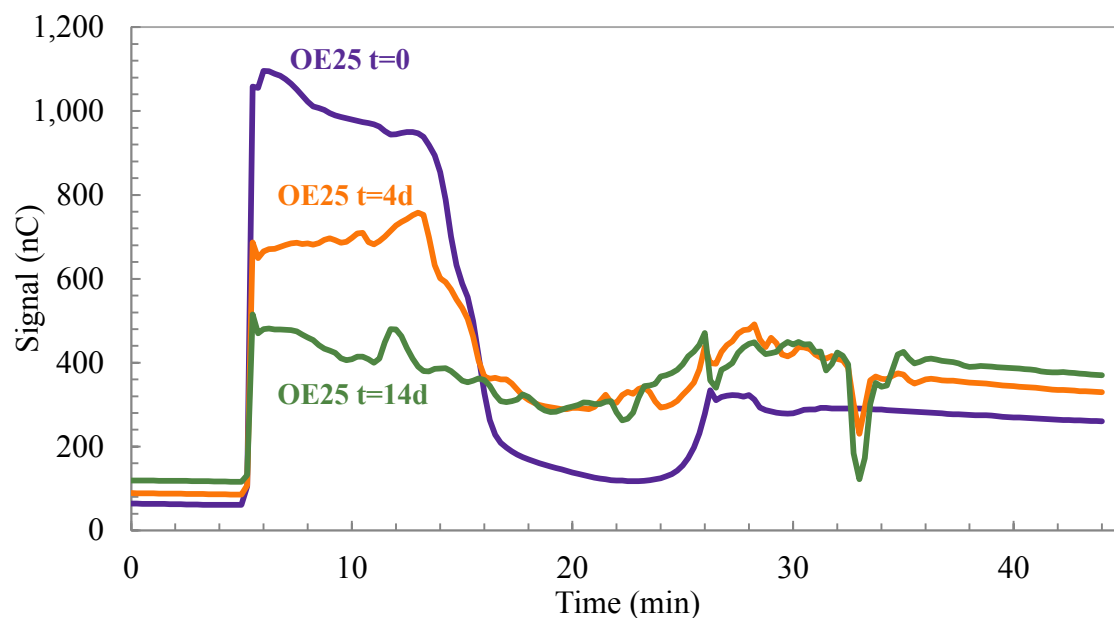


Figure 8.24: Amino acid (AA-LC) analysis of highly oxidized PZ (OE25) showing unidentified peaks (8 m PZ, 70 °C, 1400 rpm, 100 mL/min 94% O₂, 4 mM Cu²⁺, 14 days)

8.3.4 Postulated oxidation products not detected

A variety of molecules have been postulated as potential oxidation products of concentrated PZ that have not been conclusively confirmed in degraded solutions. Oxidation typically entails fragmentation of the original amine along with condensation of fragments to produce a host of possible molecules. Although PZ oxidation has not been well studied on its own, analogies to both the oxidation of the PZ moiety in larger molecules and the oxidation of alkanolamines can be made to provide suspected oxidation products for concentrated PZ. Predicting basic mechanisms of oxidation can also allow for new oxidation products to be postulated. The suspected oxidation products discussed in the following paragraphs are shown in Figure 8.25. In general, aldehydes, alcohols, ureas, amino acids, and oxidized PZ molecules are suspected.

Formaldehyde is an important aldehyde that is suspected to play an important role in the oxidation mechanisms of PZ. Formaldehyde is likely produced as an oxidized fragment of the PZ ring structure and is highly reacted. Previous oxidation experiments performed on PZ using chloride dioxide (ClO_2) as the oxidant were found to produce EDA and formaldehyde (Dennis et al., 1967). Generation of EDA is common to all medium to highly oxidized PZ solutions and in the most basic oxidative mechanism, it is expected that for each PZ oxidized, an EDA and two formaldehyde-type molecules are formed. EDA is stable and persists to be quantified, while formaldehyde reacts to other products. Attempts were made to quantify formaldehyde in liquid solution using a colorimetric method, but were unsuccessful due to the reliance on response in the visible range when degraded solutions containing metal are usually highly colored (Fregert et al., 1984; Miksch et al., 1981). Although not successfully identified and quantified, it is very likely that formaldehyde plays an important role in the production of formate and other fragmented or condensed oxidation reactants. Formaldehyde and PZ are known to react

to form polymeric PZ structures, as discussed in section 6.1.5. Other suspected aldehydes and alcohols include, but are not limited to acetaldehyde, hydroxyacetaldehyde, methanol, ethanol, and ethylene glycol.

The analogy of ciprofloxacin oxidation was discussed in section 2.4.4 where the PZ moiety was oxidized using ozone, permanganate, or photo-oxidation. The oxidation products found in that study would, by extension, be expected in this type of PZ oxidation. The analogous PZ-based oxidation products would be EDA, ammonia or ammonium, 2-piperazinone, 2,5-piperazinedione, 2-piperazinol (the carbinolamine or hemiaminal form of PZ), and N-oxide piperazine. EDA and ammonium have been identified and quantified and are not included in the figure for this reason. Both 2-piperazinone and 2,5-piperazinedione were obtained as standards and tested on all the analytical methods (anion IC, cation IC, AA-LC, and HPLC) but were not matched to unknown peaks. N-oxide PZ and 2-piperazinol were not able to be obtained as standards, likely due to their reactive, unstable nature. It is believed that either would react during analysis in the cation IC and be detected as PZ or very near it in retention time.

Finally, a few other molecules are suspected based on specific suspected oxidation pathways. Reduction-oxidation pairs of reactions are believed to be occurring which could include a reaction at the amino function of a PZ molecule where the bond between the N and the α -carbon is reduced to a double bond while a separate reaction occurs to create an oxidized product. This would leave the imine form of PZ placing a double bond at the amino function (1,2,3,6-tetrahydro pyrazine), which could also be transferred to a double bond between the two carbons on the backbone of the molecule or the enamine form of PZ (1,2,3,4-tetrahydro pyrazine). Both the imine and enamine form of PZ should be detectable as a mono or diamine, if stable. Finally, molecules are suspected that would result from a ring opening of the PZ at the α -carbon. One such

molecule would be N-(2-aminoethyl) glycine, which is the oxidized, open form of the PZ molecule.

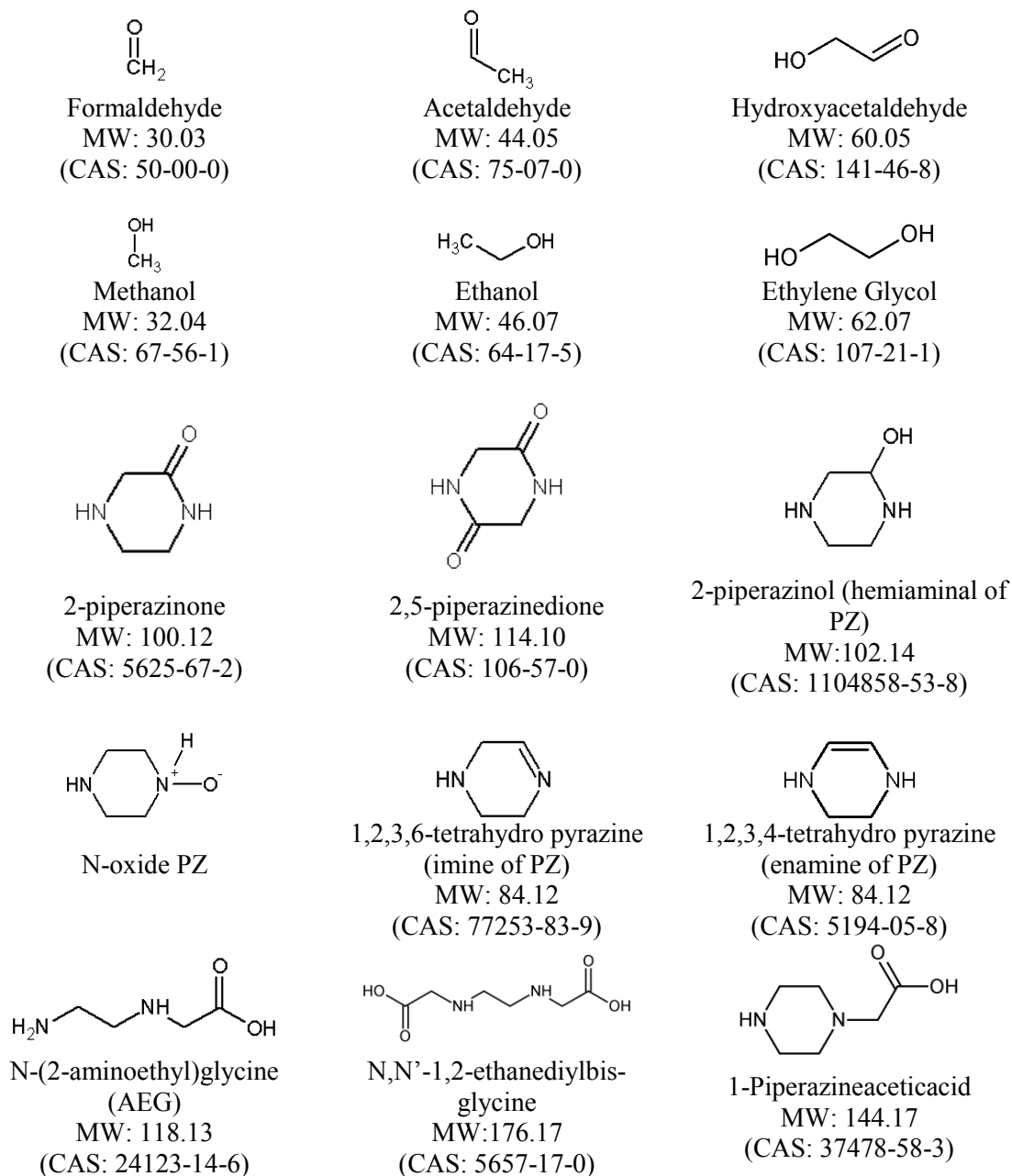


Figure 8.25: Additional suspected oxidation products

Another category of possible oxidation products are triethylenediamine (TEDA) and its oxidized forms, shown in Figure 8.26. TEDA is suspected in both oxidation and thermal degradation and its oxidized forms include 1,4-Diazabicyclo[2.2.2]octan-2-one (an amide), 1,4-Diazabicyclo[2.2.2]oct-2-ene (an enamine), and 1,4-Diazabicyclo[2.2.2]octan-2-ol (a hemiaminal). TEDA has not been found in oxidized solutions, but is suspected to be present.

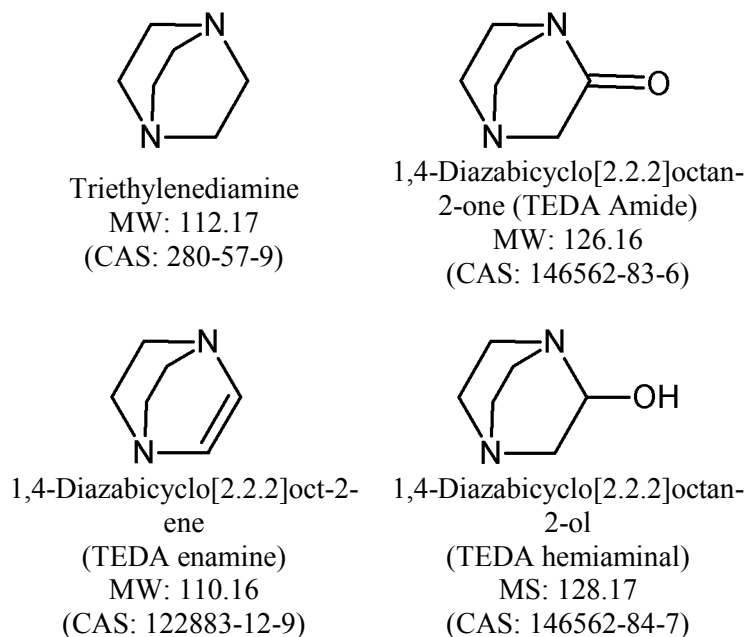


Figure 8.26: Suspected triethylenediamine-based oxidation products

8.4 EFFECT OF OXYGEN CONCENTRATION

The effect of O₂ concentration, or O₂ partial pressure, on the overall amine oxidation rate of concentrated PZ is a crucial parameter. CO₂ capture systems retrofitted to treat coal-fired power plant flue gas can expect between 5-7% O₂ entering the absorber between the bottom of the packing and the sump (Arnold et al., 1982). O₂ is absorbed by the amine solution as the flue gas rises through the packing and while retained in liquid residing in the sump. CO₂ capture systems treating natural gas flue gas can expect up to

12-15% O₂, making the amine choice in these systems very selective for oxidative resistance. The effect of O₂ concentration was examined in the presence of both stainless steel metals and Cu²⁺ for 8 m PZ.

8.4.1 Effect of oxygen on stainless-steel catalyzed oxidation

The oxidation of 8 m PZ was studied in the TOR with the standard SSM mixture (0.4 mM Fe²⁺, 0.1 mM Cr³⁺, and 0.05 mM Ni²⁺) at 55 °C, agitation at 1400 rpm and 100 mL of mixed gas with 2% CO₂, maintaining a loading of 0.3 mole CO₂ per mole alkalinity. The inlet gas also contained either 40 (OE28) or 98% O₂ (OE18), with the balance made up with N₂ in the low O₂ case.

The PZ loss and generation of degradation products for both the low and high O₂ cases are compared in Figure 8.27 and Figure 8.28, respectively. The PZ loss in both experiments is within the expected error in the oxidation experiment, as demonstrated by the baseline data shown in gray. A conclusion on the effect of O₂ is, therefore, not able to be conclusively made from the PZ loss data. On the other hand, the generation of degradation products shows an enhancement in the production of formate and total formate in high O₂ case although no EDA was detected. This enhancement demonstrates an increased rate of production of formate and formyl amides with increased O₂. Based on formate and total formate, the oxidation of PZ shows a tendency to oxidize by mechanisms that are at least first order in O₂ partial pressure. The low level of oxidation due to the weakness of stainless steel as a catalyst disallows more precise conclusions.

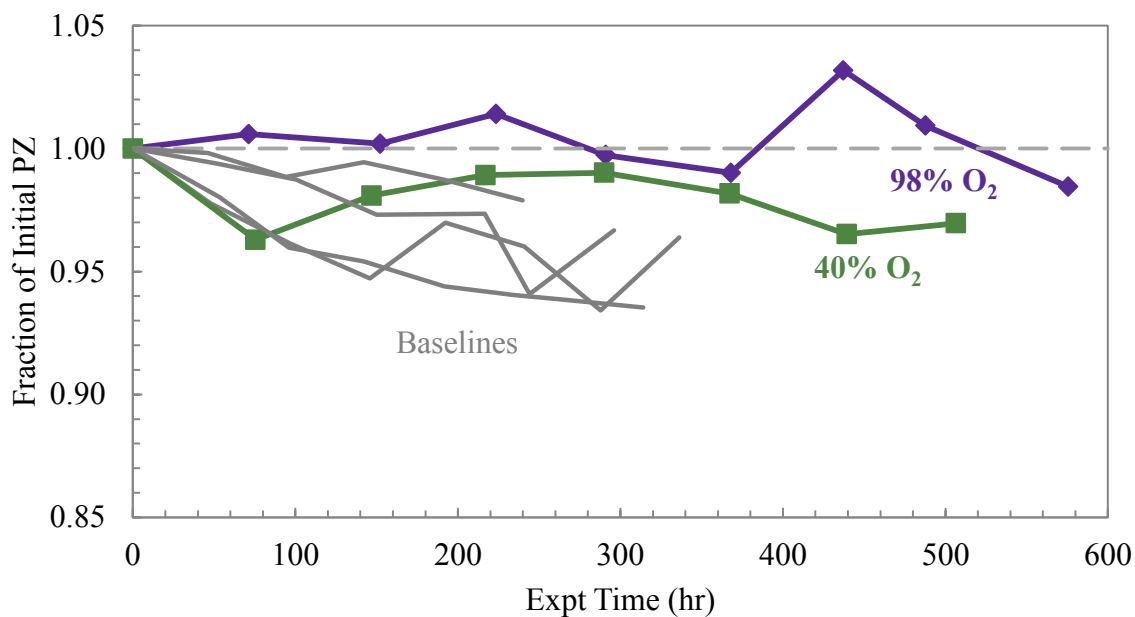


Figure 8.27: Effect of O₂ on PZ loss (TOR, 8 m PZ, 55 °C, 1400 rpm, 100 mL/min inlet gas with 40 (OE28) or 98% (OE18) O₂/2% CO₂ ($\alpha=0.3$), SSM)

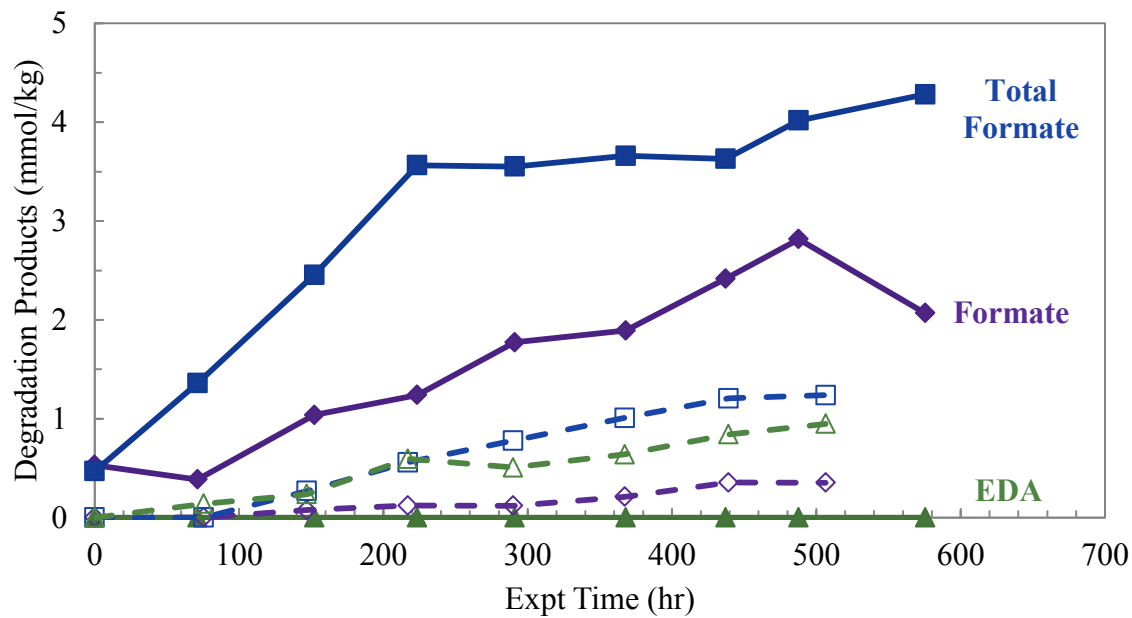


Figure 8.28: Effect of O₂ on generation of formate (◆), total formate (■), and EDA (▲) with 40% (open points, OE28) or 98% O₂ (filled points, OE18) (TOR, 8 m PZ, 55 °C, 1400 rpm, 100 mL/min inlet gas with 2% CO₂ ($\alpha=0.3$), SSM)

8.4.2 Effect of oxygen on copper-catalyzed oxidation

8.4.2.1 *Effect of oxygen on copper-catalyzed oxidation at 55 °C*

The oxidation of 8 m PZ was also investigated in the OOR and TOR with 4 mM Cu^{2+} at 55 °C, agitation at 1400 rpm and 100 mL of mixed gas with 2% CO_2 , maintaining a loading of 0.3 mole CO_2 per mole alkalinity. The inlet gas also contained either 40 (OE27, TOR) or 98% O_2 (OE2, OOR), with the balance N_2 in the low O_2 case. Provided that copper is a stronger catalyst for amine oxidation (see 9.1.3 for more detail), the effects of O_2 should be readily observable with a higher rate of oxidation.

The PZ loss and generation of degradation products for both the low and high O_2 cases are shown in Figure 8.29 and Figure 8.30, respectively. PZ loss and the generation of all three of the major degradation products are strongly enhanced by an increase in O_2 content. After 450 hours of oxidation, an increase in O_2 content from 40 to 98%, or 245%, enhanced PZ loss by approximately 240% in terms of the fraction of initial loss. PZ loss at 55 °C is therefore approximately first order in O_2 content in the inlet gas. Formate, total formate, and EDA generation were all increased with the higher O_2 content. After 450 hours of oxidation, EDA, total formate, and formate production were increased 180, 340, and 370%, respectively, as the O_2 content increased 250%. The generation of these products is not in the same ratio in each case, indicating that the O_2 content or rate of oxidation may impact the mixture of degradation products generated.

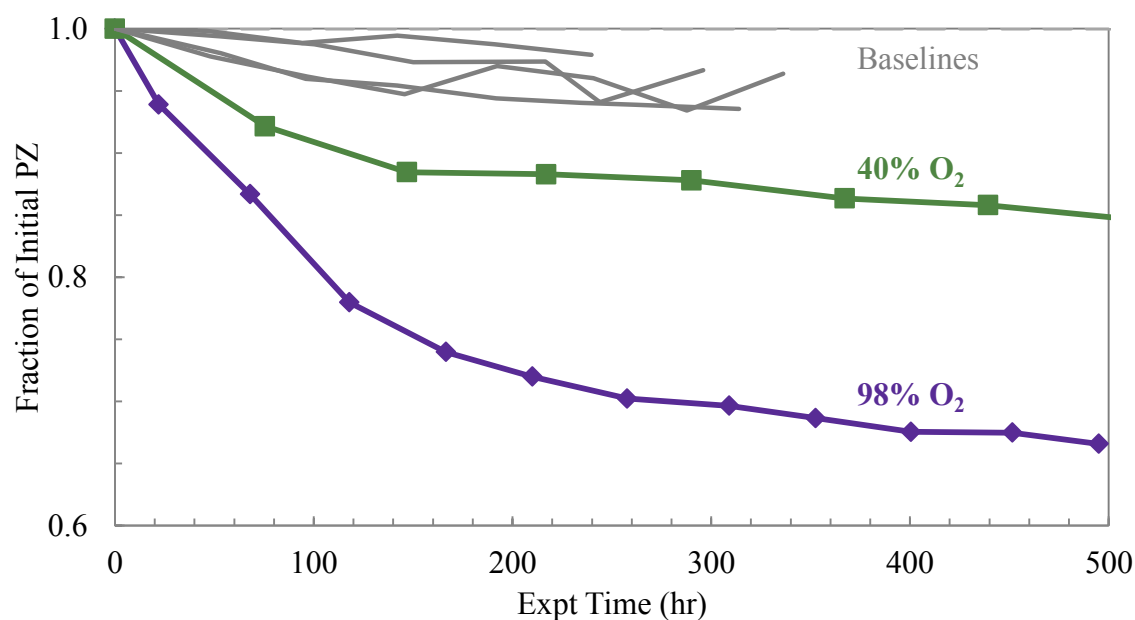


Figure 8.29: Effect of O₂ on PZ loss (8 m PZ, 55 °C, 1400 rpm, 100 mL/min inlet gas with 40 (OE27) or 98% (OE2) O₂/2% CO₂ ($\alpha=0.3$), 4 mM Cu²⁺)

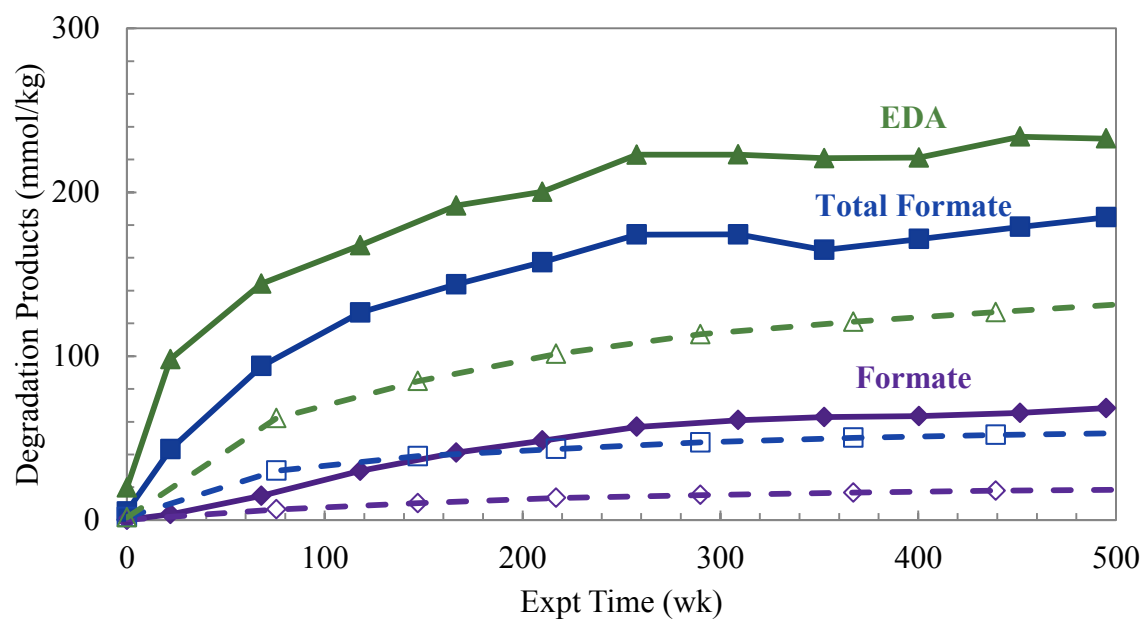


Figure 8.30: Effect of O₂ on generation of formate (♦), total formate (■), and EDA (▲) with 40% (open points, OE27) or 98% O₂ (filled points, OE2) (8 m PZ, 55 °C, 1400 rpm, 100 mL/min inlet gas with 2% CO₂ ($\alpha=0.3$), 4 mM Cu²⁺)

8.4.2.2 Effect of oxygen on copper-catalyzed oxidation at 70 °C

Finally, the effect of oxidation at high temperature was investigated. Solutions of 8 m PZ were oxidized in the TOR with 4 mM Cu^{2+} at 70 °C, agitation at 1400 rpm and 100 mL of mixed gas with 6% CO_2 , maintaining a loading of 0.3 mole CO_2 per mole alkalinity at this elevated temperature. The inlet gas also contained either 40 (OE23) or 94% O_2 (OE25), with the balance N_2 in the low O_2 case.

The PZ loss and generation of degradation products for both the low and high O_2 cases are shown in Figure 8.31 and Figure 8.32, respectively. As found in the low temperature Cu^{2+} -catalyzed experiments, the concentration of O_2 has strong effect on both PZ loss and product generation. The PZ loss is nearly doubled from 35 to 72% of the initial PZ degraded after 350 hours when the O_2 partial pressure is increased from 40 to 94% of the inlet gas. That is to say, a 235% increase in O_2 partial pressure increased PZ loss by 206%. As with the low temperature experiment, the ratio of increase in O_2 content and PZ loss is roughly the same, indicating that PZ oxidation is first order in O_2 under these conditions. For this case, however, this observation may not fully represent the system because of data quality issues in the 40% O_2 experiment (OE23). The change in PZ concentration in the initial sample was thought to be due to additional water loss because the TOR flange clamp was not fully tightened. It also may represent real PZ loss since the concentration profile for the degradation products does not seem affected. An increase in the generation of degradation products in the high O_2 experiment was observed for all three major products, supporting findings from the PZ loss data.

This direct dependence on O_2 concentration found at 55 and 70 °C indicates that for Cu^{2+} -catalyzed oxidation, the degradation could be O_2 mass transfer controlled. The PZ oxidation process uses as much O_2 as it can find in solution. The data is also consistent with a kinetic mechanism that is first order in O_2 .

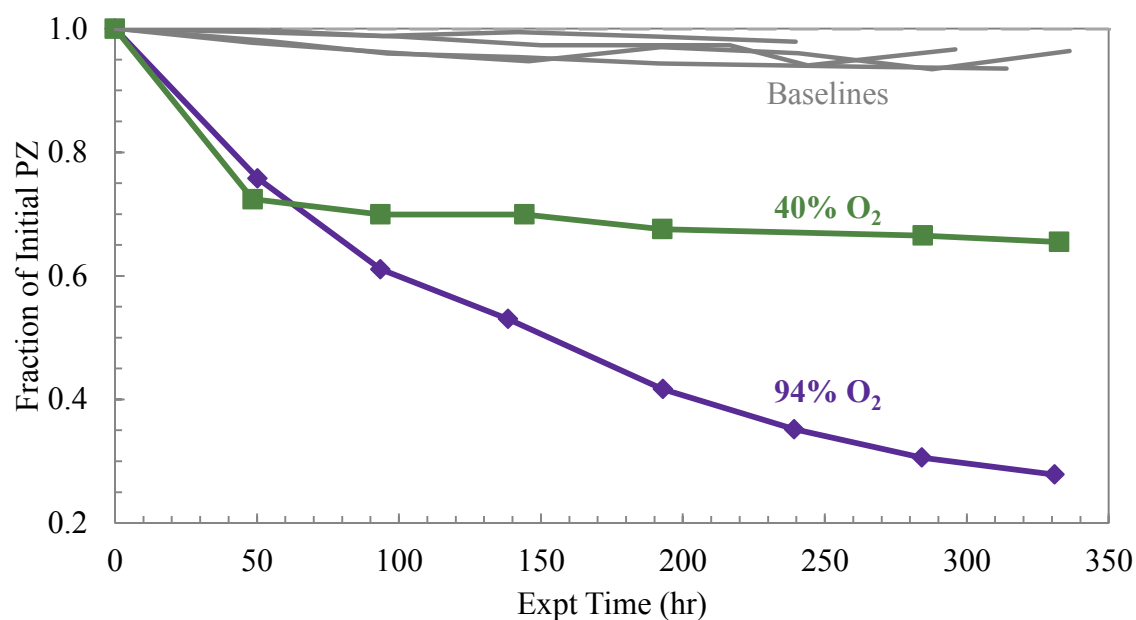


Figure 8.31: Effect of O₂ on PZ loss (TOR, 8 m PZ, 70 °C, 1400 rpm, 100 mL/min inlet gas with 40 (OE23) or 94% (OE25) O₂/6% CO₂ ($\alpha=0.3$), 4 mM Cu²⁺)

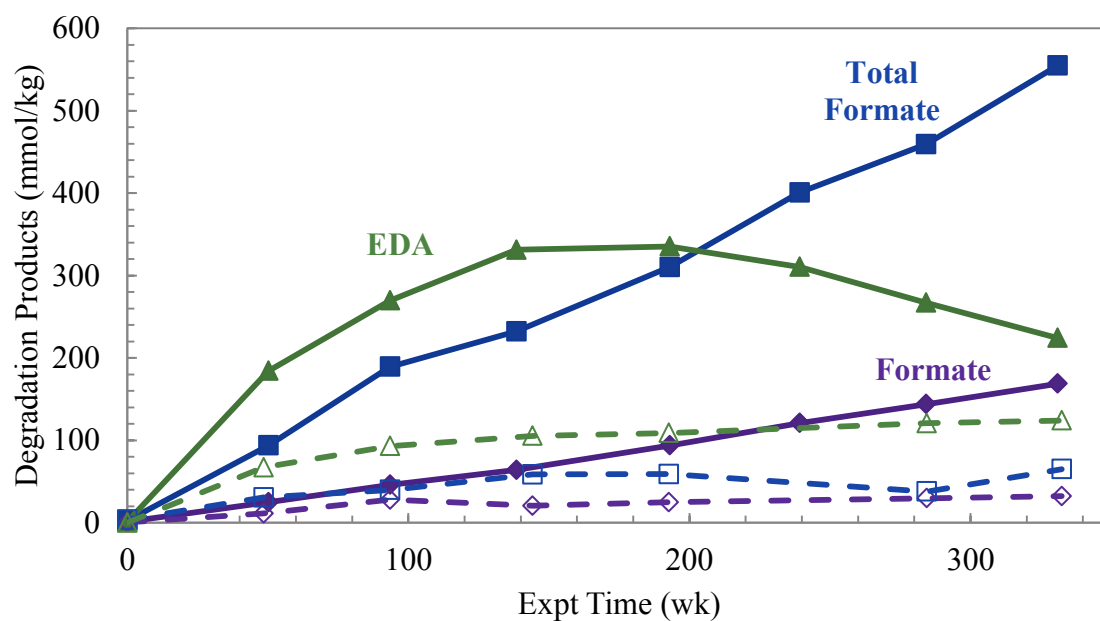


Figure 8.32: Effect of O₂ on generation of formate (♦), total formate (■), and EDA (▲) with 40% (open points, OE23) or 94% O₂ (solid points, OE25) (TOR, 8 m PZ, 70 °C, 1400 rpm, 100 mL/min inlet gas with 6% CO₂ ($\alpha=0.3$), 4 mM Cu²⁺)

8.5 EFFECT OF TEMPERATURE

PZ oxidation is expected to accelerate with increased temperature. The temperature bulge in the absorber is predicted to reach up to 70 °C, making the overall temperature range in the absorber and absorber sump 40 to 70 °C (Plaza et al., 2009). The absorber sump, where the most residence time and liquid hold up occurs, should be maintained at the lower end of the temperature range, which will minimize oxidation effects. The sump, however, is where the concentration of O₂ is likely to remain high since the sumps position directly below the flue gas inlet.

The acceleration of oxidation due to increased temperature was independently investigated in the presence of stainless steel metals and copper. For both catalysts, temperatures of 55 and 70 °C were investigated to represent the average and maximum expected temperatures.

8.5.1 Effect of temperature on stainless steel catalyzed oxidation

The oxidation of 8 m PZ was studied in the TOR with the standard SSM mixture (0.4 mM Fe²⁺, 0.1 mM Cr³⁺, and 0.05 mM Ni²⁺), agitation at 1400 rpm and 100 mL of O₂/CO₂ mixed gas. The CO₂ concentration of the inlet gas was adjusted based on the reactor temperature in order to maintain a CO₂ loading of 0.3 mole CO₂ per mole alkalinity at 55 °C (OE18: 98% O₂/2% CO₂) and 70 °C (OE25: 94% O₂/6% CO₂).

The loss of PZ and the generation of degradation products in both experiments are compared in Figure 8.33 and Figure 8.34, respectively. The higher temperature noticeably increased the loss of PZ, although both sets of data lie within the error limits established by the baseline experiments. Although perhaps not statistically significant, the increase in temperature does increase PZ loss. For the degradation products, higher concentrations of total formate and EDA were observed in the higher concentration experiment while formate production was nearly identical. It is important to note that no

EDA was observed in the 55 °C experiment while EDA levels reached nearly 30 mmole per kg in the 70 °C experiment. The undetected EDA may be a true observation, or an artifact of the difficulty in quantifying low levels of EDA while more substantial concentrations found in the high temperature experiment were more readily detected. These results indicate that the enhanced loss of PZ at 70 °C is potentially a true increase in oxidation which is also reflected in increased concentrations of degradation products.

8.5.2 Activation energy of stainless steel-catalyzed oxidation

Given the two experimental temperatures, an activation energy for PZ oxidation can be calculated for stainless-steel catalyzed oxidation. Linear rates of loss or generation of PZ, formate, total formate, and EDA have been regressed for all stainless steel experiments. This procedure is detailed in section 9.4 of the following chapter. Using the rates of experiments catalyzed by SSM, activation energies for each rate can be extracted based on an Arrhenius behavior of rate with temperature, as shown for k_1 of thermal degradation in section 5.2.

The rates for PZ loss and generation of formate, total formate, and EDA for the seven SSM containing experiments (OE1, OE15, OE18, OE19, OE22, OE26, and OE28) are shown in Figure 8.35. One experiment had loss rate of zero for PZ (OE15) while two experiments were not found to produce EDA (OE1 and OE18). For each species, an exponential trendline has been regressed through all the experimental rates and the equation shown on the graph. From the value of the constant in the exponential, the activation energy for loss or generation of that species can be calculated over this temperature range. Standard error in the activation energies were calculated based on the standard error of a linear least-squares fit of the natural log of each rate.

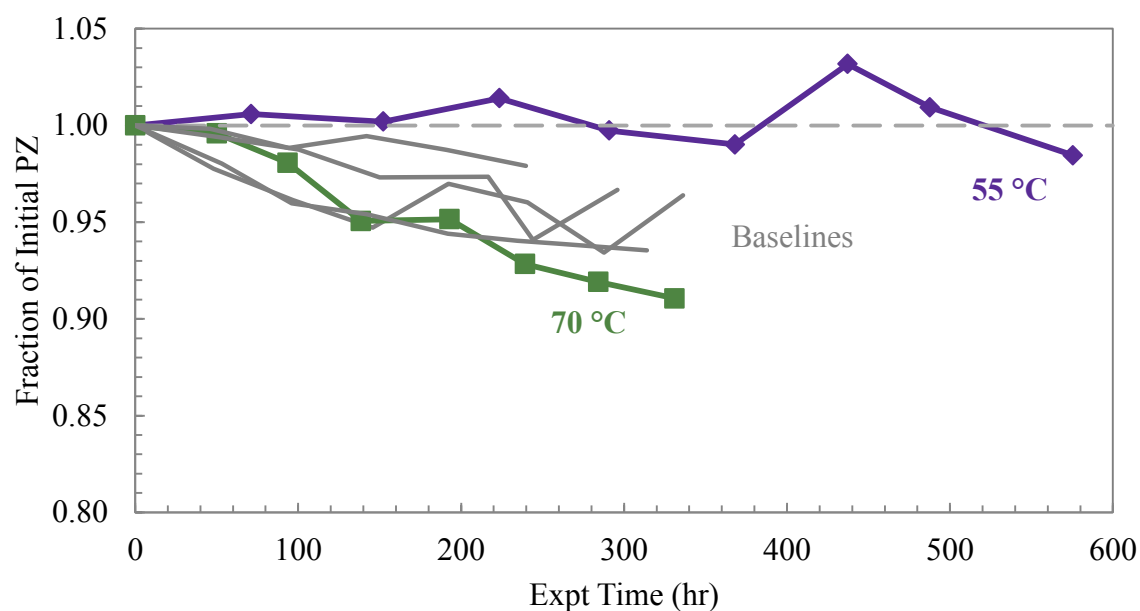


Figure 8.33: Effect of temperature on PZ loss (TOR, 8 m PZ, 1400 rpm, 100 mL/min with 2 (OE18) or 6% (OE28) CO₂ with balance O₂, $\alpha=0.3$, SSM)

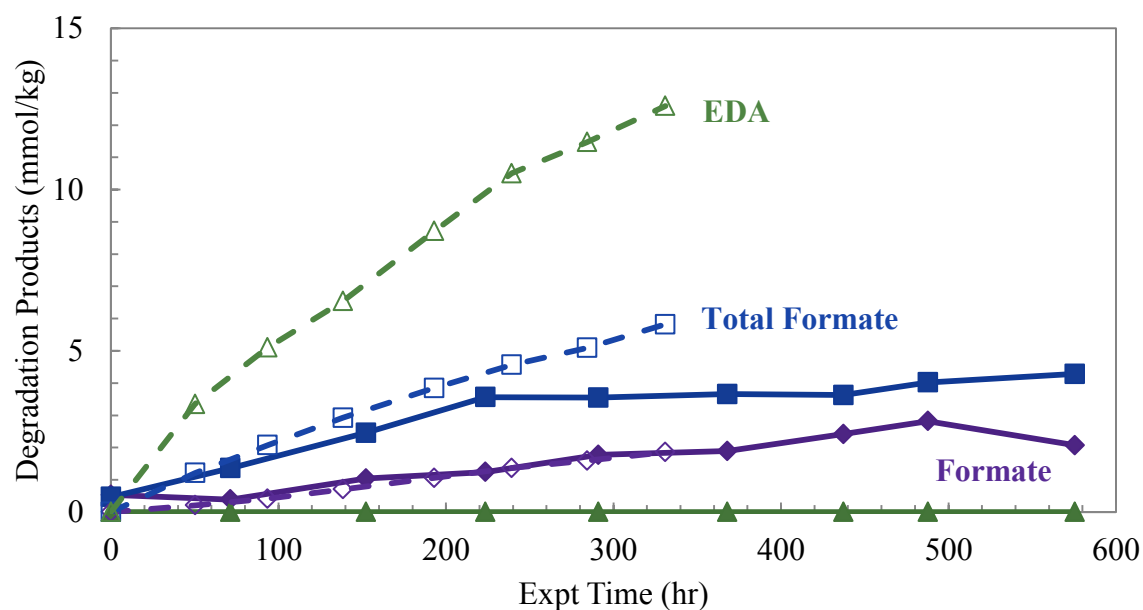


Figure 8.34: Effect of temperature on generation of formate (◆), total formate (■), and EDA (▲) at 55 (solid points, OE18) or 70 °C (open points, OE28) (TOR, 8 m PZ, 1400 rpm, 100 mL/min with 2 (OE18) or 6% (OE28) CO₂ with balance O₂, $\alpha=0.3$, SSM)

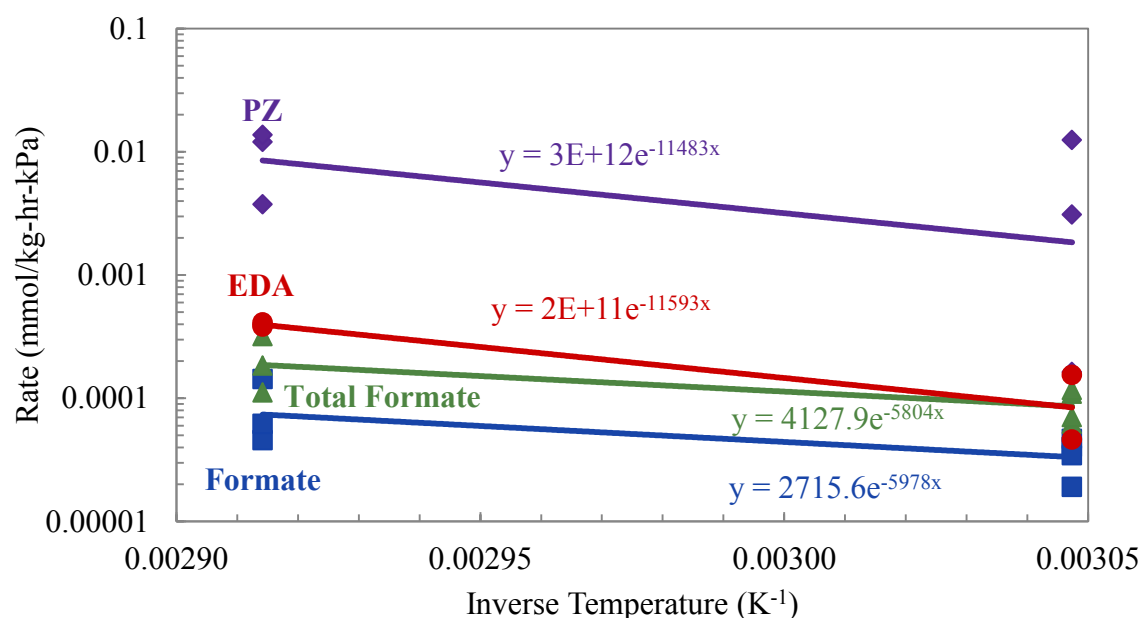


Figure 8.35: Rates of loss or production for PZ (♦), formate (■), total formate (▲), and EDA (●) for stainless-steel catalyzed oxidation

The calculated activation energies with their associated error are compared for the four species in Table 8.7. The loss of PZ and the generation of EDA were found to have very similar activation energies of 96 kJ per mole, while both formate and total formate had activation energies near 50 kJ per mole. This similarity of activation energies indicates that EDA could be generated directly at the rate of PZ oxidation. The similarity of activation energies between total formate and formate indicate that they are likely generated at a constant ratio, no matter the temperature.

Table 8.7: Activation energies for PZ loss and generation of products for stainless steel-catalyzed oxidation

Rate	Activation Energy (kJ/mol)
PZ Loss	96 ± 84
Formate Generation	50 ± 23
Total Formate Generation	48 ± 20
EDA Generation	96 ± 28

8.5.3 Effect of temperature on copper-catalyzed oxidation

A second investigation on the effect of temperature on concentrated PZ oxidation was performed in the presence of Cu^{2+} . Oxidation of 8 m PZ was performed in the OOR and TOR with 4 mM Cu^{2+} , agitation at 1400 rpm and 100 mL of O_2/CO_2 mixed gas. The CO_2 concentration of the inlet gas was adjusted based on the reactor temperature in order to maintain a CO_2 loading of 0.3 mole CO_2 per mole alkalinity at 55 °C (OE2: 98% $\text{O}_2/2\%$ CO_2) and 70 °C (OE25: 94% $\text{O}_2/6\%$ CO_2). These experiments were performed in the presence of high O_2 content (94-98% O_2). This condition would accelerate oxidation, as discussed in the previous section, making the effect of temperature more readily observed in PZ oxidation. For the interested reader, a comparison of OE23 and OE27 can be made to investigate the effect of Cu^{2+} -catalyzed oxidation between 55 and 70 °C but with low O_2 content (40%) (See Appendix E for experimental data).

The loss of PZ and generation of degradation products are compared in Figure 8.36 and Figure 8.37, respectively. The loss of PZ is markedly enhanced at the higher temperature. After 350 hours, 72% of the initial PZ is lost in the high temperature experiment compared to only 31% loss in the 55 °C experiment. This is an increase of 230% in PZ loss for an increase of 15 °C. Both experiments demonstrate statistically significant PZ loss compared to the baseline experiments.

The generation of formate, total formate, and EDA were all enhanced at higher temperature as well, as expected with increased PZ oxidation. The formate and total formate are initially generated in a linear fashion in both experiments while a leveling off effect can be seen in these products at 55 °C. This same behavior is mimicked in the low temperature PZ loss data where the oxidation has slowed due to mass transfer or kinetic limitations of the oxidation reactions. On the other hand, the formate and total formate in the 70 °C experiment continue to increase linearly without leveling off. After 350 hours,

formate and total formate concentrations reach 168.7 and 554.9 mmole per kg, respectively, compared to only 62.8 and 164.8 mmole per kg, respectively, at 55 °C. This is an increase of 270 and 340% for formate and total formate, respectively, for an increase of 15 °C. The EDA, however, demonstrates a unique behavior where a clear maximum is achieved after 150 hours at 70 °C. This behavior was not observed in other oxidation experiments and indicates that EDA is an intermediate that is generated from PZ, but then reacts to form other products. As discussed in section 8.3.1.1, it was observed that free EDA was reacting to form EDA-based amides at this point, decreasing the concentration of free EDA quantified. At the maximum of EDA concentration, at 150 hours, the EDA concentration is 170% higher than that of the low temperature experiment.

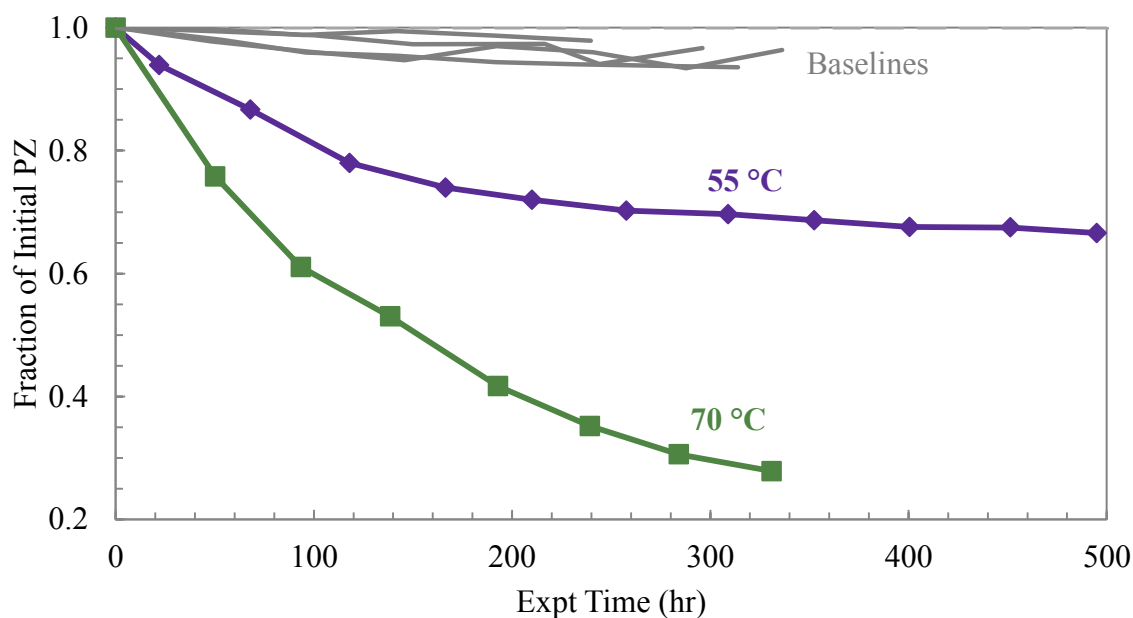


Figure 8.36: Effect of temperature on PZ loss (TOR, 8 m PZ, 1400 rpm, 100 mL/min with 2 (OE2) or 6% (OE25) CO₂ with balance O₂, $\alpha=0.3$, 4 mM Cu²⁺)

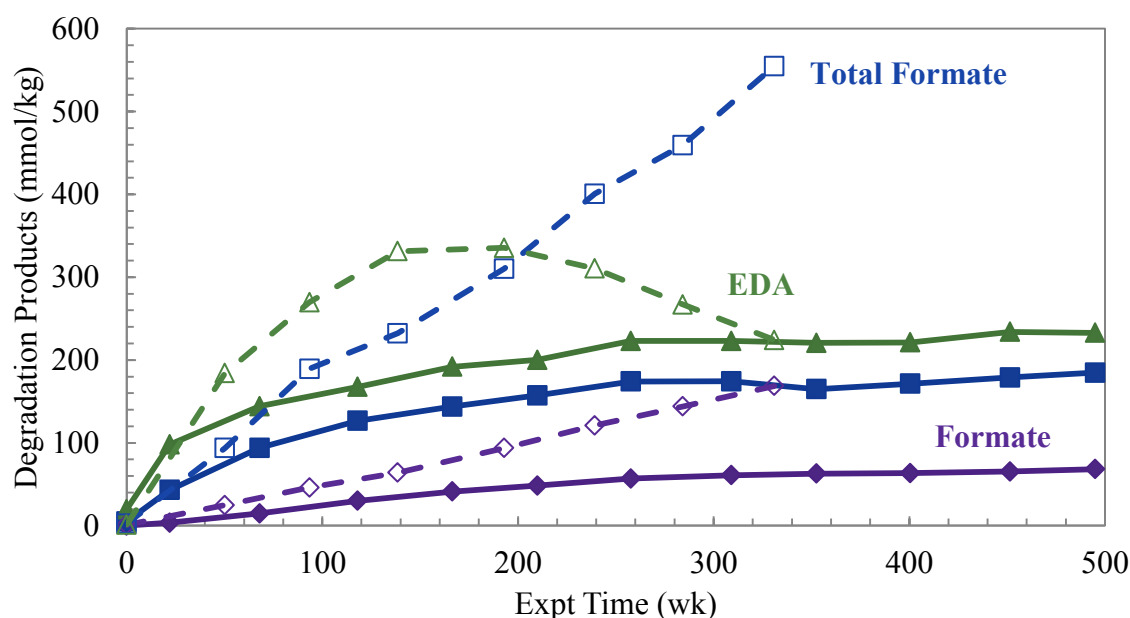


Figure 8.37: Effect of temperature on generation of formate (◆), total formate (■), and EDA (▲) at 55 (solid, OE2) or 70 °C (open, OE25) (8 m PZ, 1400 rpm, 100 mL/min with 2 (OE2) or 6% (OE25) CO₂ with balance O₂, $\alpha=0.3$, 4 mM Cu²⁺)

8.5.4 Activation energy for copper-catalyzed oxidation

That activation energy for the loss of PZ and generation of formate, total formate, and EDA during Cu²⁺-catalyzed oxidation were calculated in the same way as SSM-catalyzed oxidation (section 8.5.2). The rates for the four species are compared for four Cu²⁺-catalyzed experiments (OE2, OE23, OE25, and OE27) in Figure 8.38 and the calculated activation energies with the expected error are shown in Table 8.8.

In this case, the loss of PZ and the generation of total formate were found to have very similar activation energies of 27-29 kJ per mole, while both EDA and total formate had slightly higher activation energies of 36 and 47 kJ per mole, respectively. In comparison with SSM-catalyzed oxidation, the PZ activation energy is three times lower showing the propensity for rapid oxidation that is characteristic of Cu²⁺ catalysis. The activation energy for formate is nearly identical at around 47-49 kJ per mole while both

total formate and EDA have lower energies in the presence of Cu^{2+} . This may indicate that formate generation is not dependent on catalyst while total formate and EDA rates are more subjective to the type and concentration of catalyst. This may also suggest that formate is the best oxidation product to represent overall degradation if its behavior is more similar between catalysts. There is a more complicated equilibrium between formate and formyl amides, so these energies may indicate that the generation of formate is the dominant mechanism associated with oxidation while the generation of amides is an equilibrium phenomena based on formate concentration, not oxidation directly.

Table 8.8: Activation energies for PZ loss and generation of products for Cu^{2+} -catalyzed oxidation

Rate	Activation Energy (kJ/mol)
PZ Loss	27 ± 29
Formate Generation	47 ± 15
Total Formate Generation	29 ± 33
EDA Generation	36 ± 9

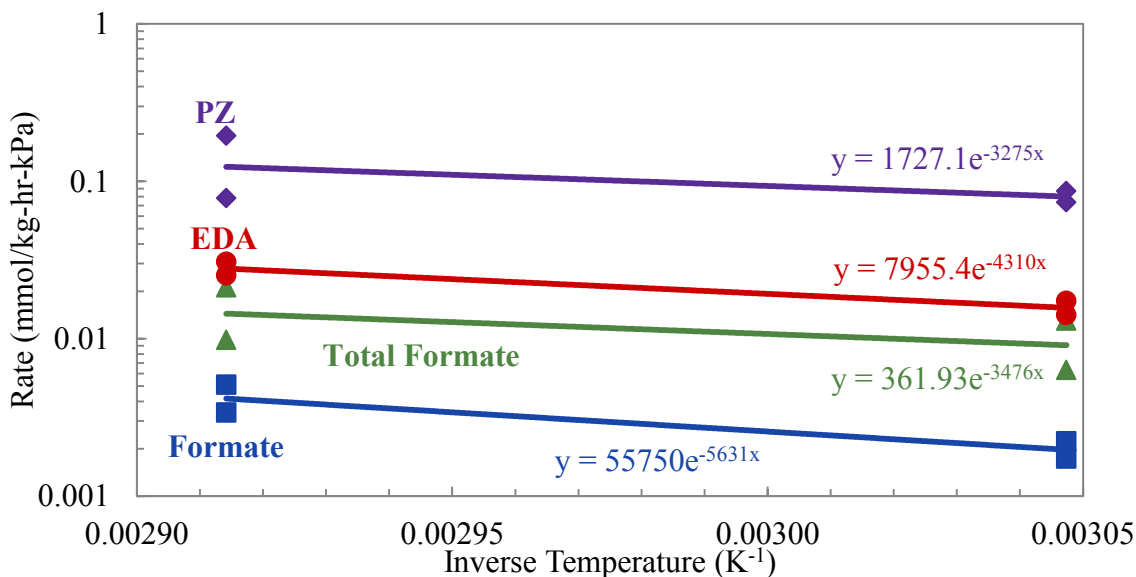


Figure 8.38: Rates of loss or production for PZ (♦), formate (■), total formate (▲), and EDA (●) for Cu^{2+} -catalyzed oxidation

8.6 EFFECT OF CO₂ CONCENTRATION

Most of the oxidation experiments in this project were performed with inlet gas streams containing the partial pressure of CO₂ needed to maintain a lean loading of approximately 0.3 to 0.32 mole CO₂ per mole alkalinity based on CO₂ solubility data. Four of the 28 experiments performed did not maintain this lean loading and the effect of CO₂ concentration can be seen in examining these four experiments. Two of these four experiments contained additives (formate and formaldehyde) that are discussed in section 8.8 below. Of the remaining two experiments, one was performed at a very lean loading of 0.26 mole CO₂ per alkalinity while the last was performed at rich loading of 0.42 mole CO₂ per mole alkalinity. The very lean experiment was performed at conditions similar to a representative lean experiment, except for an increased O₂ concentration (98 vs. 94% O₂ in the inlet gas).

The rich loaded experiment is difficult to compare directly to another lean experiment because of the reaction conditions. The rich experiment contained only 40% O₂ because 60% CO₂ was needed to achieve the rich loading at 70 °C. The two most similar experiments are not easy to compare because they differ either in temperature (55 °C instead of 70 °C) or O₂ concentration (96% instead of 40%). In the sections above, it was shown that for SSM-catalyzed oxidation, an increase of 15 °C had a stronger effect on both PZ loss and product generation in the presence of SSM than an increase from 40 to 98% O₂ (comparison of Figure 8.27 and Figure 8.33). Based on this observation, the rich loading experiment will be compared to an experiment conducted at the same temperature (70 °C) rather than the same O₂ content (40%), in an attempt to highlight the effect of CO₂ concentration. Therefore, the effect of CO₂ concentration on oxidation will be discussed in the presence of SSM at 70 °C with loadings ranging from 0.2 to 0.4 and O₂ contents ranging from 40 to 98%. This comparison does not fully

exclude the effect of O₂, but should limit the interference of the other variables (O₂ and temperature) on the effect of CO₂ loading.

The oxidation of 8 m PZ was studied in the TOR with the standard stainless steel metals mixture (0.4 mM Fe²⁺, 0.1 mM Cr³⁺, and 0.05 mM Ni²⁺) at 70 °C with agitation at 1400 rpm and 100 mL of O₂/CO₂ mixed gas. The CO₂ concentration of the inlet gas was adjusted based on the reactor temperature to produce a CO₂ loading of 0.2 (OE19: 2% CO₂), 0.3 (OE26: 6% CO₂), and 0.4 mole CO₂ per mole alkalinity (OE22: 60% CO₂). The balance of the inlet gas was O₂ in all three cases.

The PZ loss, generation of formate, and generation of total formate are compared in Figure 8.39, Figure 8.40, and Figure 8.41, respectively. The loss of PZ data indicate that increased CO₂ loadings enhance PZ oxidation, although all three data sets are within or near the boundary on error established by the baseline experiments. On the other hand, the production of both formate and total formate indicate the opposite, with the lean solution producing the highest concentrations of both species after oxidation. There is much more confidence in the accurate quantification of the degradation products, so this effect is likely more representative of the effect of loading than any observations based on the PZ loss rate. The lower O₂ content of the rich ($\alpha=0.4$) experiment will also affect interpretation. At 70 °C, a doubling of O₂ partial pressure will produce approximately a 300% increase in the production of formate and total formate based on the conclusions of section 8.5.2. This would place the rich data in line with the lean ($\alpha=0.3$) data and an enhanced rate of product generation at very lean loading ($\alpha=0.2$) would still be observed.

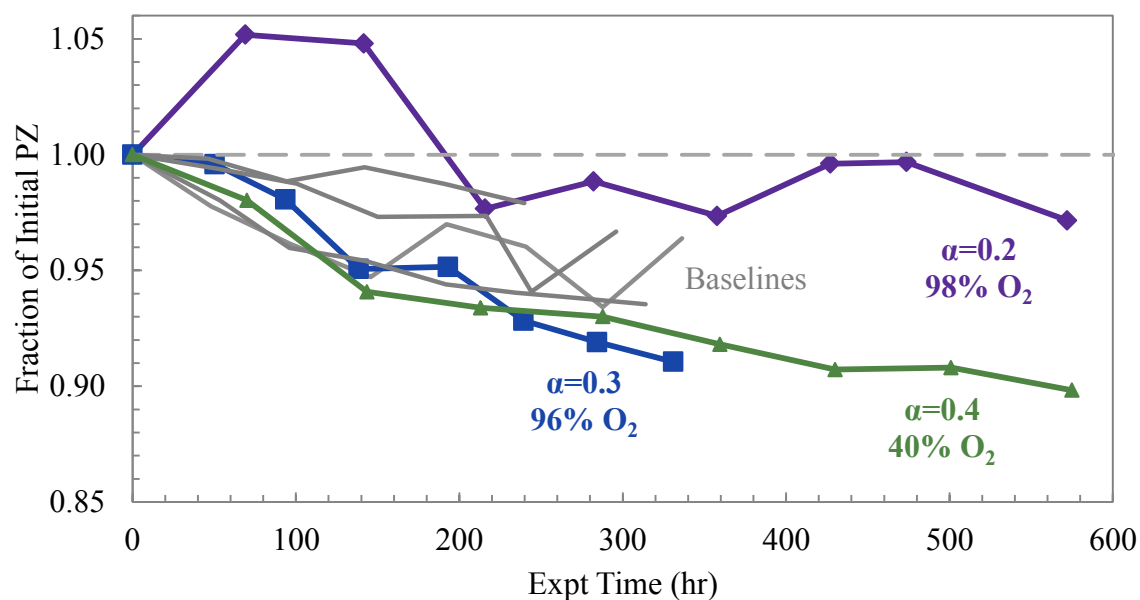


Figure 8.39: Effect of CO₂ on PZ loss (TOR, 70 °C, 8 m PZ, 1400 rpm, 100 mL/min with 2 (OE19), 6 (OE26), or 60% (OE22) CO₂ with balance O₂, SSM)

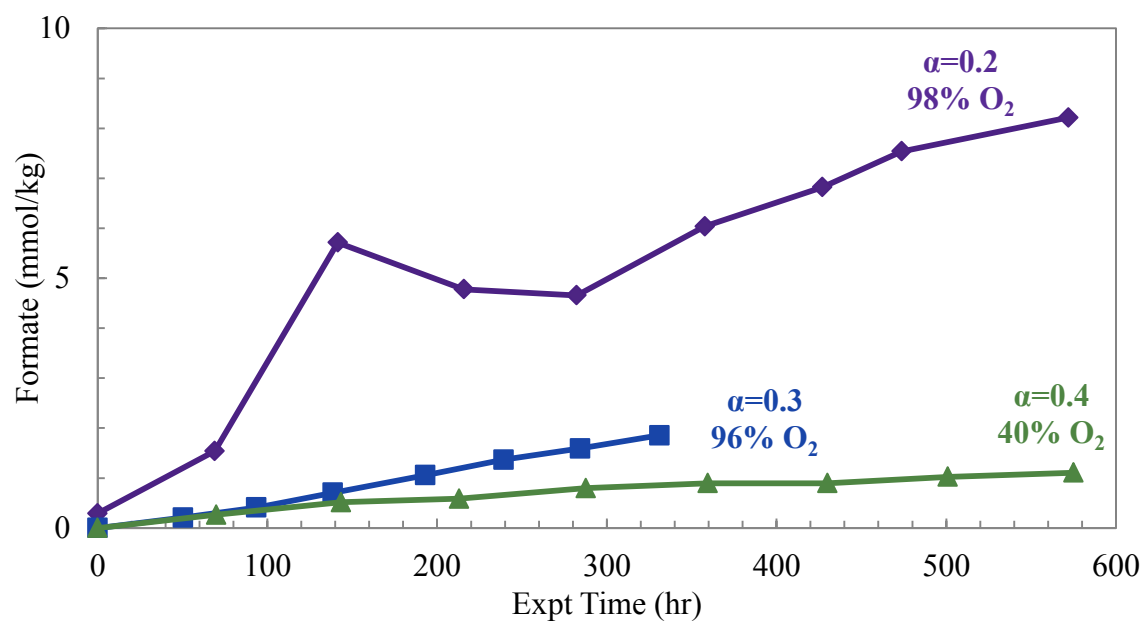


Figure 8.40: Effect of CO₂ on formate generation (TOR, 70 °C, 8 m PZ, 1400 rpm, 100 mL/min with 2 (OE19), 6 (OE26), or 60% (OE22) CO₂ with balance O₂, SSM)

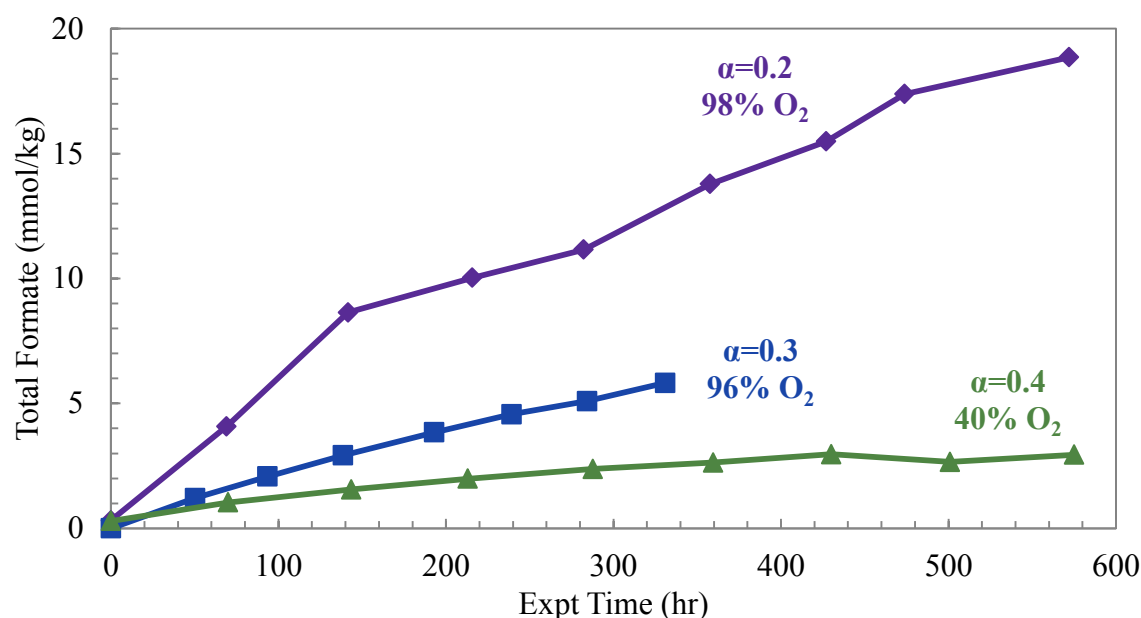


Figure 8.41: Effect of CO₂ on total formate generation (TOR, 70 °C, 8 m PZ, 1400 rpm, 100 mL/min with 2 (OE19), 6 (OE26), or 60% (OE22) CO₂ with balance O₂, SSM)

8.7 EFFECT OF PZ CONCENTRATION

Another factor explored in this chapter is the effect of PZ concentration on the oxidation of concentrated PZ. The effect of amine concentration on the oxidation of MEA has been explored previously, but not for concentrated PZ (Goff, 2005; Sexton, 2008). Within this project, the effect was not developed fully due to the importance and likely application of 8 m PZ in industrial experiments. However, a few experiments did observe the differences between 8 and 10 m PZ. In addition, previous work on PZ oxidation contains some data for 5 m PZ that will be interpreted as well. All of the experiments discussed in this section were performed at 55 °C with 100 mL per min of 98% O₂/2% CO₂ in a low gas flow reactor (OOR or TOR) with agitation at 1400 rpm. These conditions were maintained for experiments performed in this project and those

performed previously (Sexton, 2008). Only differences in PZ, catalyst, or inhibitor concentrations will be highlighted during the discussions in the rest of the section.

8.7.1 Effect of PZ concentration in stainless-steel catalyzed oxidation

With the available data, there is only one comparison to make for oxidation in the presence of stainless steel metals. Both 8 and 10 m PZ were oxidized in the presence of stainless steel metals under the abovementioned temperature, CO₂, and O₂ conditions. The experiments contained slightly different concentrations of Fe²⁺, Cr³⁺, and Ni²⁺. The 8 m PZ solution (OE18) contained 0.4, 0.1, and 0.05 mM of each metal, respectively, while the 10 m PZ solution (OE1) contained 0.23, 1.6, and 0.2 mM of each metal, respectively. It is assumed that the difference in catalyst concentration would not affect the overall conclusions of the comparison.

The loss of PZ and generation of formate and total formate are compared in Figure 8.42 and Figure 8.43, respectively. The PZ concentrations compared are close to each other and it was not expected that a large change would be seen given this small difference. However, a slightly enhanced loss of PZ and generation of degradation product can be seen in the higher concentration experiment. With 10 m PZ, the amine is steadily lost over the course of the experiment with some scatter in the data. Although the formate concentration profiles are similar between the 8 and 10 m PZ, the 10 m PZ produced roughly 3 mmole per kg more total formate. These differences are small in light of the expected experimental and analytical error demonstrated by the baseline data, but the overall picture seems to indicate that oxidation is a slight function of PZ concentration.

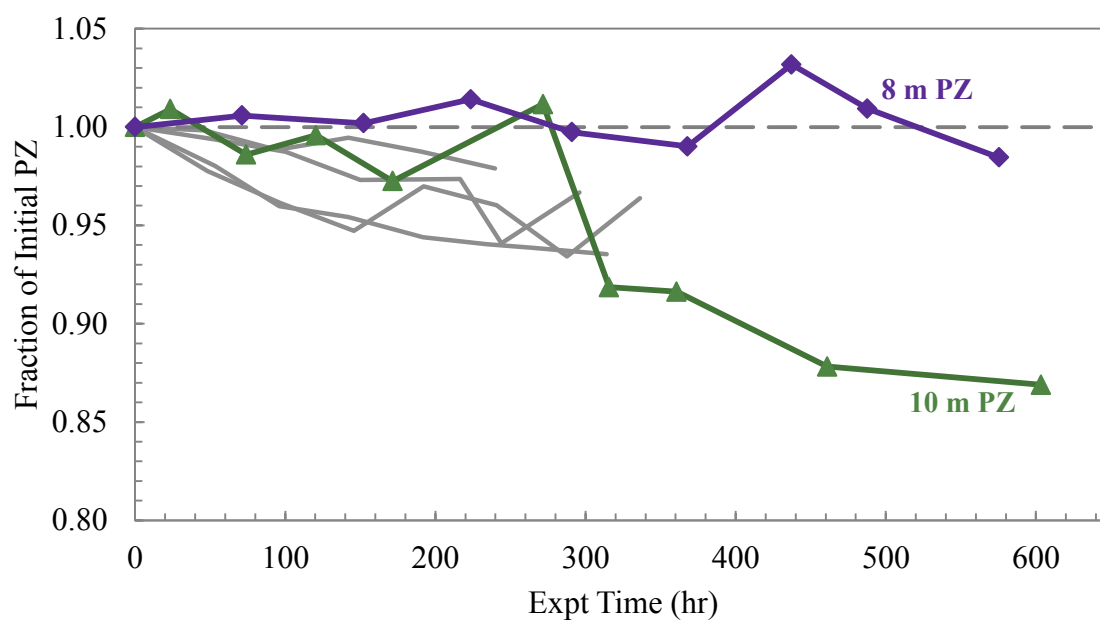


Figure 8.42: Effect of PZ concentration on PZ loss (8 m PZ (OE18) or 10 m PZ (OE1), 55 °C, 1400 rpm, 100 mL/min 98% O₂/2% CO₂, SSM)

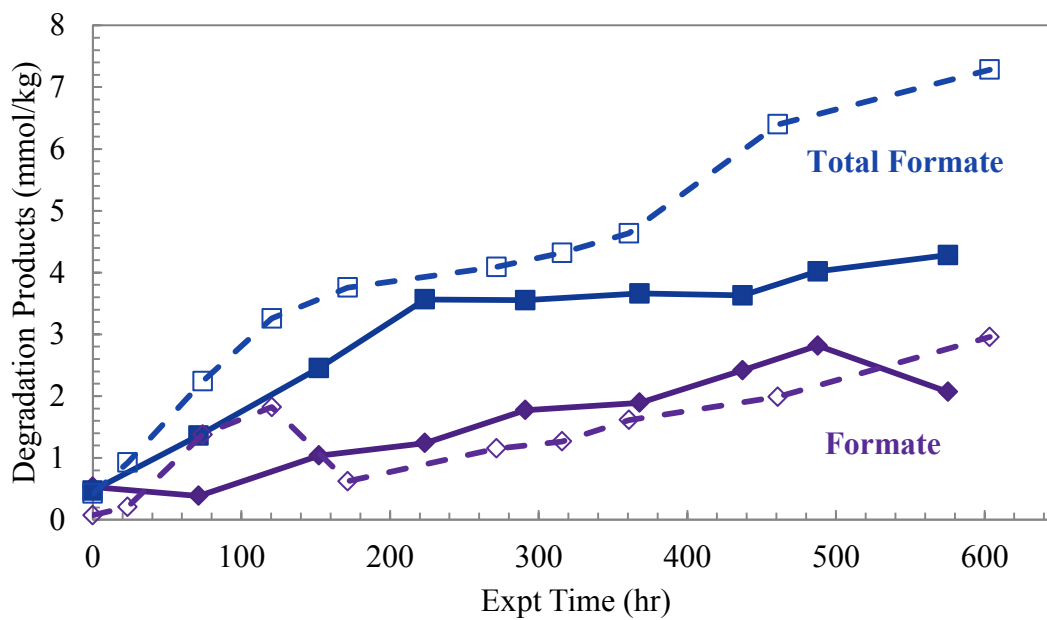


Figure 8.43: Effect of PZ concentration on generation of formate (◆) and total formate (■) for 8 m PZ (OE18, solid) and 10 m PZ (OE1, dashed) with SSM (55 °C, 1400 rpm, 100 mL/min 98% O₂/2% CO₂)

8.7.2 Effect of PZ concentration in copper-catalyzed oxidation

The effect of PZ concentration on copper-catalyzed oxidation can be observed through comparing two sets of experiments. From this project, copper-catalyzed oxidation was measured in 8 and 10 m PZ. Secondly, Sexton performed screening experiments on the oxidation of 5 m PZ in the presence of combinations of Fe^{2+} , Cu^{2+} , and Inhibitor A (Sexton, 2008). Unfortunately, the analysis performed on liquid samples was not completed to the same extent and only a few species, not including PZ in some cases, were measured. Some information can still be garnered from the degradation products that were measured. The experiments containing Cu^{2+} will be the focus since they were the most likely to produce appreciable levels of oxidation.

The oxidation of 5 m PZ in the presence of Cu^{2+} was measured by Sexton (2008) and although the data does not include PZ concentration, multiple dominant degradation products were observed and quantified. The generation of major degradation products is compared in Figure 8.44 to a 10 m PZ experiment with similar catalysts (OE2). The results from the 10 m PZ experiment are shown with filled points and solid lines while the 5 m PZ experiment is shown with open points and dashed lines. Formate (for), oxalate (oxa), total formate, total oxalate, and EDA are compared in Figure 8.44. Amides, it should be noted, were only quantified in the final sample, likely well after the initial quantification due to the development of the amine quantification procedure. The 5 m PZ experiment contained both 0.1 mM Fe^{2+} and 5 mM Cu^{2+} while the 10 m PZ experiment contained only 4 mM Cu^{2+} . The 10 m PZ experiment does not contain any Fe^{2+} but, as will be demonstrated in the next chapter, the catalytic effect of copper far outweighs the presence of 0.1 mM Fe^{2+} so these experiments are approximately comparable (section 9.1.1).

It is expected that an increase in PZ concentration would enhance oxidation and, therefore, enhance the rates of generation of degradation products. The 10 m PZ experiment produces, roughly double the EDA concentration and slightly higher total formate and total oxalate concentrations as the 5 m PZ experiment, but the production of formate is one-third less. The equilibrium between formate and formyl amides has not been well studied in highly oxidized PZ solutions, but higher concentration PZ solutions appear to favor amides over carboxylate ions. This result matches that seen in thermally degraded PZ where the ratio of formyl amides to formate increases with PZ concentration likely due to the increased free PZ concentration (section 6.4.3).

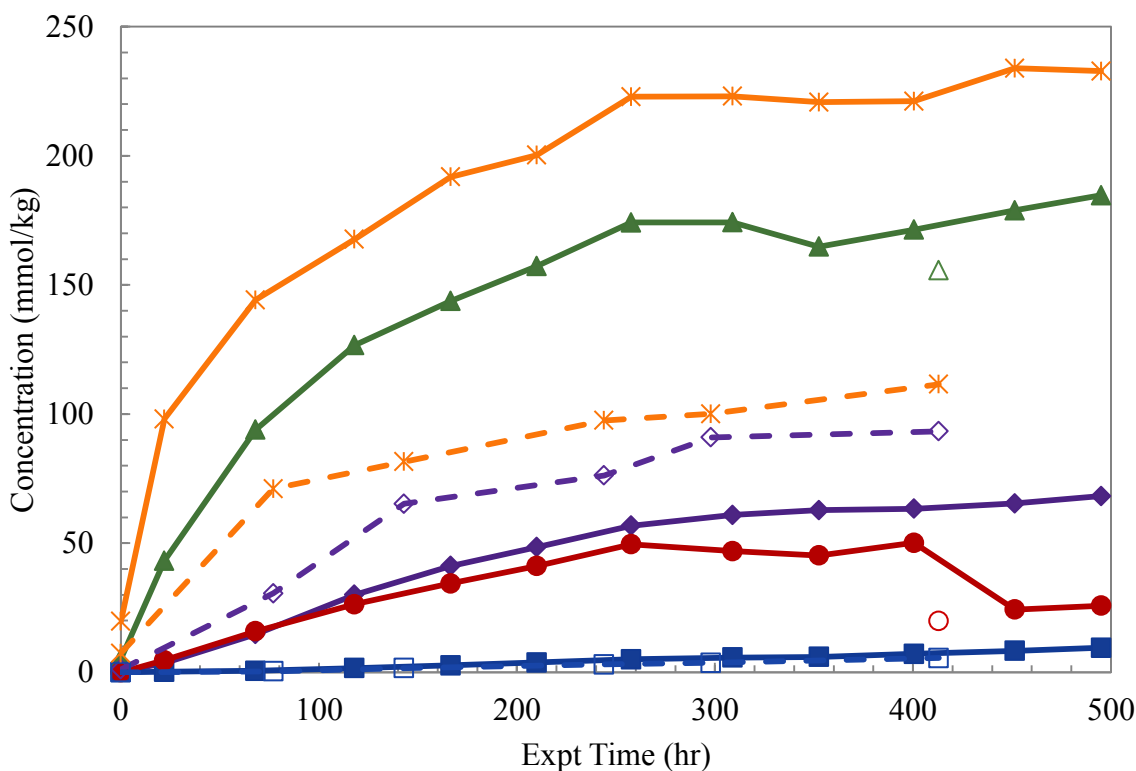


Figure 8.44: Effect of PZ concentration on generation of formate (♦), oxalate (■), total formate (▲), total oxalate (●), and EDA (*) during oxidation of 5 m PZ (open/dashed, (Sexton, 2008)) and 10 m PZ (solid, OE2) (55 °C, 1400 rpm, 100 mL/min 98% O₂/2% CO₂, 4-5 mM Cu²⁺)

A third comparison exploring PZ concentration can be made by evaluating 5 and 8 m PZ oxidation in the presence of Fe^{2+} , Cu^{2+} , and Inhibitor A. As with the previous example, the PZ concentration was not measured in the 5 m PZ experiment, and in this case neither was the total formate, oxalate, or total oxalate. Therefore, the degradation products where data is available are compared for these two experiments in Figure 8.45. In this comparison, the catalyst and inhibitor concentrations were the same at 0.1 mM Fe^{2+} , 5 mM Cu^{2+} , and 100 mM Inhibitor A. Unfortunately, the results are not easily interpreted due to the lack of low concentration data, lack of overall oxidation in PZ systems, and conflicting concentration profiles. The 5 m PZ experiment produced lower concentrations of formate, except in its final point, while it consistently produced more EDA. It was expected that the 8 m PZ experiment would demonstrate enhanced oxidation, but that conclusion cannot be drawn from this data.

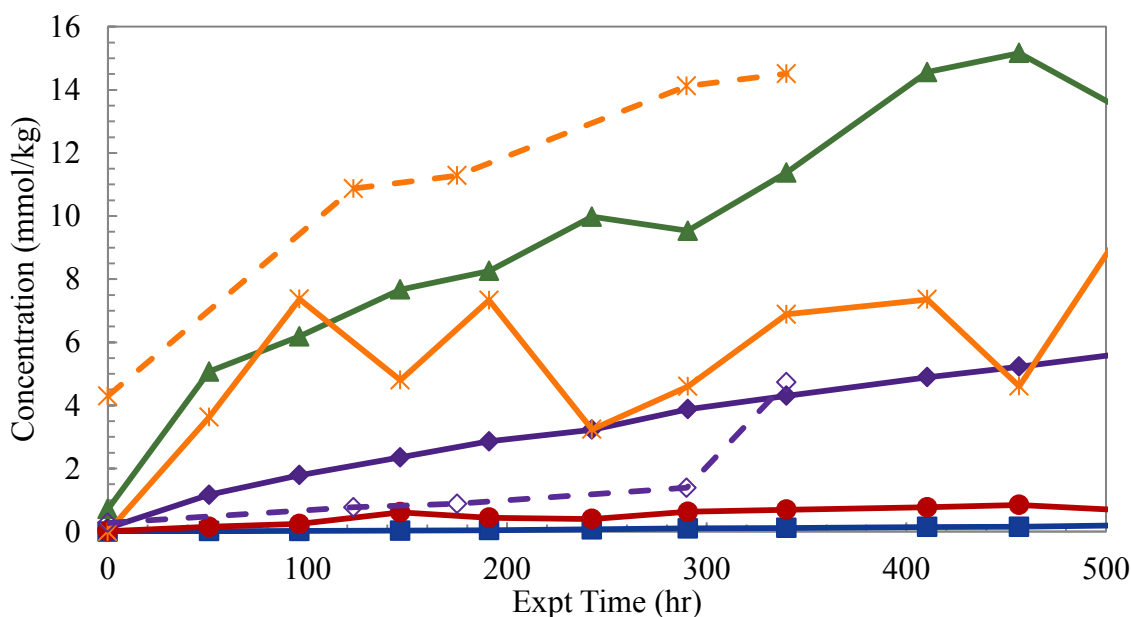


Figure 8.45: Effect of PZ concentration on generation of formate (♦), oxalate (■), total formate (▲), total oxalate (●), and EDA (*) during oxidation of 5 m PZ (open/dashed, (Sexton, 2008)) and 8 m PZ (solid, OE4) (55 °C, 1400 rpm, 100 mL/min 98% O_2 /2% CO_2 , 0.1 mM Fe^{2+} , 5 mM Cu^{2+} , 100 mM Inhibitor A)

8.8 EFFECT OF ADDITIVES

One final variable that was adjusted during this study of PZ oxidation was the use of additives to catalyze degradation, inhibit degradation or attempt to elucidate degradation pathways. The study of catalysts and inhibitors for PZ oxidation is extensively covered in Chapter 9. Other additives investigated are discussed here in terms of the individual goal of the experiment and the eventual outcome.

8.8.1 Addition of formate

An oxidation experiment was performed in the presence of the SSM (0.4 mM Fe^{2+} , 0.1 mM Cr^{3+} , and 0.05 mM Ni^{2+}) and 500 mmole per kg formate at 70 °C with agitation at 1400 rpm and 0.2 mole CO_2 per mole alkalinity. It was hypothesized that formate may be a reaction intermediate or act as an oxidation inhibitor. Previous oxidation results showed a lack of dominant degradation products and it was hypothesized that formate may be generated through oxidation of PZ and then further oxidized to CO_2 , which would not be seen in our typical analysis. If CO_2 was being generated, the loading would not necessarily change because of the agitation and constant influx of CO_2 in the headspace of the reactor. This would explain some of the gap in the C mass balance, if found to be true.

There were three predicted outcomes of this experiment. First, formate might convert to formyl amides and the total formate (500 mmole per kg) would be conserved during the experiment. In this case, the experiment would just test the equilibrium between formate and formyl amides at 70 °C. Second, formate would be oxidized to CO_2 and the total formate concentration would decrease as CO_2 is generated and lost to the headspace of the reactor. Finally, it was suspected that formate may act as an oxidation inhibitor and would also be conserved and decreased the overall PZ loss rate. As a corollary, Sexton tested formate as a potential oxidation inhibitor for 7 m MEA and

found that the addition of 500 mM formate actually accelerated MEA loss by nearly 20% in the presence of 1 mM Fe^{2+} at 55 °C (Sexton, 2008).

The concentrations of PZ, CO_2 , formate, and formyl amides for this oxidation experiment (OE20) are shown below in Figure 8.46. Trace concentrations of acetate, acetyl amides, oxalate, oxalyl amides, nitrite and nitrate were detected but are not shown in the figure. No EDA, glycolate, or glycolyl amides were detected. Over the course of 350 hours, approximately 8.8% of the initial PZ was lost. Formate acted as an inhibitor for the generation of oxidation products.

During the experiment, the overall concentration of formate was essentially conserved at 500 mmole per kg (red (×) data in Figure 8.46). The formate added to the solution at the beginning of the experiment quickly reacted with PZ in solution to form FPZ, even in the initial reactor sample. Since the initial sample was taken a few minutes after the addition of formate, there was already very quick equilibrium between formate and FPZ that manifested as formyl amides being present in the initial sample. The PZ loss is compared to an analogous experiment without formate in Figure 8.47. Outside of the second time point, the PZ loss was slightly decreased in the spiked experiment, although the error in the cation may be larger than the difference observed. This observation may indicate that formate is weak oxidation inhibitor, which is the opposite of the findings of Sexton (2008) who found formate addition accelerated MEA oxidation.

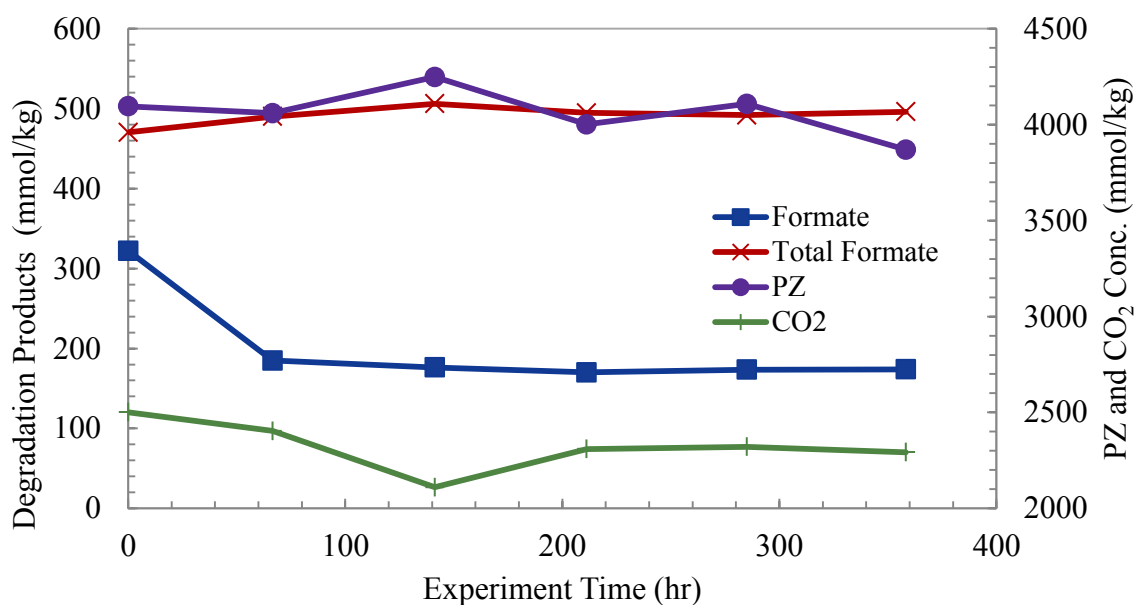


Figure 8.46: Concentration curves for OE20 (8 m PZ, 70 °C, 100 mL/min 98% O₂/2% CO₂, $\alpha=0.3$, SSM, 500 mmol/kg formate)

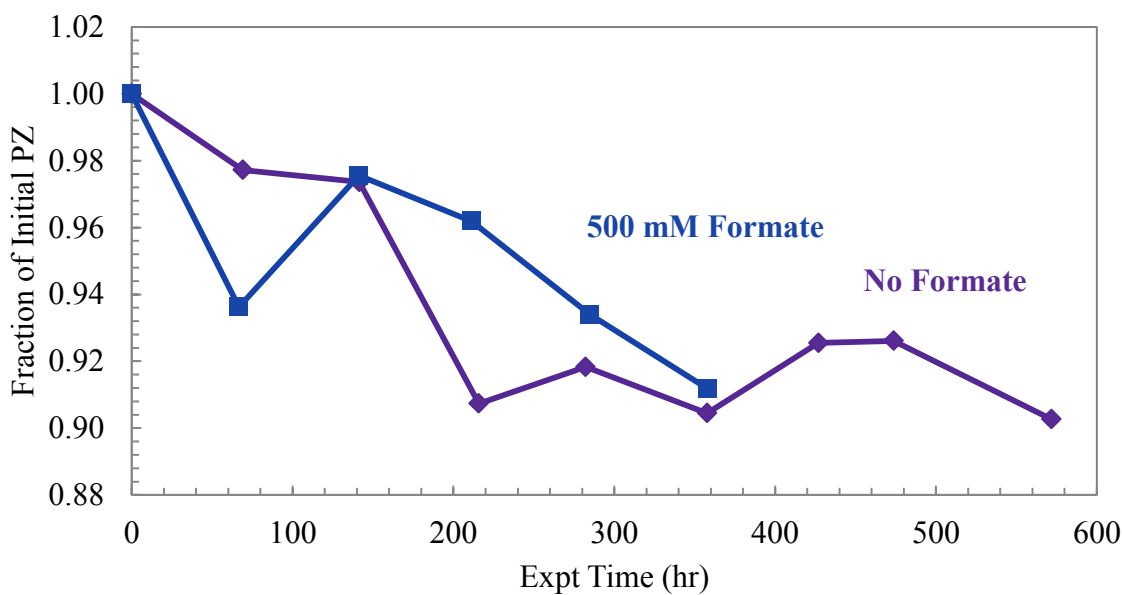


Figure 8.47: Effect of formate addition on PZ loss (8 m PZ, 70 °C, 100 mL/min 98% O₂/2% CO₂, $\alpha=0.3$, SSM,)

8.8.2 Addition of formaldehyde

As a complementary experiment to OE20, an oxidation experiment was performed in the presence of SSM (0.4 mM Fe^{2+} , 0.1 mM Cr^{3+} , and 0.05 mM Ni^{2+}) and 500 mmole per kg formaldehyde at 70 °C with agitation at 1400 rpm and 2% CO_2 (OE21). Formaldehyde was chosen as a spike in an attempt to accelerate oxidation of PZ. This species is suspected to be an important intermediate in the oxidation of PZ and it was hypothesized that the addition of this high concentration would catalyze the PZ degradation. In this way, oxidation could be more easily and confidently quantified. Sexton investigated formaldehyde as a potential oxidation inhibitor for MEA, but found the addition of 500 mM formaldehyde increased MEA loss by nearly 35% in the presence of 1 mM Fe^{2+} at 55 °C (Sexton, 2008). Since PZ is difficult to oxidize, the use of formaldehyde was tested as an accelerant of SSM-catalyzed oxidation.

Unfortunately, the concentration was much too high and generated an operational issue. When it was added, it reacted quickly to form very stable, dense, white foam on the surface of the reactor. This foam persisted even with agitation and the experiment was continued for 5 days to see how the formaldehyde and the foam would affect the results. At the conclusion of the experiment, the experimental solution was transferred to a bottle for storage. The foam persisted for at least 10 months and is shown in Figure 8.48 next to a neat PZ solution without foam

The concentrations of PZ, CO_2 , formate, formyl amides, acetyl amides, oxalyl amides, and FPZ are shown in Figure 8.49 below. No glycolate, acetate, nitrite, or nitrate was found in appreciable quantities. The concentration of FPZ tracks in agreement with that of formyl amides quantified via amide reversal indicating that FPZ is the only formyl amide of appreciable quantity. Two samples were taken at the beginning of the experiment, one before ($t = 0A$) and one after ($t = 0B$) the addition of formaldehyde. The

decrease in PZ between sample 0A and 0B indicates that PZ may have been taken up in the dense white foam that was created from the addition of formaldehyde as only the liquid below the foam was sampled for 0B.



Panel A: Neat loaded PZ solution with SSM



Panel B: OE21 final solution with SSM and stable foam

Figure 8.48: Foam created in OE21 compared with a neat PZ solution

Through the course of the 5 day experiment, 7.8% or 2.3% of the initial PZ was lost if either sample 0A or 0B, respectively, was regarded as the initial sample. FPZ was the only amide produced, which is expected with such a large addition of formaldehyde. The production of formate and total formate in an analogous experiment without formaldehyde addition is compared with this experiment in Figure 8.50. The production of formate and formyl amides was found to be decreased with the large addition of formaldehyde. Initially, the rates are similar for the two experiments but those for the spiked experiment then slow down. This was not expected since formaldehyde has been

assumed to be a very reactive intermediate in the oxidation process, and was expected to rapidly oxidize to formate under the O₂-rich conditions of the reactor.

The presence of the foam complicates the experiment since the concentration of formaldehyde in solution is not actually 500 mM. The exact composition of the foam is not known, but it is probable that it is a polymer of formaldehyde and PZ so the concentration of formaldehyde could be significantly lower than the 500 mM added. The fact that less formate was produced than a comparable solution is still unexpected even with a lower formaldehyde concentration than thought. It was anticipated that any spike of formaldehyde would increase the concentration of formate and formyl amides. The presence of the foam likely limited the amount of O₂ that was successfully absorbed into solution. Even with agitation, the foam was present and likely interfered with the mass transfer of O₂ into solution.

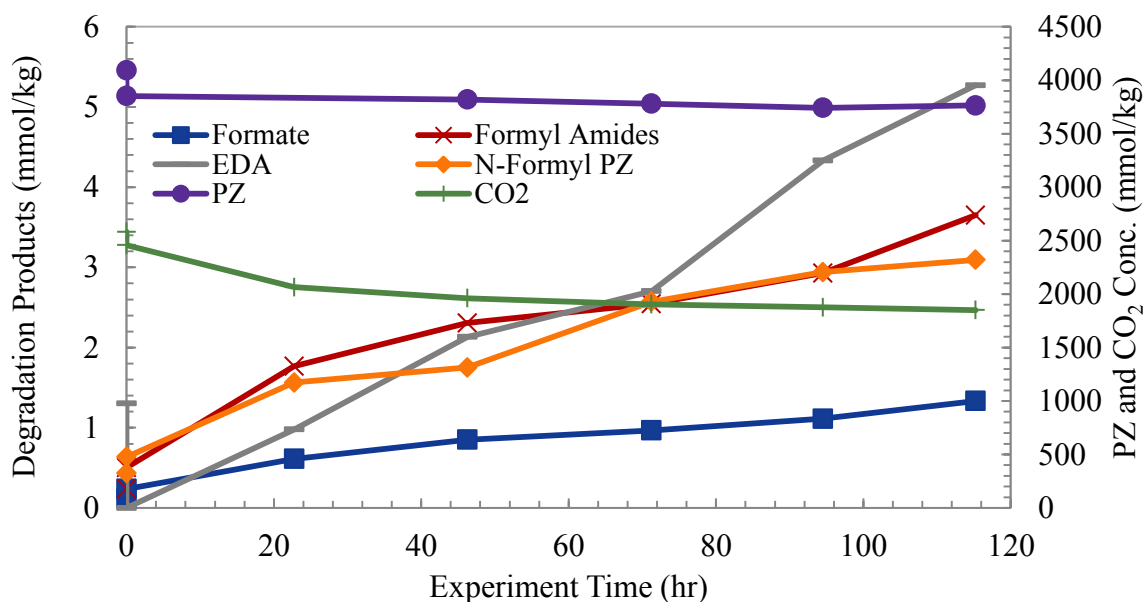


Figure 8.49: Concentration curves for OE21 (8 m PZ, 70 °C, 100 mL/min 98% O₂/2% CO₂, $\alpha=0.3$, SSM, 500 mmol/kg formaldehyde)

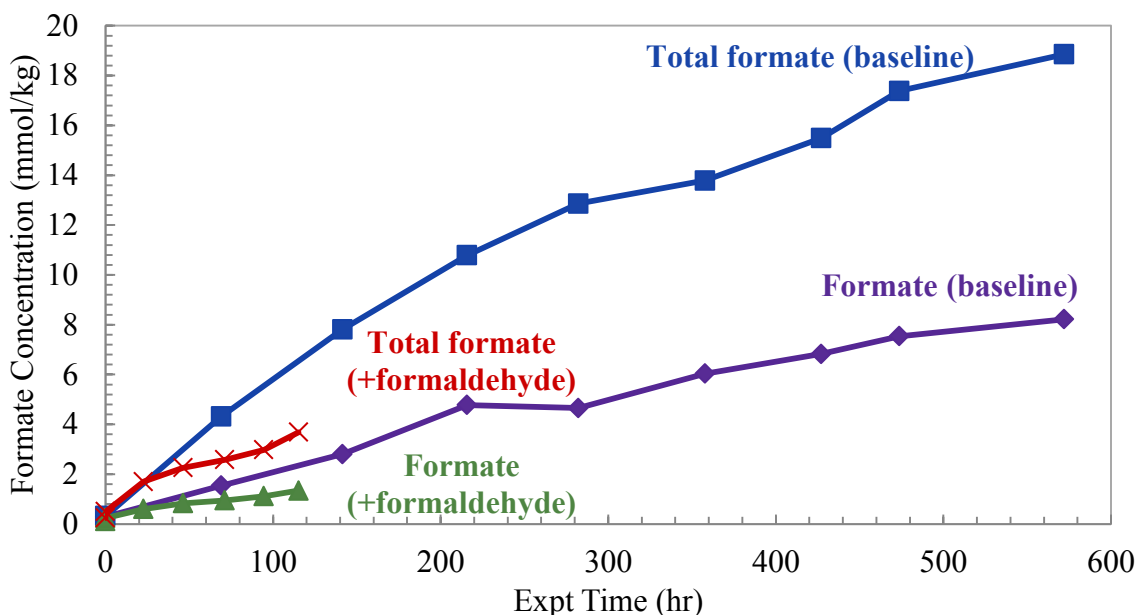


Figure 8.50: Effect of 500 mM formaldehyde addition on formate and formyl amide production (8 m PZ, 70 °C, 100 mL/min 98% O₂/2% CO₂, $\alpha=0.3$, SSM)

8.9 ANALYSIS OF FOAMING IN RELATION TO OXIDATION

Foaming in amine systems can be a significant problem for the effective mass transfer area in the absorber and, to a lesser extent, in the stripper. Previous work has analyzed the extent of foaming in experimental and neat solutions through the measurement of a foaminess coefficient (Chen et al., 2011; Thitakamol and Veawab, 2007). The method used was that of Thitakamol and Veawab (2007) which was adapted from a standard ASTM method to measure foaminess of lubricating oils (ASTM, 2000). The foaminess (F) is defined in Equation 8.12 as the ratio of volume of foam (V_g) to the superficial gas velocity (G). The volume of foam is calculated as the difference between the total steady volume (V_t) and the original liquid volume (V_0).

$$F = \frac{V_t - V_0}{G} = \frac{V_g}{G} \quad (8.12)$$

The foaminess coefficient of solutions has been measured on every PZ oxidation experiment to date, except for a few cases where the solution was not available for testing. A summary of the foaming results for all the oxidation experiments performed during this project are shown in Table 8.9. A neat solution of 8 m PZ was analyzed by Chen and is included as the first entry in the table (Chen et al., 2011). All experiments were performed on 8 m PZ except for OE1 and OE2 which were 10 m PZ. The type of reactor was changed from the OOR to the TOR starting with OE17. Experiments OE1, OE2, OE3, and OE14 were not tested because the solutions were discarded before the apparatus was built or there was no final solution. The foam stability of OE4 was not measured. OE21 was not tested because the addition of 500 mM formaldehyde to the reactor created very stable white foam that persists in the final solution. The total formate at the end of the experiment is included in the table as an indication of the overall level of degradation.

Foaminess results have been used in some cases to make the argument for PZ oxidation where the analysis of products was not conclusive. Unfortunately, the results have been contradictory and all of the foaming results are analyzed to determine the reliability of the measurements for oxidized PZ solutions.

Foaminess to this point has been fairly inconclusive. Earlier researchers have had some success with the comparison of foaming between solutions (Chen et al., 2011). Qualitatively, PZ solutions are frequently difficult to test because the same solution can foam differently on a different day for unknown reasons between the same or different researchers. As evidence of this unknown variability, oxidation experiments performed with the same experimental conditions sometimes have different foaminess coefficients. This is demonstrated in Table 8.9 as OE9 and OE10 are the same experiment but the foaminess ranges from 2.5 to $20 \times 10^{-3} \text{ m}^2\text{-s}$. These two values differ and are also wildly

different from the neat PZ solution value $78.8 \times 10^{-3} \text{ m}^2\text{-s}$. This experiment was a blank solution where a loaded PZ solution was exposed to a gas mixture of 98% N_2 /2% CO_2 at 55 °C for 3 weeks. There should not have been any oxidation with this experiment and the foaminess should have been similar to that of neat, loaded PZ.

As another example of the inconsistency of foaminess as a measure of oxidation, the results from OE15 and OE16 are not conclusive. Inhibitor A has been previously shown to decrease degradation and, therefore, foaming of oxidized PZ solutions (Chen et al., 2011). Thus it was expected that the foaminess coefficient would be lower in OE16 where 10 mM of Inhibitor A was present. The experimental results, however, were opposite with the foaminess coefficient of OE16 being 50% higher than that of OE15 while neither experiment had significant oxidation.

The inconsistencies noticed in the foaming data can be demonstrated further when looking at the four experiments that were degraded only in the presence of Fe^{2+} : OE5, OE5B, OE13, and OE17 under similar conditions. These experiments are highlighted in bold in Table 8.9. The foaminess coefficients for these four experiments are 85, 300, 8, and $17 \times 10^{-3} \text{ m}^2\text{-s}$, respectively, while the foam stability is >600, >600, 8, and 19 seconds, respectively. The experiments have differences such as reactor type and degradation time, but the range in the data is striking and suggests that all the foaming data should be reconsidered. The high foaminess coefficient found for OE5B has been used as a rationale for the hypothesis that PZ is oxidizing while degradation products cannot be found in solution. This assumption is questionable in light of the other foaming results for oxidation, with 1.0 mM Fe^{2+} yielding similar concentrations of total formate (OE5, OE13, and OE17).

Table 8.9: Summary of foaming tests performed on oxidized PZ

Expt.	Expt. Additives ^a	Rxtr. Temp.	Deg. Time	Total Formate	Before Foaming ^c	Foaminess Coefficient ^c	Foam Stability ^c
	mM	°C	hr	mmol/kg	day	10 ⁻³ m ² -s	sec
Neat	-	-	-			78.8-86	29
PP	100 A	-	-			43.8	12
OE1	0.2 Fe, 1.6 Cr, 0.2 Ni	55	606	7.3	NT	NT	NT
OE2	4 Cu	55	495	184.7	NT	NT	NT
OE3	0.1 Fe, 0.1 V	55	381	10.5	NT	NT	NT
OE4	1 Fe, 5 Cu, 100 A	55	742	20.5	195	300	NT
OE5	1 Fe	55	70	2.4	1	85	>600
OE5B	1 Fe	55	163	2.1	0	300	>600
OE6	1 Fe, 100A	55	70	1.3	1	92	>600
OE6B	1 Fe, 100A	55	163	1.4	0	68	>600
OE7	30 B	55	164	0.6	1	380	>600
OE8	30 C	55	168	18.4	1	88	>600
OE9	-	55	336	2.5	283	3	10
OE10	-	55	336	4.7	207	20	40
OE11	-	55	314	2.4	198	11	37
OE12	-	55	296	1.8	225	18	19
OE13	1 Fe	55	523	3.7	112	8	18
OE14	1 Fe, 100A	55	381	3.6	NT	NT	NT
OE15	0.4 Fe, 0.1 Cr, 0.05 Ni	55	427	4.8	82	10	22
OE16	0.4 Fe, 0.1 Cr, 0.05 Ni, 10 A	55	427	1.3	82	16	25
OE17	1 Fe	55	424	3.4	156	17	19
OE18	0.4 Fe, 0.1 Cr, 0.05 Ni	55	576	4.3	49	117	45
OE19	0.4 Fe, 0.1 Cr, 0.05 Ni	70	572	18.9	11	195	35
OE20	0.4 Fe, 0.1 Cr, 0.05 Ni, 500 Formate	70	358	NA ^b	1	110	140
OE21	0.4 Fe, 0.1 Cr, 0.05 Ni, 500 Formaldehyde	70	115	3.7	NT	NT	NT
OE22	0.4 Fe, 0.1 Cr, 0.05 Ni	70	575	3.0	32	26.25	85

^a Abbreviations: Fe is Fe²⁺, Cr is Cr³⁺, Ni is Ni²⁺, Cu is Cu⁺, V is V⁵⁺, A is Inhibitor A, B is Inhibitor B, C is Inhibitor C.

^b NA = Not applicable since formate was an additive

^c NT = not tested

The difficulty of understanding the oxidation of PZ has been discussed in regards to the lack of detectable degradation products. Only formate, total formate, and

occasionally EDA are present most oxidized solutions. It has been hypothesized separately that either the total formate concentration or foaminess of a solution should represent the overall PZ oxidation rate in lieu of accurately quantifying PZ loss during the experiment. The foaminess coefficient is plotted against the total formate concentration at the end of the experiment in Figure 8.51 below. The experiments with the same additives have been indicated using different colored data points. The experiments with 1.0 mM Fe^{2+} have blue squares while those with 0.4 mM Fe^{2+} , 0.1 mM Cr^{3+} , and 0.05 mM Ni^{2+} are indicated with green triangles. The inconsistency of the data can easily be seen in this figure.

Unfortunately, there is not a dependable relationship between the two variables and this inconsistency indicates that both cannot represent PZ oxidation as a whole. The three experiments with the highest concentrations of total formate (OE4, OE8, and OE19) have foaminess coefficients ranging from 88 to $300 \times 10^{-3} \text{ m}^2\text{-s}$. However, what does not seem to make sense is that two of the experiments with the highest foaminess coefficients (OE5B and OE7) have very low total formate concentrations of 2.4 and 0.6 mmole per kg, respectively, at the end of each experiment. The four experiments with 1.0 mM Fe^{2+} (blue squares) have a wide range of foaminess coefficients with consistent levels of total formate at the end of the experiment.

The stability or shelf-life of oxidized PZ solutions after the conclusion of an experiment was a primary concern considering the conflicting foaminess data. To analyze this, the number of days between the end of the oxidation experiment and the foaminess test was calculated for all the foaming tests performed. The number of days between the experiment end and the test are plotted against the foaminess coefficient in Figure 8.52.

With the exception of the data from OE4 (195 days, $300 \times 10^{-3} \text{ m}^2\text{-s}$), there is a correlation between the number of days and the overall foaminess coefficient. No measurements past 60 days resulted in foaminess coefficients of more than $25 \times 10^{-3} \text{ m}^2\text{-s}$, except OE4. This suggests that the contaminants or degradation products in solution that cause foaming during the foaming tests continue to react while on the shelf and can greatly affect test results. If this is the case, there is significant error in the foaminess test since the protocol does not require the test be performed consistently. Comparing the number of days between the experiment end and the foaming test as a function of the foam stability also produces a very clear correlation (Figure 8.53). High foam stability values cannot be achieved with longer wait times. It is important to note that the foam stability was not measured for OE4.

The measurement of foaminess coefficient is not a reliable or consistent analytical technique. It varies widely for similar solutions and any conclusions taken from foaminess data should be considered qualitative at best. Since the degradation products that are responsible for foaming have not been determined, it is not known which variables in these experiments most affect the measured foaminess coefficient. At this point, the time between the experiment end and the measurement has the most impact on the results.

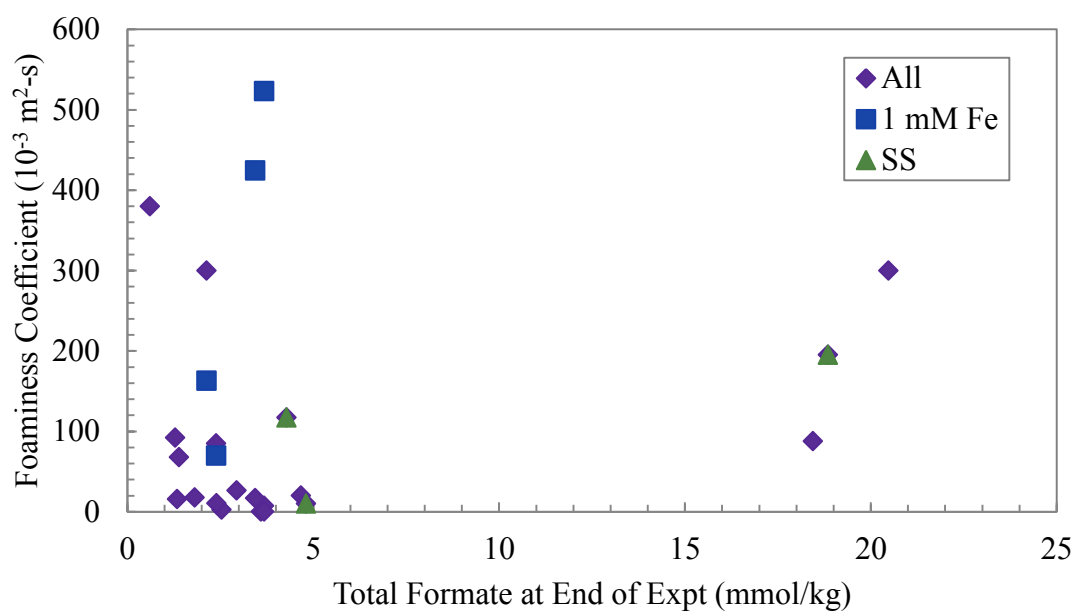


Figure 8.51: Relationship between the foaminess coefficient and total formate production

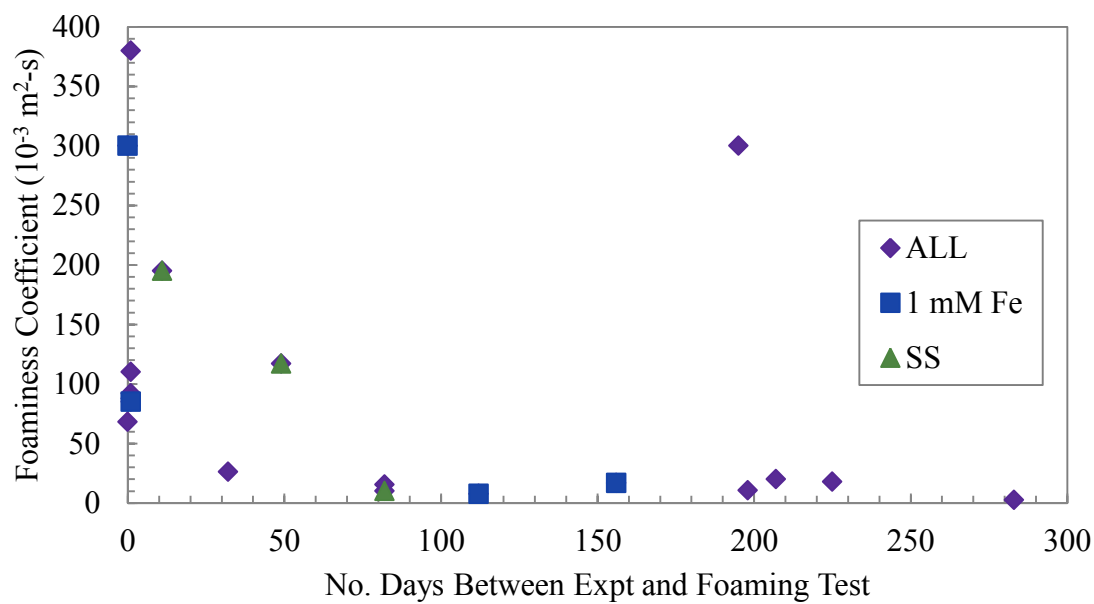


Figure 8.52: Relationship of foaminess coefficient and the delay in measurement

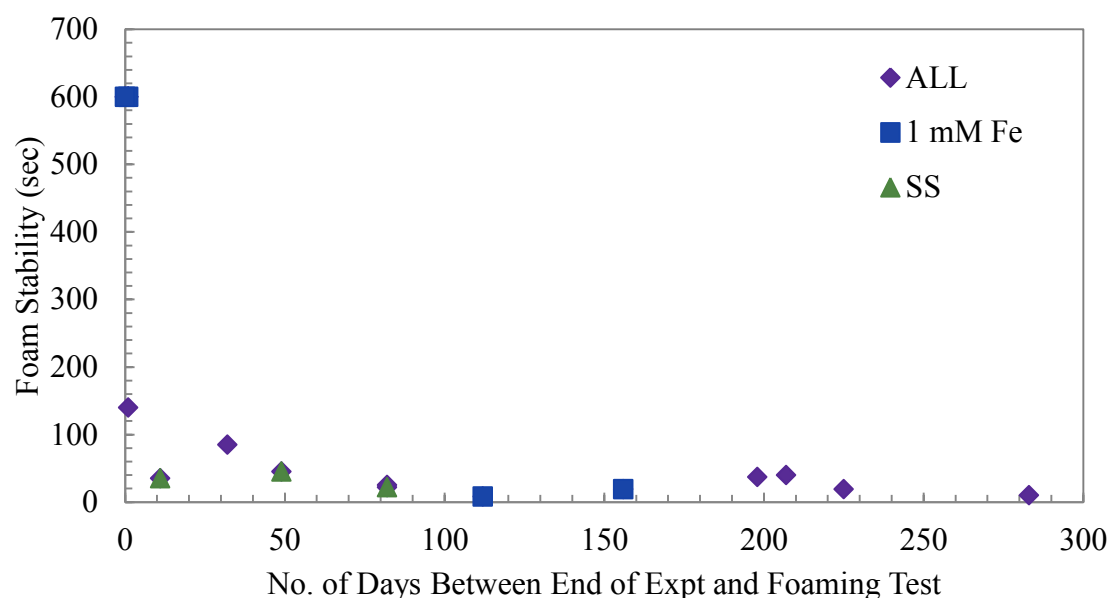


Figure 8.53: Relationship of foam stability and the delay in measurement

8.11 CONCLUSIONS

Oxidation of concentrated PZ from 55 to 70 °C in the presence of Cu^{2+} was found to be consistent with a mechanism that is first order in O_2 partial pressure. A 245% increase in O_2 partial pressure from 40 to 98 kPa enhanced PZ loss by 240% at 55 °C. The production of formate, total formate, and EDA increased by 180, 340, and 370%, respectively, for the same increase in O_2 partial pressure. At 70 °C in the presence of Cu^{2+} , PZ loss was enhanced 206% with a 235% increase in O_2 partial pressure. This data indicates a first order dependence of PZ oxidation on O_2 . In the presence of SSM, the oxidation rate was too slow to see a large change in PZ loss, but the generation rate of degradation products increased with higher O_2 partial pressures, consistent with the Cu^{2+} experiments.

In Cu^{2+} -catalyzed systems, an increase in reactor temperature from 55 to 70 °C increased the PZ loss rate by 230%. A change of 15 °C in reactor temperature, therefore,

has the same effect as an increase in O₂ content by 245% in Cu²⁺-catalyzed systems. At the same time, the production of formate, total formate, and EDA increased by 270, 340, and 170%, respectively. The activation energy for PZ loss in this temperature range was determined to be 27.2 kJ per mole in Cu²⁺-catalyzed systems. This low activation energy indicates the propensity of PZ to degrade in the presence of Cu²⁺. Activation energies for the generation of formate, total formate, and EDA were calculated to be 47, 29, and 36 kJ per mole, respectively, in the presence of Cu²⁺. Since the activation energy for formate generation is higher than that of total formate, it is likely that formate generation is an oxidation mechanism while the formation of amides is dependent on formate concentration, rather than oxidation directly.

In SSM-catalyzed systems, an increase of 15 °C, from 55 to 70 °C, produced a small but noticeable increase in PZ loss. The activation energy for PZ loss in SSM-catalyzed systems was determined to be 96 kJ per mole, 3.5 times higher than in the presence of Cu²⁺. Activation energies for the generation of formate, total formate, and EDA were calculated to be 50, 48, and 96 kJ per mole, respectively, in the presence of SSM.

The activation energy for the generation of formate is approximately the same in the presence of Cu²⁺ and SSM at 47-49 kJ per mole. The oxidation mechanism that is responsible for formate may not be dependent on the catalyst type. Formate is likely the most representative product to indicate oxidation when PZ data is unreliable.

CO₂ concentration was found to have a weak effect on PZ oxidation compared to O₂ and temperature. A decrease from 0.3 to 0.2 mole CO₂ per mole alkalinity produced a decreased PZ loss rate, but enhanced rate of generation of formate and total formate. Data with a high loading (0.4 mole CO₂ per mole alkalinity) demonstrated counteractive effect of low O₂ partial pressure and was not conclusive.

PZ concentration was also found to have only a weak effect on PZ oxidation from 5 to 10 m PZ. Higher concentration PZ was found to preferentially produce amides over the corresponding free carboxylate ion, matching observations in thermally degraded PZ experiments. The effect of PZ concentration is small compared to that of O₂ and temperature.

Baseline oxidation experiments performed in the absence of metal catalysts experienced 2 to 7% PZ loss over 350 hours, representing the PZ loss due to overall experimental error. Tracers were not effective at maintaining the water balance in the reactor.

The identified oxidation products of PZ include EDA, carboxylate ions (formate, oxalate, acetate), amides (formyl amides, oxalyl amides, and acetyl amides of PZ, EDA, and ammonia), and ammonium (NH₄⁺). Glycolate, nitrite and nitrate are minor products that were inconsistently generated. In highly oxidized solutions, unidentified peaks on both anion IC and cation IC have been classified as either monoamines, polyamines, and amides, but are significantly smaller in area to the primary degradation products.

Analysis of TOC and TN indicated the presence of unidentified liquid phase degradation products. Both a baseline experiment and a heavily oxidized solution in the presence of Cu²⁺ were found to have maintained the TOC concentration in the liquid phase during the experiment, indicating unquantified liquid phase oxidation products. Both experiments also experienced a quantifiable decrease in TN concentration, indicating the loss of volatile N compounds not containing C. Ammonia (NH₃) has been confirmed as one volatile product while NO_x species are also suspected.

N and C mass balances on oxidized solutions were poor, especially with low rates of oxidation. In OE11, a baseline experiment, only 2.5% and 1.7% of the N and C, respectively, lost as PZ was recovered. Inclusion of an estimate of the volatile N from

the TN analysis increased the N balance to 75% of the lost PZ. For OE18, an experiment with SSM, only 3.4% and 5.2% of the N and C lost as PZ was recovered in products. In OE25, the most heavily oxidized PZ solution in the study, 27% and 23% of the N and C, respectively, from the lost PZ was recovered as liquid phase products. With the inclusion of an estimate of 2650 mmole volatile N per kg from TN, 69% of the lost PZ N was recovered.

A combination of the mass balance and TOC results suggest a significant concentration of degradation products that have not been identified in the liquid phase. More sophisticated liquid phase analyses are needed to identify the important oxidation products of concentrated PZ. Amino acid detection indicates that this may be an important function group in oxidation products, but no amino acids were identified. It is suspected that aldehydes (e.g. formaldehyde, acetaldehyde, and hydroxyacetaldehyde), alcohols (e.g. methanol, ethanol, and, ethylene glycol), ureas of PZ, amino acids (e.g. N-(2-aminoethyl) glycine, N,N'-1,2-ethanediylbis-glycine), and oxidized PZ molecules (2-piperazinone, 2,5-piperazinedione, 2-piperazinol, 1,2,3,6-tetrahydro pyrazine, 1,2,3,4,-tetrahydro pyrazine, 1-piperazineaceticacid) are a significant portion of the unidentified products.

The addition of 500 mM formate to 8 m PZ eliminated the production of EDA, suggesting that PZ oxidation was significantly decreased. However, the change in the loss rate of PZ was small and possibly not statistically significant. Formate is not oxidized to CO₂ in PZ oxidation experiments but may act as a weak oxidation inhibitor for PZ.

The addition of 500 mM formaldehyde to 8 m PZ created stable, dense, white foam that persisted through the oxidation experiment. The foam is likely a polymer of formaldehyde and PZ that was stable for over 10 months.

The foaminess coefficient is not a consistent measurement technique and does not produce repeatable results. The amount of time between the end of an experiment and the foaminess test appears to impact results, which is an unforeseen problem in the assay. The foaminess coefficient also does not accurately represent the overall degradation of an oxidized PZ solution.

Chapter 9 – Catalysts and Inhibitors for the Oxidation of Concentrated, Aqueous PZ

The oxidation of concentrated PZ systems can be greatly affected by the presence of metal catalysts or inhibitors. Metal catalysts are likely to be present in industrial CO₂ capture systems due to corrosion of the materials of construction, presence of metals in industrial chemicals, and through the use of inhibitors or other additives. This chapter explores the catalytic effect iron (II) (Fe²⁺), copper (II) (Cu²⁺), a combination of Fe²⁺, chromium (III) (Cr³⁺), nickel (II) (Ni²⁺), and a combination of Fe²⁺ and vanadium (V) (V⁵⁺). Three inhibitors are investigated to determine their efficacy at decreasing metal-catalyzed oxidation. Portions of this chapter are excerpted from a previous publication relating to PZ oxidation (Freeman et al., 2010a).

9.1 METAL CATALYSTS FOR OXIDATION OF PIPERAZINE

Metal catalysts are known to enhance oxidation rates of amines in the presence of elemental oxygen (O_2) (Goff, 2005; Sexton, 2008). The effect of metal catalysts on the oxidation of PZ has only been studied to a small degree by Sexton. Sexton focused on low concentration solutions, always below 5 molal (m) PZ (Sexton, 2008). The work in this section focuses on metal catalysis of oxidation of 8 m PZ.

The discussion of catalytic impact of metals will rely on comparisons to the four baseline experiments discussed in section 8.2.1. These experiments in the absence of metal catalysts or inhibitors represent the range of expected experimental error over the course of a typical experiment. Any loss of PZ in a catalyzed experiment that is close the level shown in the baseline experiments indicates a weak catalyst for PZ oxidation or data that should be interpreted with caution. Strong catalysts and conditions will demonstrate PZ losses that are noticeably faster than the baseline experiments. Differences in experiments in terms of O_2 concentration, CO_2 concentration, and PZ concentration will be noted, but the data will be plotted together for efficiency. Only experiments with differences in metal catalyst and temperature will be presented separately in this chapter.

9.1.1 Effect of iron (Fe^{2+})

In industrial CO_2 capture systems constructed of carbon steel, aqueous iron or iron particulates are expected to be present in amine solutions due to corrosion of the columns, column internals, storage tanks, and piping. If carbon steel is to be used for PZ-based CO_2 capture systems, the catalytic effect of aqueous iron on the oxidation of PZ needs to be understood in order to mitigate the effect, if possible. This concentration of iron was based on concentrations observed to accumulate in commercial acid gas treating systems lacking a corrosion inhibitor. Reports of CO_2 capture systems in service without corrosion inhibition using a variety of amines, typically alkanolamines such as

monoethanolamine (MEA) or diethanolamine (DEA), have reported concentrations up to 6000 ppm iron (Hall and Barron, 1981; Holub et al., 1998). Sexton had previously studied lower concentration PZ oxidation found that Fe^{2+} -catalyzed oxidation of PZ was very slow compared to 7 m MEA (Sexton, 2008). Sexton also observed no difference in oxidation when the Fe^{2+} was varied from 0.1 to 5 mM.

To simulate the effects of carbon steel corrosion, 8 m PZ was oxidized in the presence of 1 mM Fe^{2+} . Three experiments, OE4, OE13, and OE17, were performed on 8 m PZ in the presence of 1 mM Fe^{2+} at 55 °C with agitation at 1400 rpm and 100 mL per minute of 98% O_2 /2% CO_2 in the headspace. The PZ loss data from these three experiments are compared to the baseline experiments in Figure 9.1. Sexton performed an experiment in 5 m PZ with 5 mM Fe^{2+} under similar reactor conditions in an attempt to maximize Fe^{2+} -catalytic impact and these data are compared as well.

Initially, the PZ loss rates in all four experiments appear to be faster than the baseline experiments. After 100 hours, however, the data for the high Fe^{2+} experiment becomes more scattered and the final points recover the initial PZ concentration. The remaining three experiments demonstrate some disagreement but all oxidize faster than the baseline experiment. After 160 hours, the loss of PZ ranges from 7 to 14%, above the baseline cases ranging from 1 to 5%. There is a significant level of scatter in the high Fe^{2+} data, but the high level of Fe^{2+} does not enhance oxidation above the levels seen in the 1 mM experiments.

The production of total formate and ethylenediamine (EDA) are compared for the same four experiments and four baseline experiments in Figure 9.2 and Figure 9.3, respectively. The productions of both of these major degradation products are close to the four baseline experiments and do not demonstrate repeatability. There is significant scatter in the total formate data for OE5 and the high Fe^{2+} experiment. The other two

experiments have the expected trend, but are not statistically significant compared to the baseline experiments. EDA, which is difficult to quantify accurately at low concentrations, was detected in all four experiments, but not consistently or at levels above the baseline experiments.

Overall, Fe^{2+} appears to be only a very weak catalyst for PZ oxidation, even up to 5 mM Fe^{2+} , based on PZ loss. The generation of degradation products is not consistent between experiments and is within the concentrations produced in the baseline experiments. Fe^{2+} may catalyze PZ oxidation to a small extent, but no more than a 7% loss of PZ after 300 hours as found in the baseline experiments.

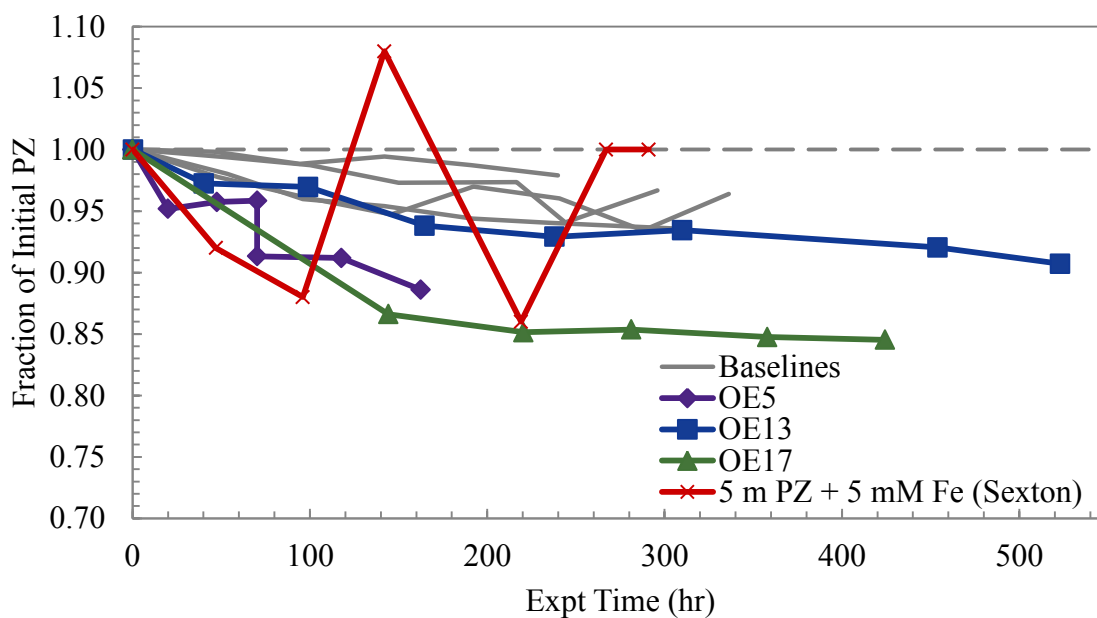


Figure 9.1: Catalytic effect of Fe^{2+} on PZ Loss (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O_2 /2% CO_2 , 1 or 5 mM ($\times$) Fe^{2+})

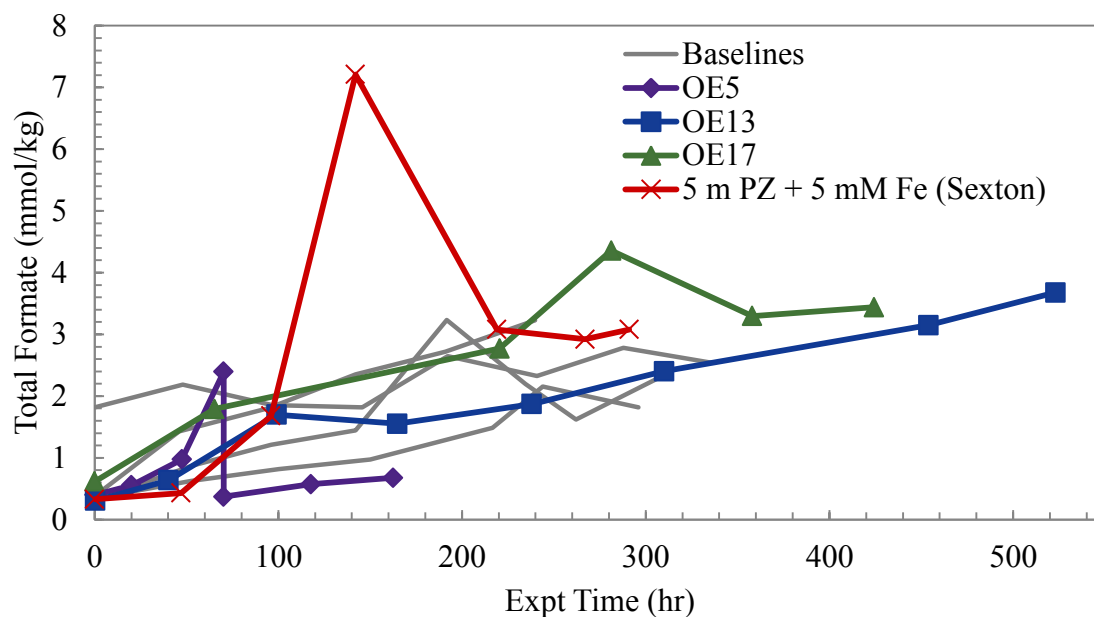


Figure 9.2: Production of total formate in the presence of 1 or 5 mM ($\times$) Fe^{2+} (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O_2 /2% CO_2)

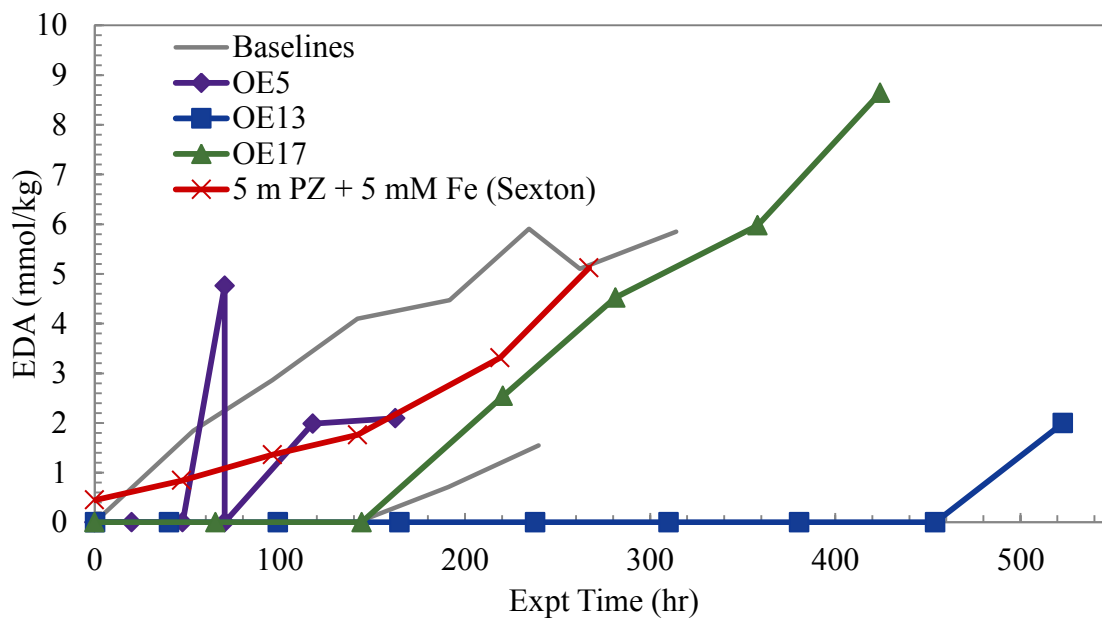


Figure 9.3: Production of EDA in the presence of 1 or 5 mM ($\times$) Fe^{2+} (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O_2 /2% CO_2)

9.1.2 Effect of stainless steel metals (Fe^{2+} , Cr^{3+} , and Ni^{2+})

Stainless steel will more likely be used as the material of construction for absorber-stripper systems due to its enhanced resistivity to corrosion. If any corrosion does occur, low concentrations of Fe^{2+} , Cr^{3+} , and Ni^{2+} can exist as aqueous species in amine solutions. To simulate the catalytic effect of stainless steel metals, concentrated PZ was oxidized in the presence of 0.4 mM Fe^{2+} , 0.1 mM Cr^{3+} , and 0.05 mM Ni^{2+} , also known as the standard stainless steel metal (SSM) mixture. This combination was determined to be representative of the expected concentrations of each species and relative concentrations to each other in a stainless steel system without corrosion inhibitors. This concentration mixture was maintained for all of the experiments containing SSM, with one exception. In the first oxidation experiment, 10 m PZ was oxidized in the presence of 0.26 mM Fe^{2+} , 1.6 mM Cr^{3+} , and 0.26 mM Ni^{2+} before the standard SSM mixture was developed.

9.1.2.1 Effect of stainless steel metals at 55 °C

In total, four concentrated PZ experiment were performed in the presence of SSM at 55 °C. Three experiments, OE15, OE18, and OE18, were performed on 8 m PZ with the standard SSM mixture, while a fourth, OE1, was a 10 m PZ experiment with varied concentrations of metals, as described above. The PZ loss for these four experiments is compared to the four baseline experiments in Figure 9.4. The 10 m PZ experiment is indicated in the figure to highlight the difference in PZ and metals concentrations. The experiments with 8 m PZ and the SSM mixture demonstrated PZ loss data well within the range of the four baseline experiments and appear to demonstrate a small level of oxidation inhibition. The 10 m PZ experiment demonstrated slightly enhanced PZ loss after 300 hours of oxidation that was statistically significant above the baseline experiments.

The generation of total formate and EDA for the four experiments and four baseline experiments is compared in Figure 9.5 and Figure 9.6, respectively. As was expected after analyzing the PZ loss, the generation rate of total formate and EDA in all four experiments is low and falls within the boundaries established by the baseline experiments. The generation of products at similar levels as the baseline indicates there is not inhibition, but very low rates of oxidation. Overall, the SSM are a weak catalyst for PZ oxidation when examined in terms of both PZ loss and the generation of degradation products. As with Fe^{2+} -catalysis, SSM may catalyze PZ oxidation to some extent, but no more than the baseline 7% loss of PZ after 300 hours as found in the baseline experiments.

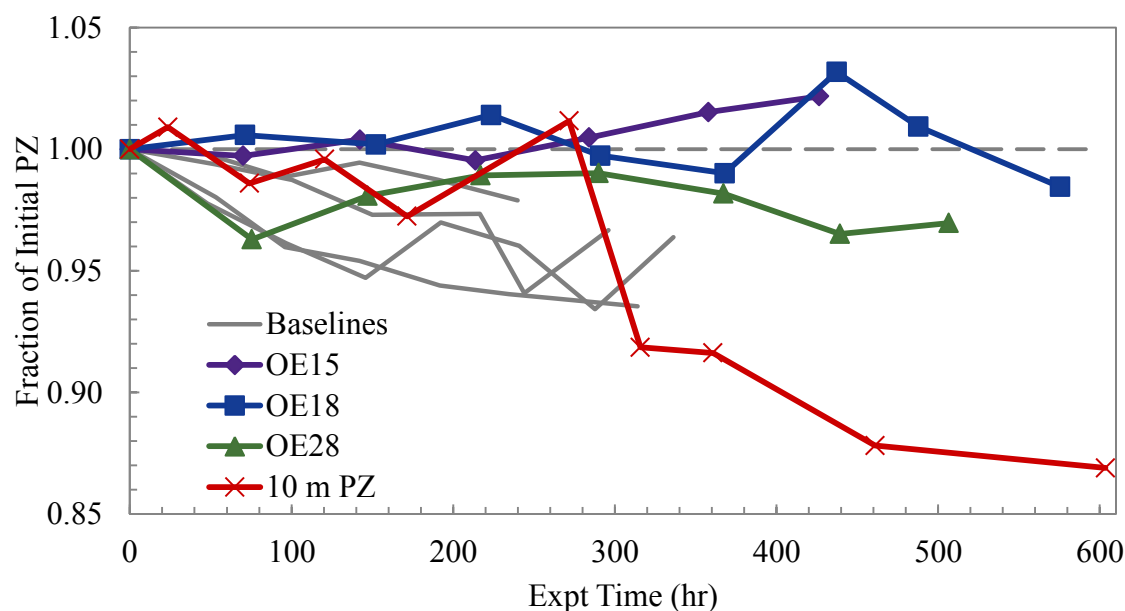


Figure 9.4: Catalytic effect of SSM on PZ Loss (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O_2 /2% CO_2 , 0.4 mM Fe^{2+} , 0.1 mM Cr^{3+} , 0.05 mM Ni^{2+})

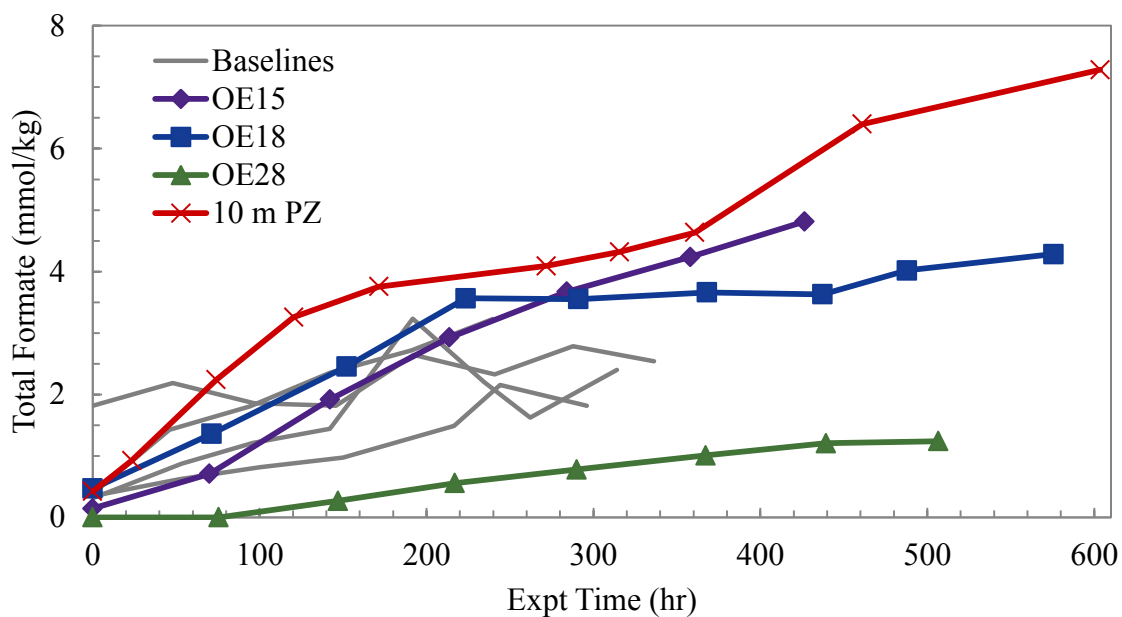


Figure 9.5: Production of total formate in the presence of SSM (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O₂/2% CO₂, 0.4 mM Fe²⁺, 0.1 mM Cr³⁺, 0.05 mM Ni²⁺)

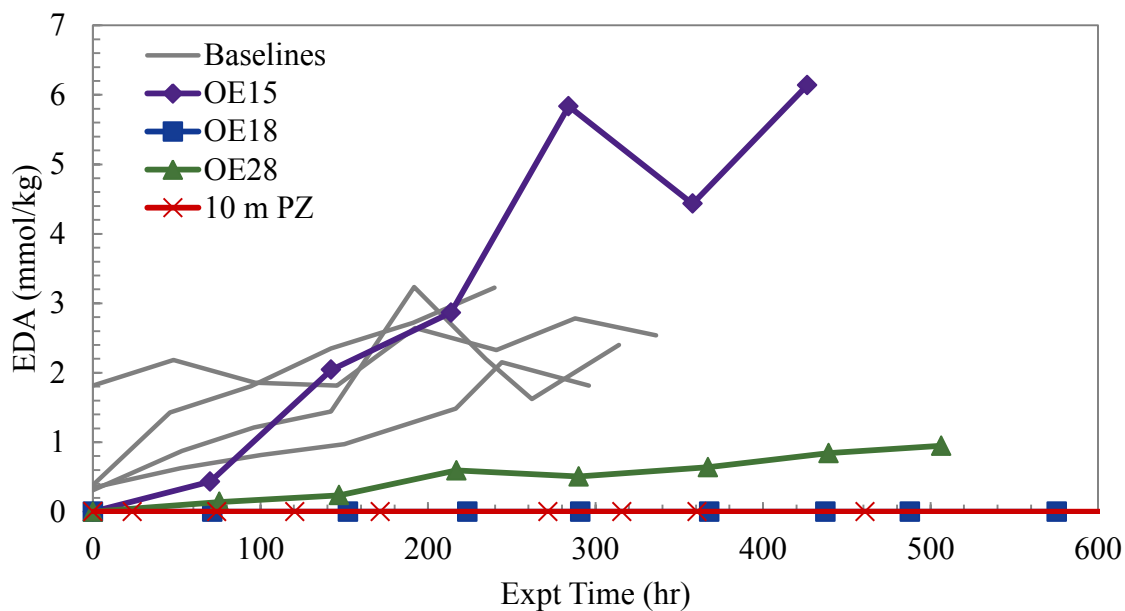


Figure 9.6: Production of EDA in the presence of SSM (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O₂/2% CO₂, 0.4 mM Fe²⁺, 0.1 mM Cr³⁺, 0.05 mM Ni²⁺)

9.1.2.2 Effect of stainless steel metals at 70 °C

The catalytic effect of stainless steel metals was also investigated at the higher temperature of 70 °C. High temperature experiments were performed in order to accelerate degradation in order to analyze PZ oxidation more accurately. Unfortunately, no baseline experiments were performed at 70 °C, so it is not possible to understand if there are any mechanistic differences in the reactor operation or water balance due to the increased temperature. Since the water and amine volatility will increase at 70 °C, the water balance will be strongly affected due to increased water losses. The water balances were carefully monitored for high temperature experiments and the water added to the pre-saturator was also monitored starting with OE19, the first high temperature experiment. This was done in an effort to maintain the water balance as closely as possible.

In total, three concentrated PZ experiment, OE19, OE22, and OE26, were performed in the presence of the standard stainless steel metal mixture at 70 °C. PZ loss for these three experiments is compared to the four baseline experiments at 55 °C in Figure 9.7. Unfortunately, the three experiments do not demonstrate a high degree of repeatability in terms of the PZ loss data. Both OE22 and OE26 demonstrate PZ loss that is slightly more than that observed in the baseline experiments, indicating that the presence of SSM at 70 °C may enhance PZ oxidation rates above the baseline noise of the experiment, while OE19 falls within the range of the baselines. OE22 had a lower O₂ content (40%) than the other two experiments (96-98%), but the PZ loss data shows that OE19 had the lowest loss rate of PZ.

The generation of total formate and EDA for the four experiments and four baseline experiments are compared in Figure 9.8 and Figure 9.9, respectively. The total formate and EDA data have opposite trends as those seen in the PZ loss data for

experiments OE19 and OE22. For OE22, where PZ loss up to 10% was observed, the total formate concentration is within the noise of the baselines. For OE19, which did not have significant PZ loss, the highest concentration of both products was observed. Overall, SSM are not a strong catalyst for concentrated PZ oxidation, even at the elevated temperature of 70 °C. There is some evidence that at this temperature, oxidation is starting to be accelerated, but more data at even higher temperatures would be needed to fully confirm this observation. The loss of PZ in this condition is at most 10% of the initial PZ after 400 hours.

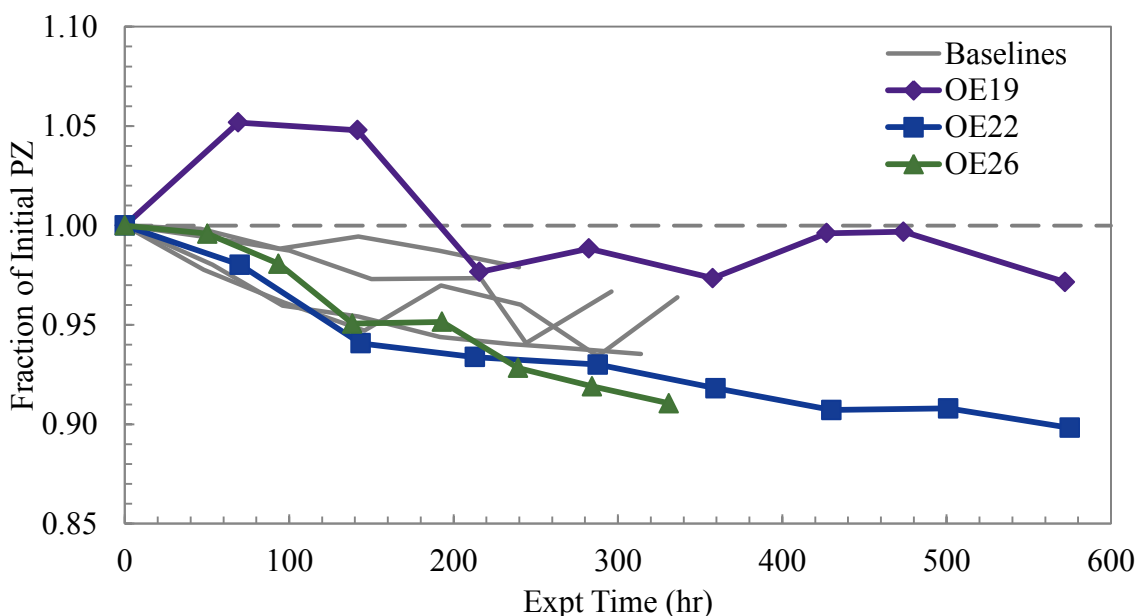


Figure 9.7: Catalytic effect of SSM on PZ Loss (8 m PZ, 70 °C, 1400 rpm, 100 mL/min 40-98% O₂/2-6% CO₂, 0.4 mM Fe²⁺, 0.1 mM Cr³⁺, 0.05 mM Ni²⁺)

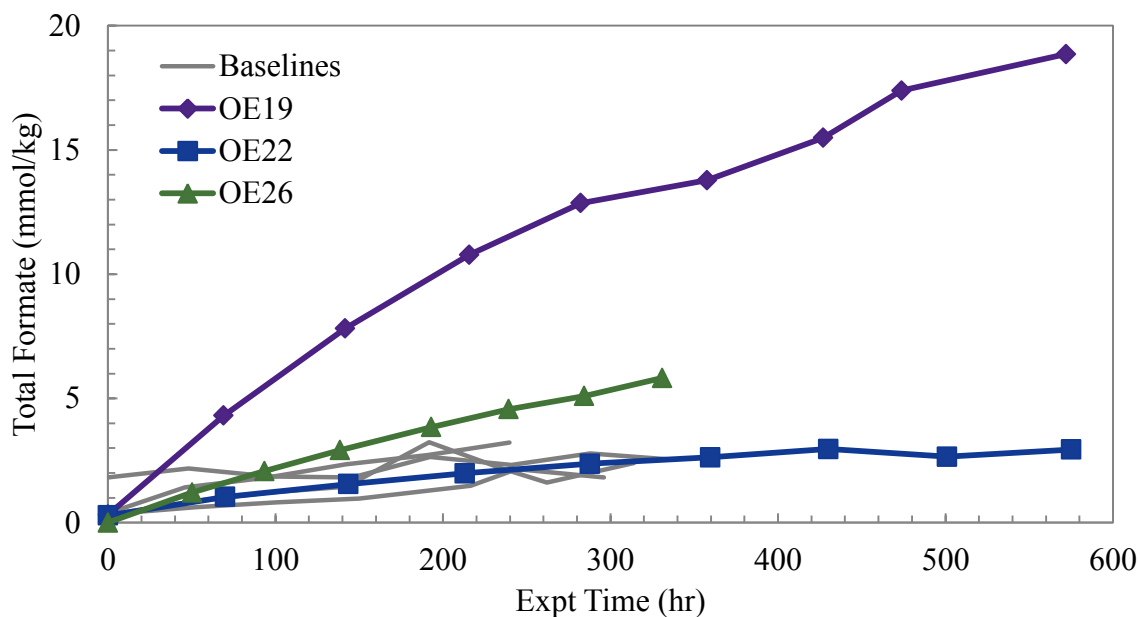


Figure 9.8: Production of total formate in the presence of SSM (8 m PZ, 70 °C, 1400 rpm, 100 mL/min 40-98% O₂/2-6% CO₂, 0.4 mM Fe²⁺, 0.1 mM Cr³⁺, 0.05 mM Ni²⁺)

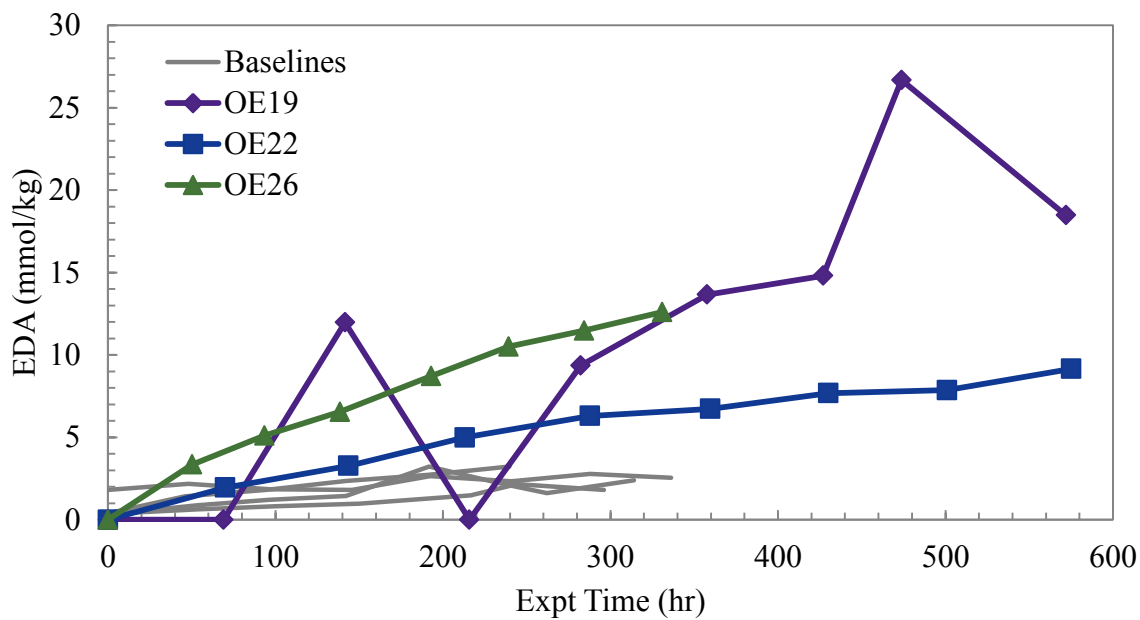


Figure 9.9: Production of EDA in the presence of SSM (8 m PZ, 70 °C, 1400 rpm, 100 mL/min 40-98% O₂/2-6% CO₂, 0.4 mM Fe²⁺, 0.1 mM Cr³⁺, 0.05 mM Ni²⁺)

9.1.3 Effect of copper (Cu^{2+})

Copper salts have been used as a corrosion inhibitor in industrial gas treating systems and are also a well-known catalyst for amine degradation. To determine the extent of copper-catalyzed oxidation, 8 m PZ was degraded in the presence of 4.0 mM Cu^{2+} , or roughly 250 ppm Cu^{2+} . This concentration of Cu^{2+} was chosen to match those proposed for Cu^{2+} -based corrosion inhibitors (Pearce, 1984; Reed, 1945). Cu^{2+} has been identified previously to have the strongest catalytic effect on oxidation of MEA and the same behavior was expected for concentrated PZ (Goff and Rochelle, 2006; Sexton and Rochelle, 2009b). As demonstrated in the previous two sub-sections, PZ degradation is slow in the presence of either Fe^{2+} or SSM and Cu^{2+} -catalyzed degradation was used to rapidly achieve oxidation with the purposes of identifying degradation products.

9.1.3.1 Effect of copper (Cu^{2+}) at 55 °C

The effect of Cu^{2+} on PZ oxidation at 55 °C was explored in two experiments, OE2 and OE27. These two experiments were compared in section 8.4.2.1 to demonstrate the effect of O_2 partial pressure. The PZ loss for these two experiments is compared to the baseline data in Figure 8.29 while the generation of degradation products in both experiments is compared to the baselines in Figure 8.30.

Copper is clearly an exceedingly strong catalyst for PZ oxidation under both low (OE27) and high O_2 (OE2) conditions. After 500 hours of oxidation, either 16 or 33% of the initial PZ is lost for the low and high O_2 conditions, respectively. In agreement with the PZ loss data, the generation of formate, total formate, and EDA are all well above that of the baseline experiments, demonstrating the strength of Cu^{2+} as a PZ oxidation catalyst at 55 °C.

9.1.3.2 Effect of copper (Cu^{2+}) at 70 °C

The effect of Cu^{2+} on PZ oxidation at 70 °C was explored in two experiments, OE23 and OE25, with either 40 or 94% O_2 . These experiments were discussed in section 8.4.2.2 to demonstrate the effect of O_2 partial pressure on high temperature, Cu^{2+} -catalyzed oxidation. The PZ loss for these two experiments is compared to the baseline data in Figure 8.31 while the generation of formate, total formate, and EDA are compared in Figure 8.32.

As expected, Cu^{2+} is a very strong catalyst for PZ oxidation under both low and high O_2 conditions at 70 °C. Between 35 and 72% of the initial PZ is oxidized in these experiments, indicating the superior efficacy of Cu^{2+} as an oxidation catalyst. The generation of total formate and EDA are in agreement with the PZ loss data. High concentrations of the degradation products were seen in both experiments, with up to 170, 555, and 335 mmole per kg of formate, total formate, and EDA, respectively, seen in the high O_2 experiment. The low O_2 experiment also demonstrates the generation of significant concentrations of both products, well above what was quantified in the baseline experiments. Aqueous Cu^{2+} is a clear catalyst for oxidation of concentrated PZ at 70 °C.

9.1.4 Effect of vanadium (V^{5+})

V^{5+} is a component of some corrosion inhibitors and can be used at variable concentrations (Ranney, 1976). The potential catalytic effect of low concentration V^{5+} was assessed for concentrated PZ. A solution of 8 m PZ with 0.1 mM V^{5+} and 0.1 mM Fe^{2+} was oxidized at 55 °C with agitation at 1400 rpm with 100 mL per minute 98% O_2 /2% CO_2 in the headspace (OE3). This low concentration was chosen to match the expected concentration of V^{5+} based corrosion inhibitors (Mago, 1974; Mago and West, 1976; Nieh, 1983). Fe^{2+} was added to simulate a system where corrosion would

lead to small concentrations of Fe^{2+} in solution. Sexton observed a strong catalytic effect of V^{5+} on MEA oxidation, where MEA was oxidized half as fast as when in the presence of Fe^{2+} , a strong catalyst for MEA oxidation (Sexton, 2008). V^{5+} -catalyzed oxidation has not been studied for concentrated PZ systems.

The PZ loss for the V^{5+} experiment is compared with the four baseline PZ oxidation experiments in Figure 9.10. The PZ loss is virtually negligible and falls well within the error experienced in the baseline experiments. The generation of total formate, the dominant degradation product in the V^{5+} experiment, is compared with the baseline experiments in Figure 9.11. As with PZ loss, the total formate data is very close to the baseline data. After 200-250 hours of oxidation, the concentration of total formate continues to climb, indicating an enhanced production of this product compared to the baseline cases. There may be a delay in total formate production in the presence of this catalyst and a longer experiment would clarify this phenomenon.

Both the PZ and total formate data appear to indicate that V^{5+} is a weak catalyst for PZ oxidation at 55 °C. Sexton observed that V^{5+} had a stronger catalytic effect on PZ than Fe^{2+} , but his observations were based on experiments at 2.5 m PZ and 5 mM V^{5+} (Sexton, 2008). The effect of V^{5+} on 8 m PZ is difficult to assess with only low concentration V^{5+} data available. Oxidation performed with 5 mM V^{5+} may demonstrate that a high concentration of V^{5+} is required to observe a catalytic effect. Based on the data obtained in this project, V^{5+} -catalyzed oxidation occurs slower than a loss of 7% of the initial PZ after 300 hours, the baseline rate.

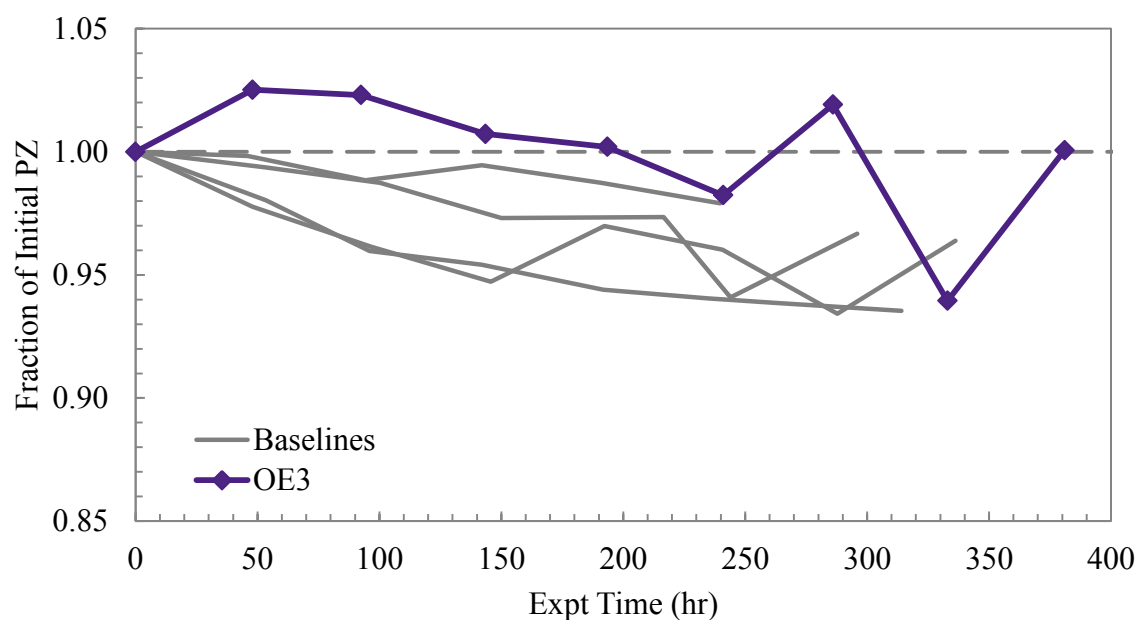


Figure 9.10: Catalytic effect of 0.1 mM V^{5+} and 0.1 mM Fe^{2+} (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O_2 /2% CO_2)

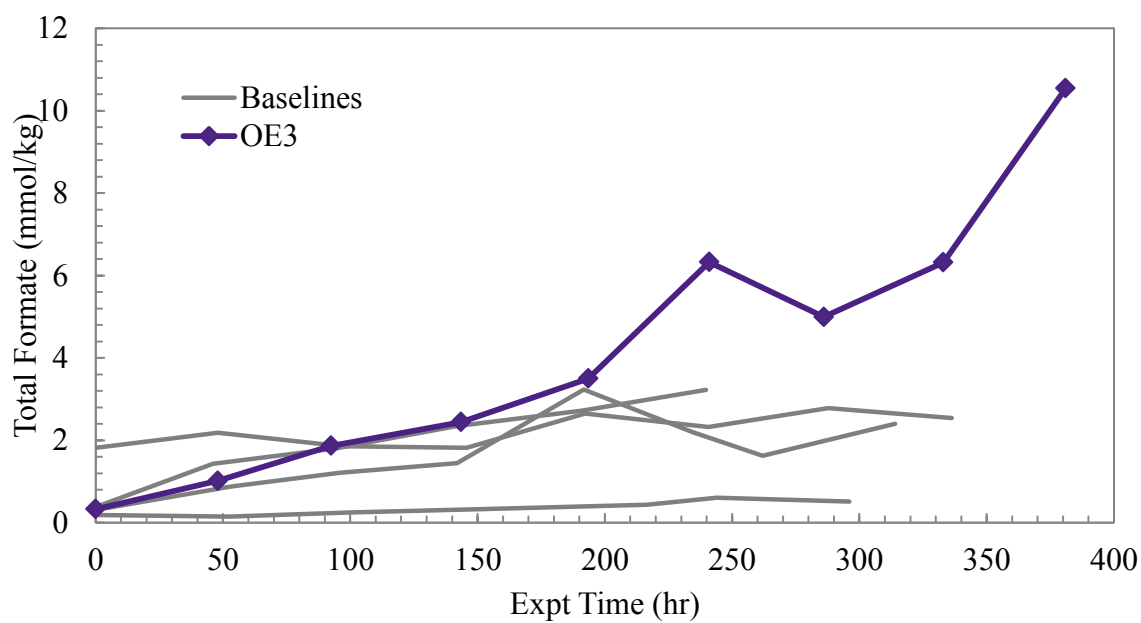


Figure 9.11: Production of total formate in the presence of 0.1 mM V^{5+} and 0.1 mM Fe^{2+} (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O_2 /2% CO_2)

9.2 COMPARISON OF METAL CATALYZED OXIDATION OF CO₂ CAPTURE AMINES

9.2.1 Iron-catalyzed oxidation of CO₂ capture amines

In the presence of iron, many amines are known to oxidize readily, especially as the iron concentration increases (Goff, 2005; Sexton, 2008). Oxidation of PZ has been performed in the presence of 1 mM Fe²⁺ while previous amine oxidation studies went as high as 5 mM Fe²⁺ in order to rapidly catalyze oxidation (Goff, 2005; Sexton, 2008). PZ, MEA, EDA, Diglycolamine[®] (DGA), and DEA have all been oxidized at similar conditions in the low gas flow reactor with 1 mM Fe²⁺ at 55 °C with agitation at 1400 rpm and a flow of 100 mL per minute of 98% O₂/2% CO₂ in the headspace (Sexton, 2008; Zhou et al., 2010). The amine loss is compared between all five amines in Figure 9.12. Amine solutions discussed were 8 m PZ, 7 m MEA, 8 m EDA, 4 m DGA, or 4 m DEA, where concentrations differed based on the individual solvent system (Sexton, 2008; Zhou et al., 2010).

In the absence of any other metal catalyst or inhibitor, 8 m PZ loses 8% of the original amine after 450 hours. In the same time, 44% of 7 m MEA is lost. PZ is 5.5 times more resistant to Fe²⁺-catalyzed degradation than the comparable MEA system. EDA oxidizes slowly at first, and then suffers Fe²⁺-catalyzed oxidation after an initial lag of 50 hours. Although the experiment was shorter than that for PZ, EDA would be expected to have more oxidation than PZ after the initial lag phase based on the slope of the data. DGA is very resistant to Fe²⁺-catalyzed oxidation. Some error in the water balance or analytical techniques led to an increase of DGA through the course of the experiment which can be interpreted as an overall lack of oxidation. Finally, DEA rapidly oxidized in the presence of Fe²⁺ catalyst and has initial oxidation rates similar to that of MEA.

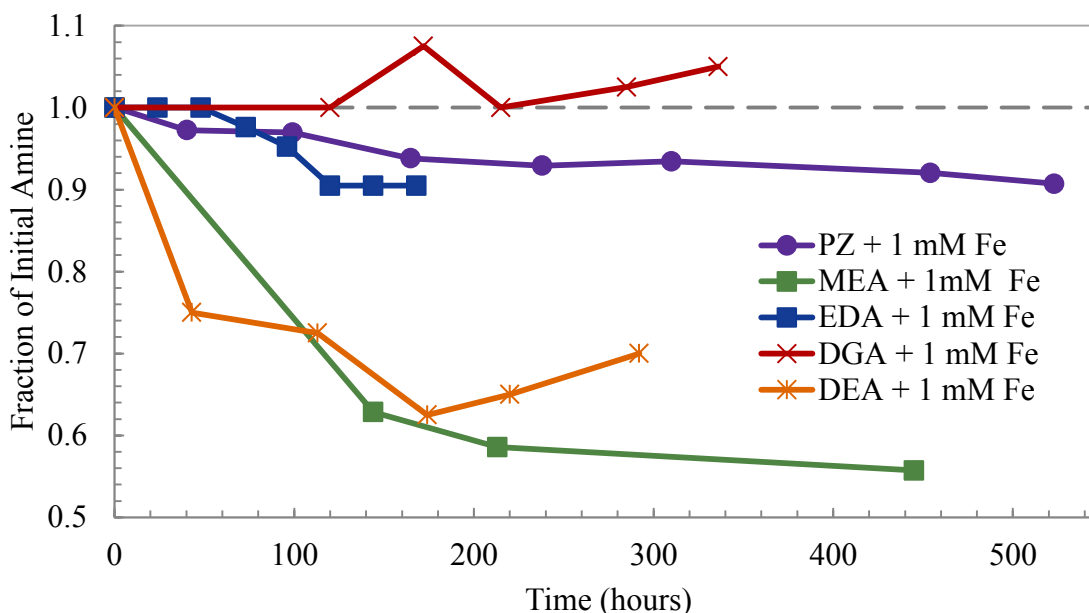


Figure 9.12: Comparison of PZ, MEA, EDA, DGA, and DEA loss in the presence of 1 mM Fe²⁺ (55 °C, 1400 rpm, 100 mL/min 98% O₂/2% CO₂) (Sexton, 2008; Zhou et al., 2010)

9.2.2 Stainless steel metal-catalyzed oxidation of CO₂ capture amines

Understanding the catalytic impact of SSM on amines is valuable because stainless steel is the expected material of construction for industrial CO₂ capture applications. PZ, MEA, and 3-(methylamino)propylamine (MAPA) have been oxidized in the same manner in the presence of the standard stainless steel SSM mixture (0.4 mM Fe²⁺, 0.1 mM Cr³⁺, and 0.05 mM Ni²⁺) at 55 °C with agitation at 1400 rpm and 100 mL per minute of 98% O₂/2% CO₂ in the headspace (Sexton, 2008; Vevelstad, 2010). The amine loss is compared in Figure 9.13. Experiments compared in this figure were performed on 8 m PZ, 7 m MEA, and 9 m MAPA (Sexton, 2008; Vevelstad, 2010). The amine concentrations differed slightly as each amine has a preferred concentration for CO₂ capture applications (Rochelle, 2010a). After 350 hours, only 1%, of the original PZ has oxidized while the MEA experiment shows a loss of 35%. MAPA is completely

oxidized within 120 hours. The resistance of PZ and, to a lesser extent, MEA, to oxidation catalyzed by stainless steel metals is clearly demonstrated.

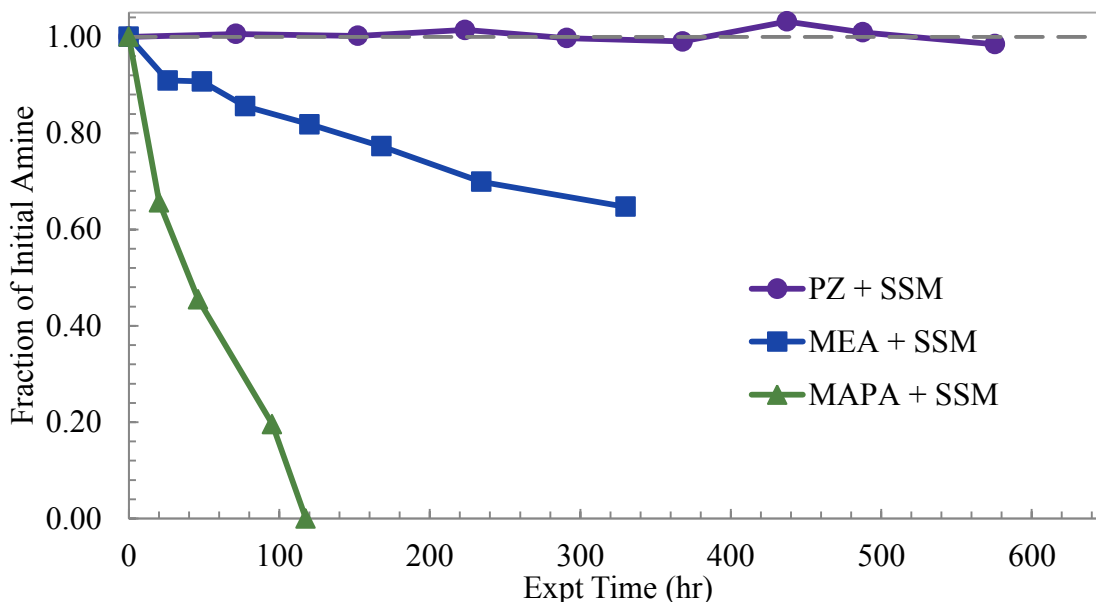


Figure 9.13: Comparison of PZ and MEA loss in the presence of SSM (55 °C, 1400 rpm, 100 mL/min 98% O₂/2% CO₂) (Sexton, 2008; Vevelstad, 2010)

9.2.3 Copper-catalyzed oxidation of CO₂ capture amines

Finally, Cu²⁺ is a well-studied oxidation catalyst that may be present in system utilizing a Cu²⁺-based corrosion inhibitor. PZ, MEA, 2-amino-2-methyl-1-propanol (AMP), and EDA have been oxidized in the presence of Cu²⁺ at 55 °C with agitation at 1400 rpm and 100 mL per minute of 98% O₂/2%CO₂ in the headspace. The concentration of metals was slightly different between the experiments. The PZ, AMP, and EDA experiments contained 4, 5, and 5 mM Cu²⁺, respectively, while the MEA experiment contained both 1 mM Fe²⁺ and 5 mM Cu²⁺ (Sexton, 2008). A comparable MEA experiment was not performed with only Cu²⁺ present. The concentration of amines also differed slightly depending on the solvent system. The experiments

discussed were performed on 8 m PZ, 7 m MEA, 4 m AMP, and 3.5 m EDA (Sexton, 2008).

The loss of amine for each of these experiments is compared in Figure 9.14. Although the metals concentrations are not exactly the same, the effect of copper on amine oxidation is clearly demonstrated. After 220 hours, 28% of the PZ had been degraded while 73% of the MEA was degraded. Even though PZ showed 2.6 times less degradation than 7 m MEA, the 28% degradation observed was nearly four times more than both Fe^{2+} - and SSM-catalyzed PZ oxidation. AMP and EDA, as observed by Sexton (2008), are both more stable to Cu^{2+} -catalyzed oxidation than both PZ and MEA. The EDA concentration studied is lower than would be typically used in a CO_2 capture system, but the resistance to Cu^{2+} -catalyzed oxidation can be assumed to extend to higher EDA concentrations. At higher EDA concentrations, the oxidation rate may increase slightly, but it would still be more resistant to oxidation than either PZ or MEA.

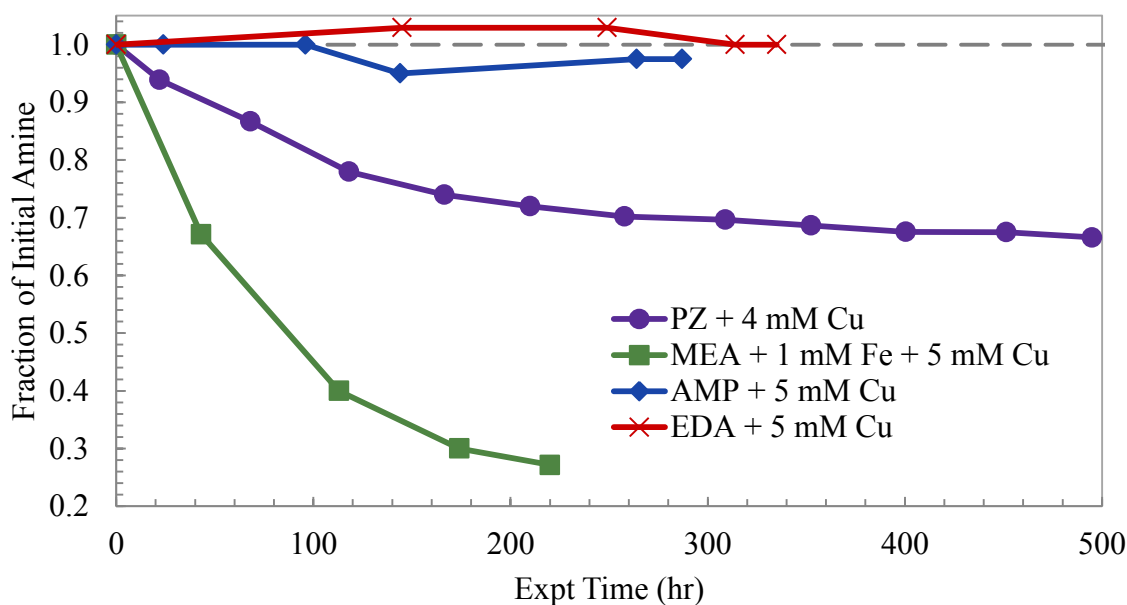


Figure 9.14: Comparison of PZ, MEA, AMP, and EDA loss in the presence of 4-5 mM Cu^{2+} (55 °C, 1400 rpm, 100 mL/min 98% O_2 /2% CO_2) (Sexton, 2008)

9.3 INHIBITION OF THE OXIDATION OF PIPERAZINE

Inhibition of oxidation is a topic closely related to metal-catalyzed oxidation. In industrial systems, corrosion that leads to metals contamination of the amine solution can be mitigated with an inhibitor that can effectively decrease the catalytic effect of the metals. One of the most potent inhibitors investigated in the Rochelle group is Inhibitor A. Inhibitor A is a trade secret compound that can be added to concentrations of up to 100 mM. Inhibitor A has been proven effective at impeding both Fe^{2+} - and Cu^{2+} -catalyzed degradation in other amines such as MEA and 7 m MEA/2 m PZ blends (Goff and Rochelle, 2006; Sexton, 2008). Sexton also demonstrated that Inhibitor A decreased the production of degradation products for 2.5 and 5 m PZ. The efficacy of Inhibitor A to inhibit Fe^{2+} -, stainless steel metal, and Cu^{2+} -catalyzed oxidation was tested with 8 m PZ during the course of this project. Two alternative inhibitors, Inhibitor B and Inhibitor C were also tested for their efficacy at decreasing Fe^{2+} -catalyzed oxidation.

9.3.1 Efficacy of Inhibitor A with Iron (Fe^{2+})

Inhibitor A was tested on 8 m PZ containing 1 mM Fe^{2+} and either 0 or 100 mM Inhibitor A. The first set of experiments exploring the inhibitor was conducted in connection with analysis for foaming characteristics. In these experiments, both solutions were oxidized at 55 °C with 1400 rpm and 100 mL per min of 98% O_2 /2% CO_2 for 70 hours, then removed from the low gas flow reactor and subjected to foaming tests (see section 8.9). Then, both solutions were returned to their respective reactors to be further oxidized for another 93 hours. This was an unusual experiment and the effect of removing the solution from the reactor and returning it was not known at that time. There was a period of 5 days where the solution sat before the foaming tests were performed. The solutions were then returned to the reactors and restarted shortly after completing the foaming tests.

The efficacy of Inhibitor A to decrease Fe^{2+} -catalyzed oxidation is demonstrated in Figure 9.15 when comparing the uninhibited (OE5) and inhibited (OE6) experiments. Fe^{2+} -catalyzed oxidation of concentrated PZ is a slow process and Inhibitor A effectively inhibits the oxidation further. In the inhibited system, no degradation was statistically observable. The PZ concentration actually slightly increased during the course of the experiment. This increase reveals the experimental error due to the water balance in the reactor changing during the experiment and the cumulative error involved in the analytical process. The baseline Fe^{2+} -catalyzed oxidation with 1 mM Fe^{2+} had a 10% loss of PZ after 500 hours of oxidation and the addition of Inhibitor A makes oxidation negligible.

The multiple points present at 70 hours indicate the last point before the solutions were removed for the foaming test and the first point when the solutions were returned to the reactors. The difference between the two points for the 1 mM Fe^{2+} experiment is unfortunately quite large. The solutions were handled with care when transferred, but some changes to the composition of the solution may have occurred. During the foaming test itself, N_2 is sparged through the system and may impact the composition of the solution. It is likely that the water content of the solution was affected by evaporation and any degradation compounds with appreciable volatility would have escaped from solution due to gas sparging.

The formate, total formate, and EDA quantified in these experiments are compared in Figure 9.16. Overall, the formate concentration tracks very well between the experiments with and without Inhibitor A, which was not expected. No EDA was detected in the inhibited solution, indicating effectiveness at decreasing the generation of EDA during oxidation. Both the total formate and EDA concentrations, however, appeared to have been affected by the transfer of the solutions for the foaming test. Both

appear to be building up prior to the solutions removal from the reactor and then are diminished when the oxidation test is restarted. This may indicate that the N₂ sparging stripped out some of the volatile degradation products or shifted the degradation reactions during the foaming test. The lowering of total formate indicates that the formyl amides were strongly affected, which have unknown volatility in comparison to non-volatile heat stable salts. The impact of the foaming test, unfortunately, compounds the fact the experiments were short and produced low concentrations of degradation products that are near the error limits of the anion and cation IC. Despite the impact of the foaming test, the change in PZ loss and lack of EDA production indicate that Inhibitor A is effective at decreasing Fe²⁺-catalyzed oxidation.

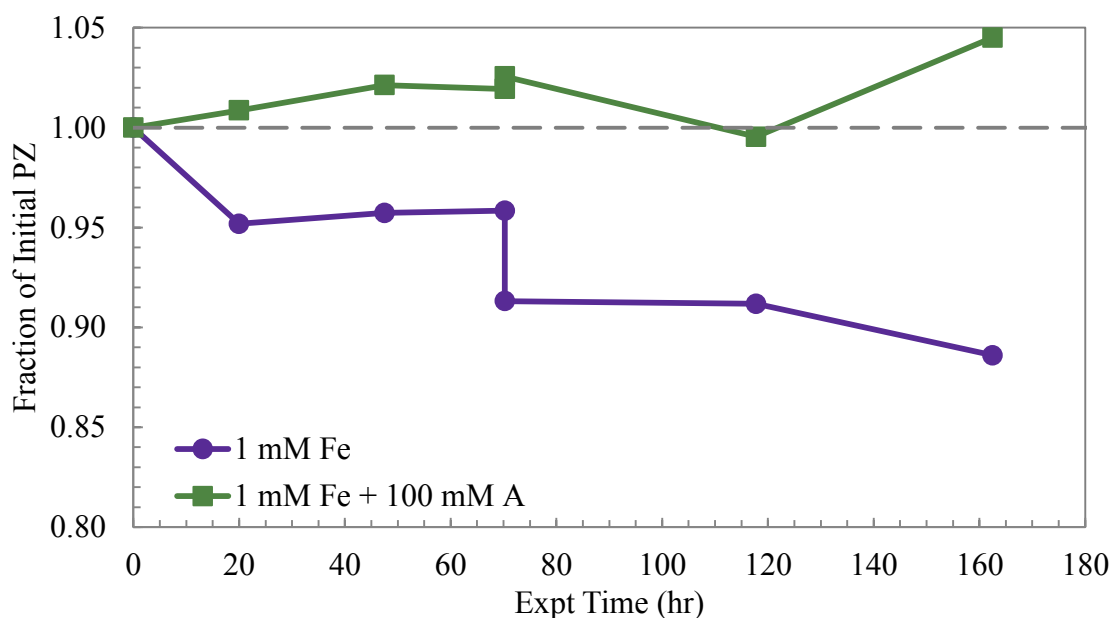


Figure 9.15: Effect of 100 mM Inhibitor A on PZ loss either uninhibited (●) or inhibited (■) (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O₂/2% CO₂, 1 mM Fe²⁺)

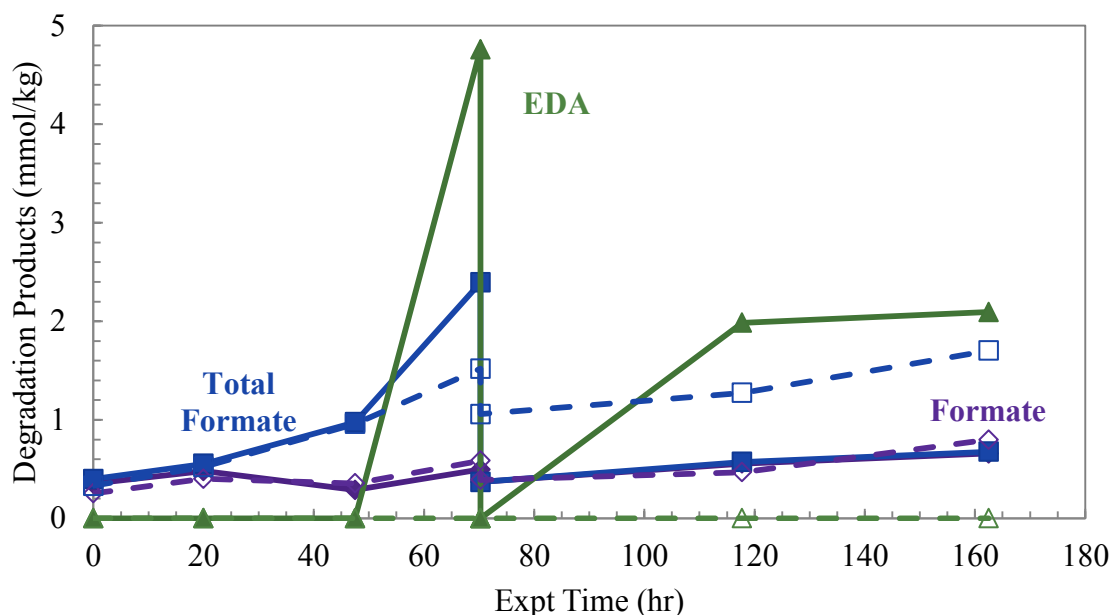


Figure 9.16: Effect of 100 mM Inhibitor A on generation of formate (◆), total formate (■), and EDA (▲) either uninhibited (solid) or inhibited (open) (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O₂/2% CO₂, 1 mM Fe²⁺)

In a second set of experiments, 8 m PZ was oxidized at 55 °C with 1400 rpm and 100 mL per min of 98% O₂/2% CO₂ with either 0 (OE13) or 100 mM Inhibitor A (OE14). This set of experiments was a repeat of the previous set with the goal of avoiding the issues experienced due to the mid-experiment foaming test. The PZ loss during the experiments is shown in Figure 9.17 while the production of formate and total formate are compared in Figure 9.18. The PZ loss data indicates that Inhibitor A is successful at inhibiting Fe²⁺-catalyzed oxidation in 8 m PZ. There is significant scatter in the inhibited solution that demonstrates the overall error in the experiment. No EDA was detected in either experiment, unlike the previous comparison. Unexpectedly, more formate and total formate were generated in the inhibited solution. The concentrations overall are very low, and some error is expected as demonstrated by the outliers. The cause for this higher level of degradation products in the inhibited solution is unknown.

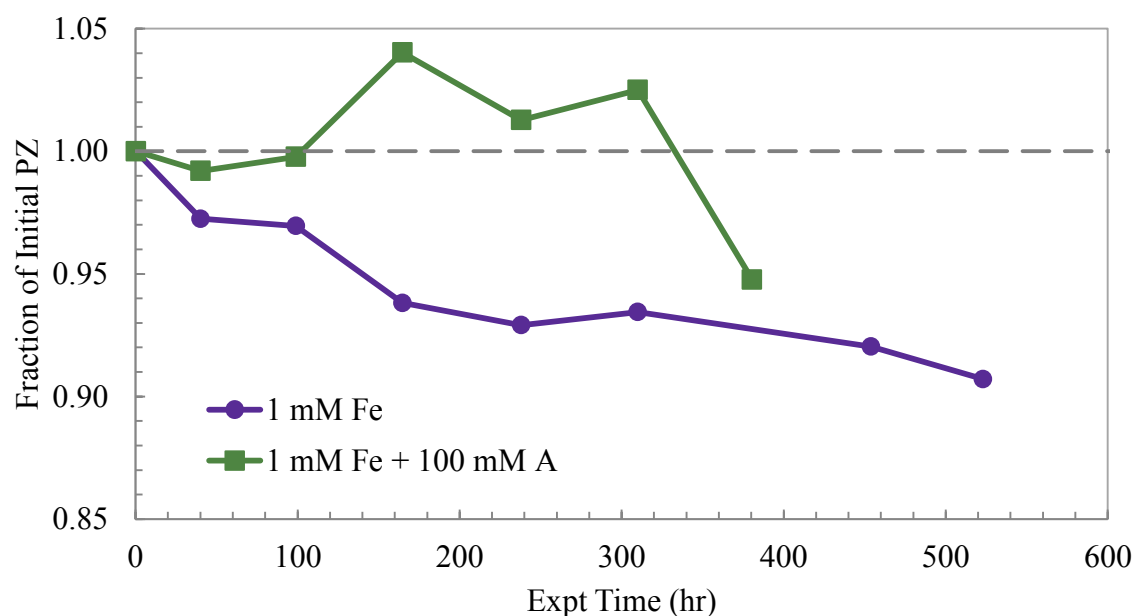


Figure 9.17: Effect of 100 mM Inhibitor A on PZ Loss either uninhibited (●) or inhibited (■) (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O₂/2% CO₂, 1 mM Fe²⁺)

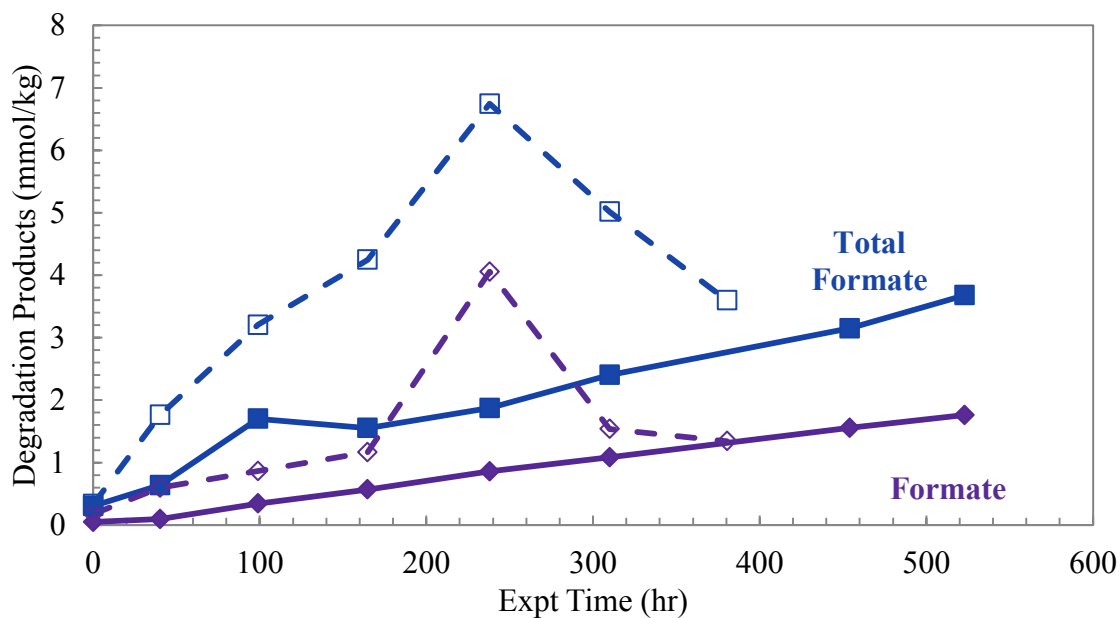


Figure 9.18: Effect of 100 mM Inhibitor A on generation of formate (◆) and total formate (■) either uninhibited (solid) or inhibited (open) (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O₂/2% CO₂, 1 mM Fe²⁺)

Oxidation can be detected either by the loss of PZ or the production of degradation products. In the case of these four experiments, some of the results are contradictory. Overall, Inhibitor A does appear to inhibit Fe^{2+} -catalyzed PZ oxidation, although the production of degradation products is not always substantially decreased in every case. The weak catalytic effect of Fe^{2+} made observing the effect of Inhibitor A on PZ oxidation difficult.

9.3.2 Efficacy of Inhibitor A with Stainless Steel Metals (Fe^{2+} , Cr^{3+} , and Ni^{2+})

The effectiveness of Inhibitor A to mitigate stainless steel metal catalyzed corrosion has not been tested previously on concentrated PZ. In order to determine the efficacy of Inhibitor A, 8 m PZ with the standard SSM mixture (0.4 mM Fe^{2+} , 0.1 mM Cr^{3+} , and 0.05 mM Ni^{2+}) was oxidized at 55 °C with 1400 rpm and 100 mL per min of 98% O_2 /2% CO_2 with either 0 (OE15) or 10 mM Inhibitor A (OE16). The loss of PZ is shown in Figure 9.19 while the generation of degradation products is compared in Figure 9.20. Both solutions lose very little PZ during the course of the 420 hour experiment, with the inhibited experiment actually losing more PZ than the uninhibited case. It is important to remember that the baseline experiments described in Section 8.2.1 showed 3 to 7% PZ loss simply due to the operation error of the experiment.

In this case with little overall oxidation the production of degradation products is more informative. The inhibited solution has lower concentrations of formate and total formate and no detected EDA. A significant drop in the total formate is seen, but the concentrations are all below 7 mmole per kg. Although only 10 mM of Inhibitor A was used it noticeably decreased the generation of degradation products. The degradation products clearly indicates that Inhibitor A is successful in hindering SSM-catalyzed oxidation where PZ loss data is not statistically significant due to low oxidation rates.

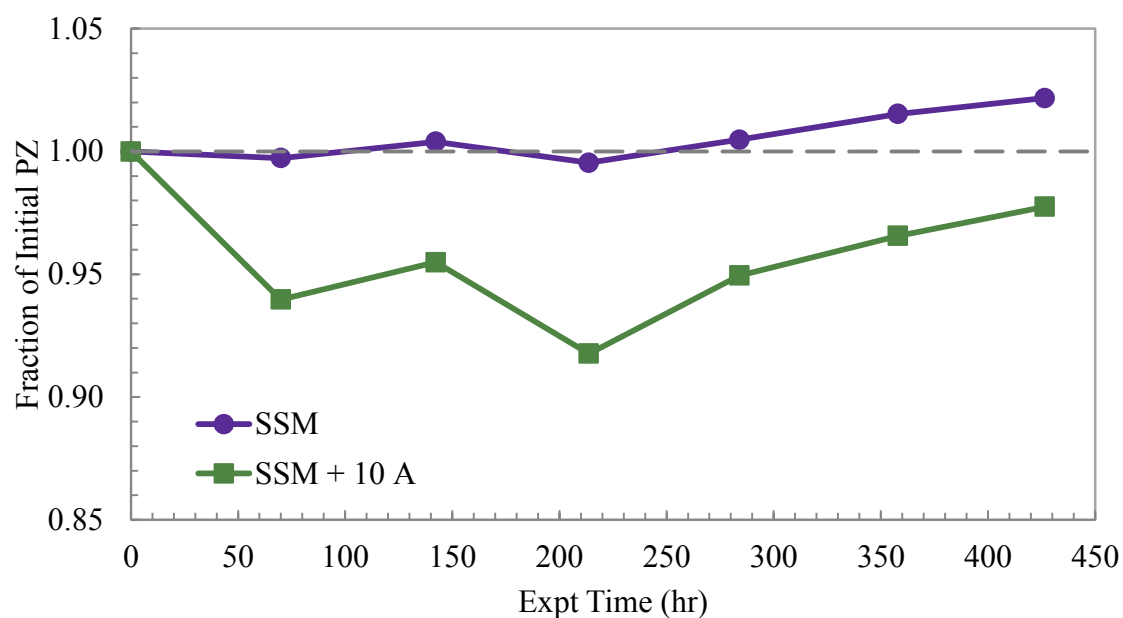


Figure 9.19: Effect of 10 mM Inhibitor A on PZ Loss either uninhibited (●) or inhibited (■) (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O₂/2% CO₂, SSM)

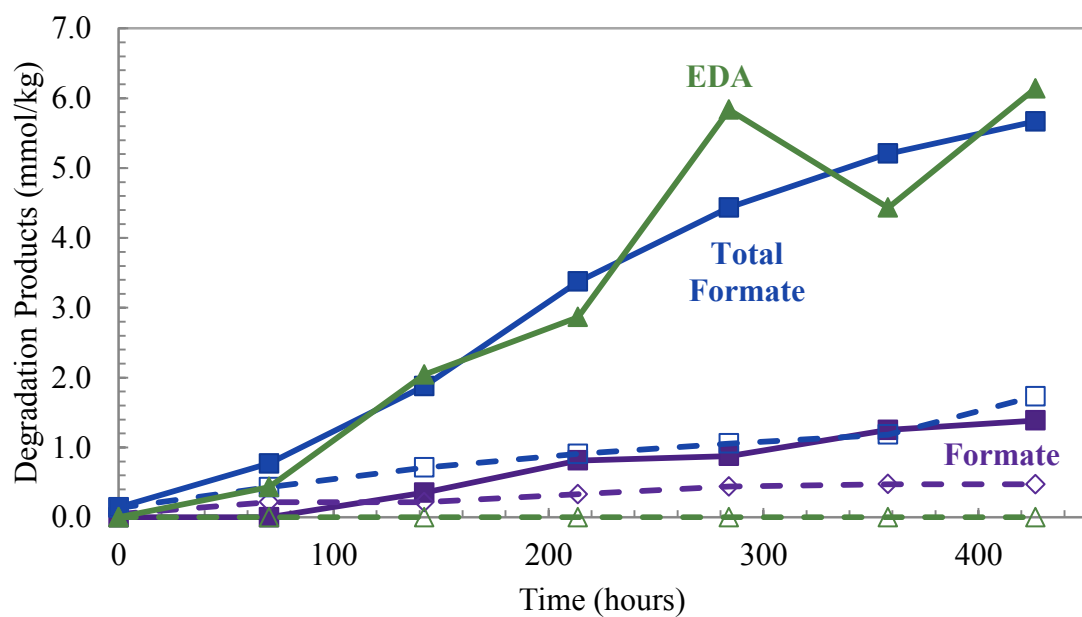


Figure 9.20: Effect of 10 mM Inhibitor A on generation of formate (◆), total formate (■), and EDA (▲) either uninhibited (solid) or inhibited (open) (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O₂/2% CO₂, SSM)

9.3.3 Efficacy of Inhibitor A with Copper (Cu^{2+})

Inhibitor A has previously been investigated for its ability to inhibit Cu^{2+} -catalyzed oxidation of low concentration PZ. Sexton observed that 100 mM Inhibitor A was highly effective and decreased the generation of formate and EDA by 90% in 5 m PZ at 55 °C with 5 mM Cu^{2+} (Sexton, 2008). PZ concentrations were not measured for the experiments discussed by Sexton, but it can be assumed that PZ loss was also decreased by a similar degree through the addition of Inhibitor A.

9.3.3.1 Efficacy of Inhibitor A with Copper (Cu^{2+}) at 55 °C

The effectiveness of Inhibitor A was tested on 8 m PZ in the presence of Cu^{2+} at 55 °C. Two experiments were performed in which PZ was oxidized uninhibited in the presence of 4 mM Cu^{2+} (OE2) or in the presence of 5 mM Cu^{2+} , 0.1 mM Fe^{2+} , and 100 mM Inhibitor A (OE4). The metals concentrations differed both in Cu^{2+} concentration and in the addition of Fe^{2+} to the inhibited experiment. As discussed in section 9.2 above, the catalytic impact of 0.1 mM Fe^{2+} is minimal in comparison with the presence of any concentration of Cu^{2+} . The higher concentration present in the inhibited solution will only further test the efficacy of Inhibitor A at decreasing Fe^{2+} and Cu^{2+} -catalyzed degradation.

The efficacy of Inhibitor A at decreasing Cu^{2+} -catalyzed PZ oxidation is clearly demonstrated in the PZ loss data in Figure 9.21. After 500 hours, PZ loss is decreased by three times as 34% PZ was lost in the uninhibited case compared to 11% in the inhibited case. The higher starting concentration of Cu^{2+} did not decrease the inhibitory power of Inhibitor A. The generation of formate, total formate, and EDA are compared in Figure 9.22 for the uninhibited and inhibited experiments. In concurrence with the PZ loss data, the generation of all three dominant degradation products is significantly decreased in the inhibited solution. After 500 hours, the concentration of formate, total formate, and EDA

were decreased by 92, 93, and 96%, respectively. These decreases mimic what was observed for 5 m PZ (Sexton, 2008).

In order to gauge the full effectiveness of Inhibitor A on Cu^{2+} -catalyzed oxidation, the two experiments were performed at high temperature. Solutions of 8 m PZ were oxidized in the presence of 4 mM Cu^{2+} at 70 °C agitated at 1400 rpm with 100 mL per minute of 40% O_2 /6% CO_2 either uninhibited (OE23) or with 100 mM Inhibitor A (OE24). The PZ loss in each case is compared in Figure 9.23. As with the lower temperature experiments, the effectiveness of Inhibitor A at decreasing PZ loss in the presence of Cu^{2+} is clear. Inhibitor A decreased the loss of PZ by five times as the uninhibited experiment lost 35% of the initial PZ while the inhibited experiment lost only 6%.

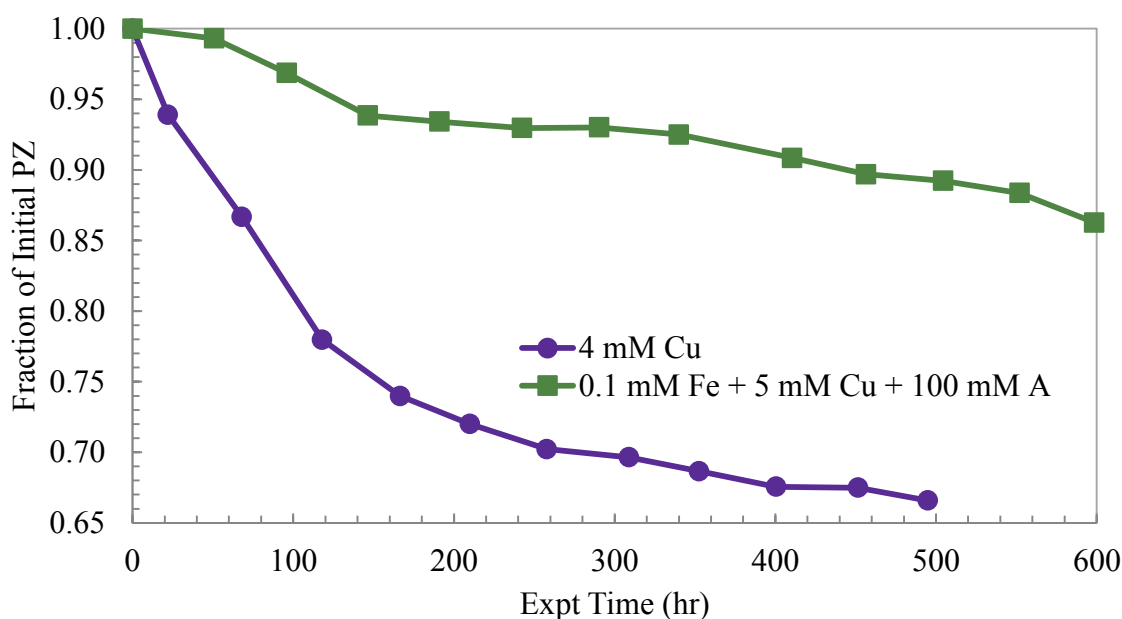


Figure 9.21: Effect of 100 mM Inhibitor A on PZ loss either uninhibited (●) or inhibited (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O_2 /2% CO_2 , 4 mM Cu^{2+} (uninhibited) or 0.1 mM Fe^{2+} and 5 mM Cu^{2+} (inhibited))

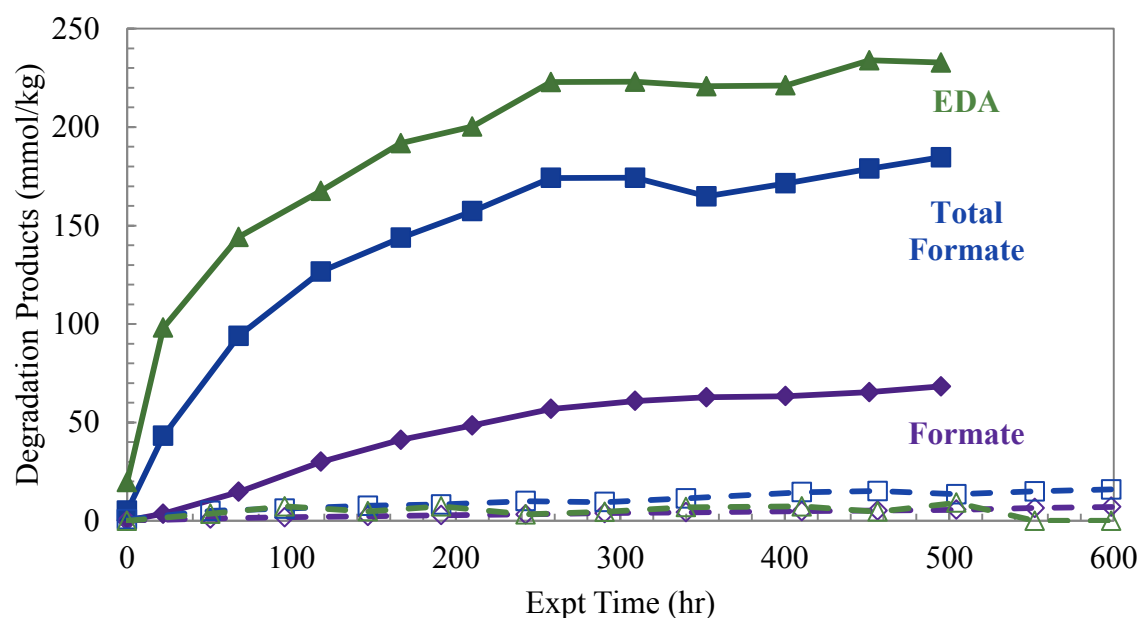


Figure 9.22: Effect of 100 mM Inhibitor A on generation of formate (◆), total formate (■), and EDA (▲) either uninhibited (solid) or inhibited (open) (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O₂/2% CO₂, 4 mM Cu²⁺)

9.3.3.2 Efficacy of Inhibitor A with Copper (Cu²⁺) at 70 °C

The production of formate, total formate, and EDA, the major degradation products are compared in Figure 9.24 for the uninhibited and inhibited experiments. In agreement with the PZ data, the production of all three degradation products is visibly decreased by the presence of Inhibitor A. After 330 hours, the production of formate, total formate, and EDA were each decreased by 87, 81, and 90%, respectively. This decrease is very similar to the decrease seen with both 5 and 8 m PZ at 55 °C. Inhibitor A is extremely effective at decreasing high temperature oxidation of PZ in the presence of Cu²⁺.

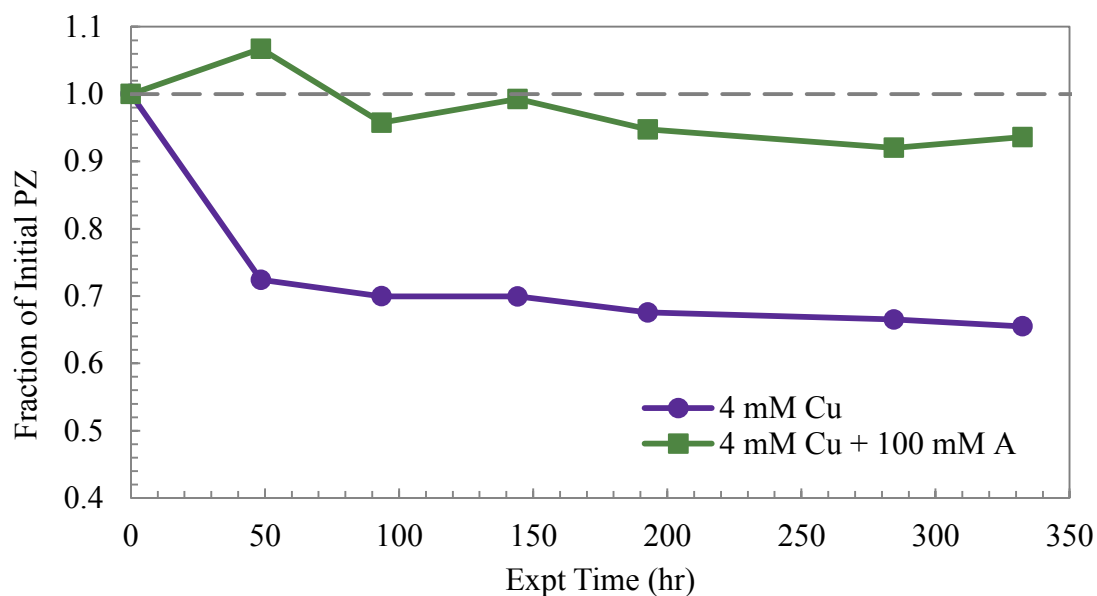


Figure 9.23: Effect of 100 mM Inhibitor A on PZ loss either uninhibited (●) or inhibited (■) (8 m PZ, 70 °C, 1400 rpm, 100 mL/min 40% O₂/2% CO₂, 4 mM Cu²⁺)

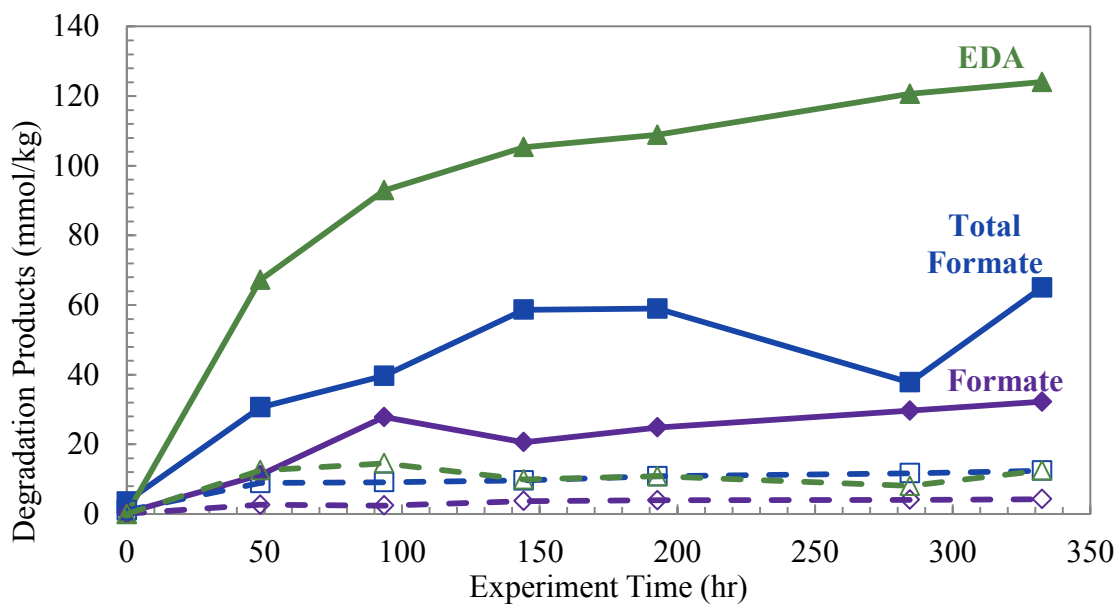


Figure 9.24: Effect of 100 mM Inhibitor A on generation of formate (◆), total formate (■), and EDA (▲) either uninhibited (solid) or inhibited (open) (8 m PZ, 70 °C, 1400 rpm, 100 mL/min 40% O₂/2% CO₂, 4 mM Cu²⁺)

9.3.3.2 Activation energy of copper-catalyzed oxidation with Inhibitor A

That activation energies for the loss of PZ and generation of formate, total formate, and EDA during Cu^{2+} -catalyzed oxidation with 100 mM Inhibitor A were also calculated in the same way as SSM- and Cu^{2+} -catalyzed experiments in sections 8.5.2 and 8.5.4. The rates for the four species are compared for two Cu^{2+} -catalyzed experiments (OE4 and OE24) in Figure 9.25. An estimation of error was not able to be performed because there were only two data points for the regression, making the degrees of freedom zero for the calculation of activation energy.

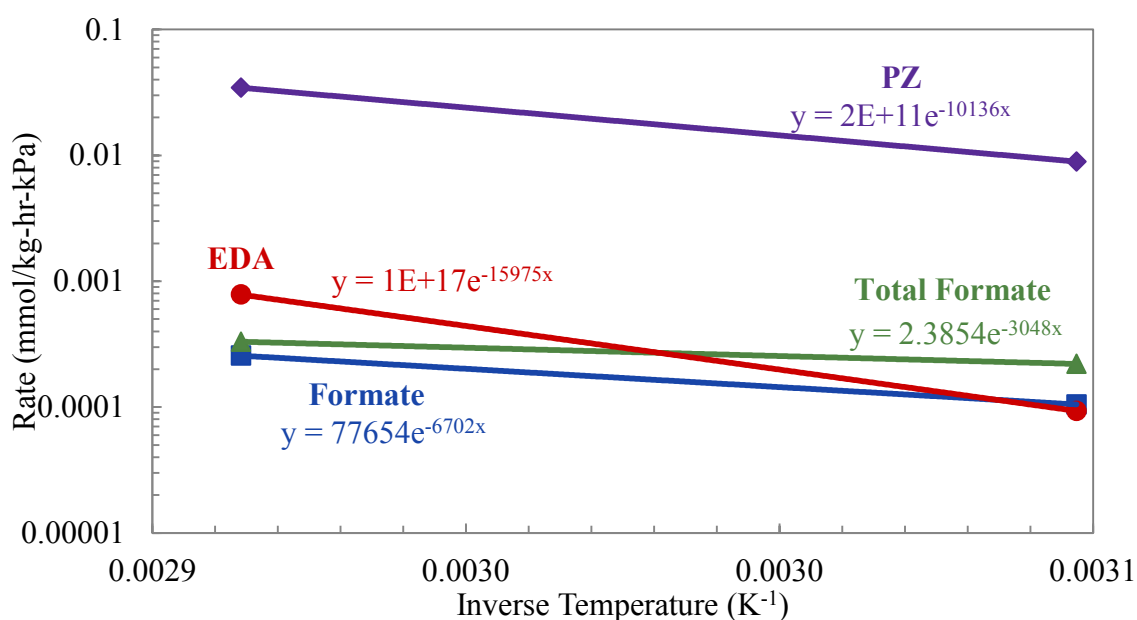


Figure 9.25: Rates of loss or production for PZ (♦), formate (■), total formate (▲), and EDA (●) for Cu^{2+} -catalyzed oxidation with 100 mM Inhibitor A

The calculated activation energies are compared for the four species in the presence of Cu^{2+} and with and without 100 mM Inhibitor A in Table 9.1. The first column of data is taken from Table 8.8. The most striking effect of Inhibitor A is the sharp increase in the activation energy for EDA. Inhibitor A may work directly to minimize the reactions responsible for EDA production in Cu^{2+} -catalyzed oxidation of

PZ. The activation energy for PZ itself is increased by three times, to a level almost as high as SSM-catalyzed oxidation. The formate generation energy is slightly high, but in the same range as that of both SSM- and Cu^{2+} -catalyzed oxidation suggesting that Inhibitor A may not be effective at interfering with the mechanisms that generate formate.

Table 9.1: Activation energies for PZ loss and generation of products for Cu^{2+} -catalyzed oxidation with and without 100 mM Inhibitor A

Rate	Cu^{2+}	$\text{Cu}^{2+} + 100 \text{ mM Inhibitor A}$
	Activation Energy (kJ/mol)	Activation Energy (kJ/mol)
PZ Loss	27 ± 29	84
Formate Generation	47 ± 15	56
Total Formate Generation	29 ± 33	25
EDA Generation	36 ± 9	133

9.3.4 Efficacy of Inhibitor B with Iron (Fe^{2+})

Inhibitor B is a trade secret oxidation inhibitor that has been classified as a reaction mechanism inhibitor. Previous work by Sexton has shown the effectiveness Inhibitor B at inhibiting oxidation of MEA in the presence of Fe^{2+} by decreasing MEA loss by up to 75% (Sexton, 2008). Unpublished work of the Rochelle group has indicated that Inhibitor B may enhance oxidation of MEA in the presence of both Fe^{2+} and Cu^{2+} . Inhibitor B was tested for its effectiveness at inhibiting Fe^{2+} -catalyzed oxidation of 8 m PZ. A solution of 8 m PZ was oxidized at 55 °C with 1 mM Fe^{2+} and 20 mM Inhibitor B with agitation at 1400 rpm and 100 mL per minute 98% O_2 /2% CO_2 .

The loss of PZ is compared for this inhibited experiment and a comparable uninhibited experiment in Figure 9.26. The loss of PZ is very similar in both experiments, with and without Inhibitor B. There is scatter in the inhibited data that leads to the increase in the final data point. Overall, the loss of PZ is very small in both

experiments over this short time range. Then generation of formate and total formate are compared in Figure 9.27. No EDA was detected in either experiment. The degradation product data appears to conclusively show that Inhibitor B does, in fact, decrease the production of formate and formyl amides in concentrated PZ. Both concentrations in the inhibited solution are almost negligible after 170 hours of degradation, reaching only 0.6 mmole per kg. A longer experiment would be needed to confirm the decrease in PZ loss that should accompany this decrease in degradation production formation.

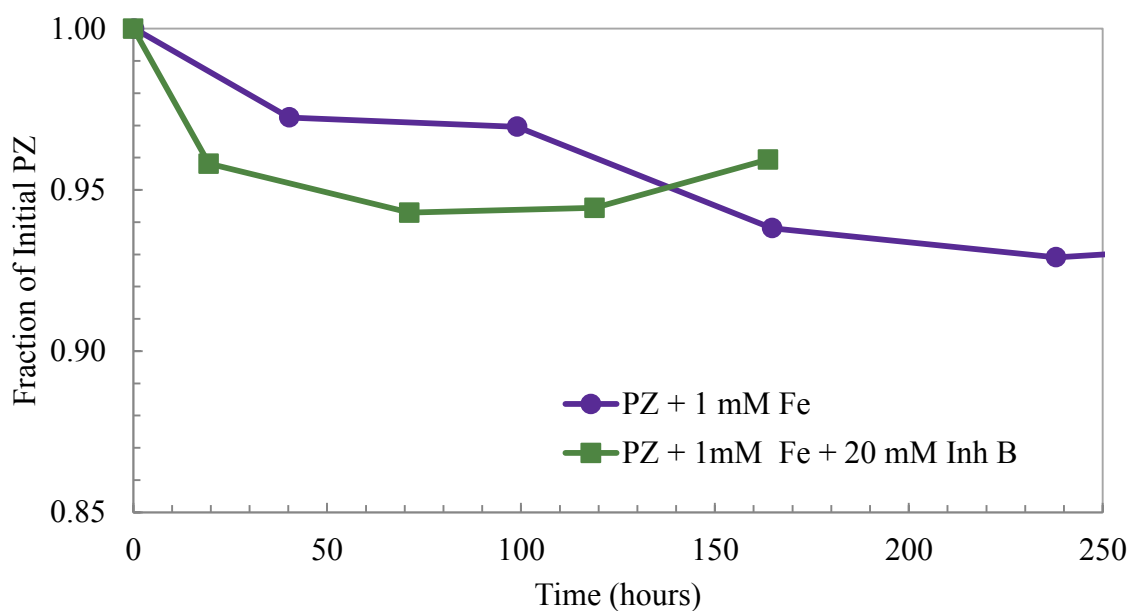


Figure 9.26: Effect of 20 mM Inhibitor B on PZ loss either uninhibited (●) or inhibited (■) (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O₂/2% CO₂, 1 mM Fe²⁺)

9.3.5 Efficacy of Inhibitor C with Iron (Fe²⁺)

Inhibitor C is another trade secret inhibitor that is classified as a chelating agent. Unpublished work from within the Rochelle group has shown that Inhibitor C is effective at decreasing both Fe²⁺- and Cu²⁺-catalyzed oxidation of MEA. The effectiveness of Inhibitor C to decrease PZ oxidation was investigated in the presence of 1 mM Fe²⁺

through the oxidation of 8 m PZ was oxidized at 55 °C with 30 mM Inhibitor C, agitation at 1400 rpm and 100 mL per minute 98% O₂/2%CO₂.

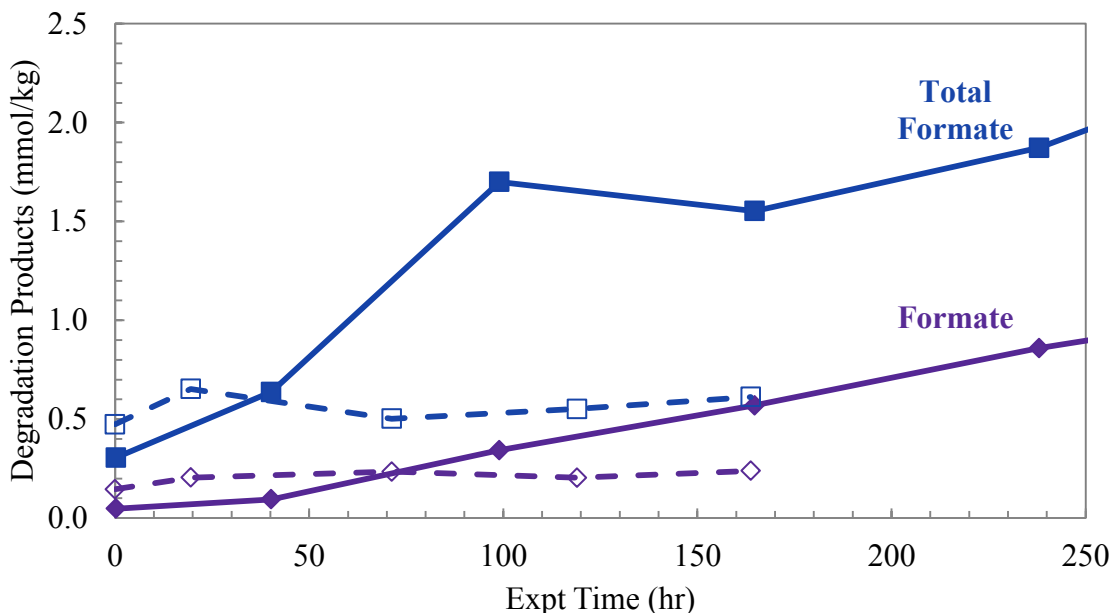


Figure 9.27: Effect of 20 mM Inhibitor B on generation of formate (♦) and total formate (■) either uninhibited (solid) or inhibited (open) (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O₂/2% CO₂, 1 mM Fe²⁺)

The loss of PZ for the inhibited and uninhibited experiments is compared in Figure 9.28. The PZ data suggests that Inhibitor C has no effect on PZ loss. The production of formate, total formate, and EDA is compared for the two experiments in Figure 9.29. There is a striking increase in the production of all three of the dominant degradation products, formate, formyl amides, and EDA, in the presence of 30 mM Inhibitor C. This observation does not match the PZ loss data which suggests a similar rate of oxidation. It is possible that the inhibitor itself is oxidizing and this is reflected in the increased product generation. Despite the uncertainty of the fate of Inhibitor C in solution, it is clear that Inhibitor C is not a useful inhibitor of oxidation in concentrated PZ solutions and may, in fact, catalyze the generation of oxidation products.

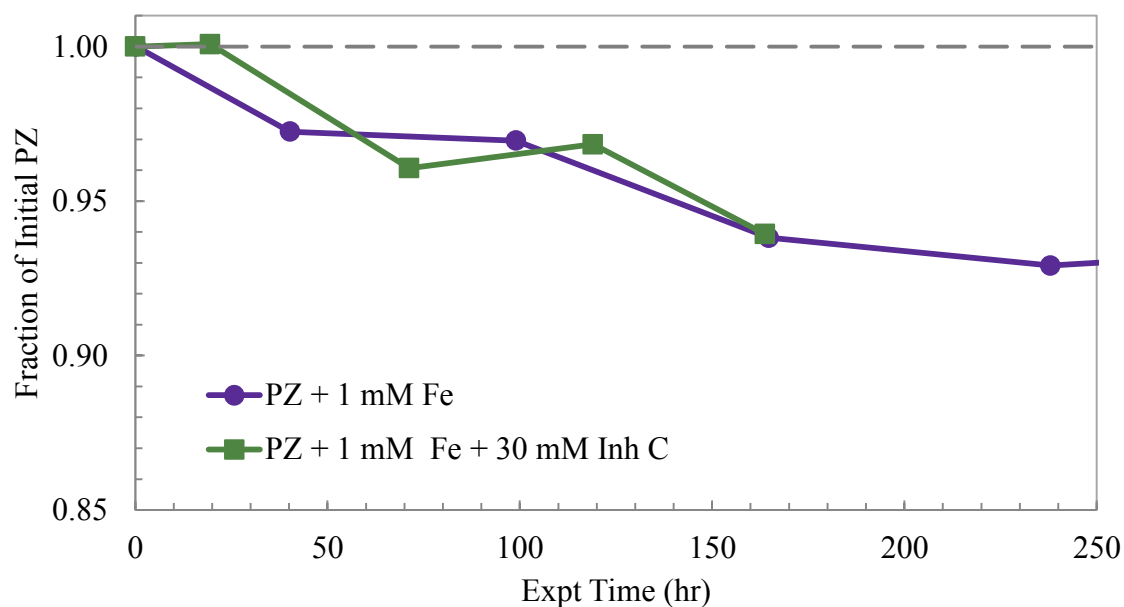


Figure 9.28: Effect of 30 mM Inhibitor C on PZ loss either uninhibited (●) or uninhibited (■) (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O₂/2% CO₂, 1 mM Fe²⁺)

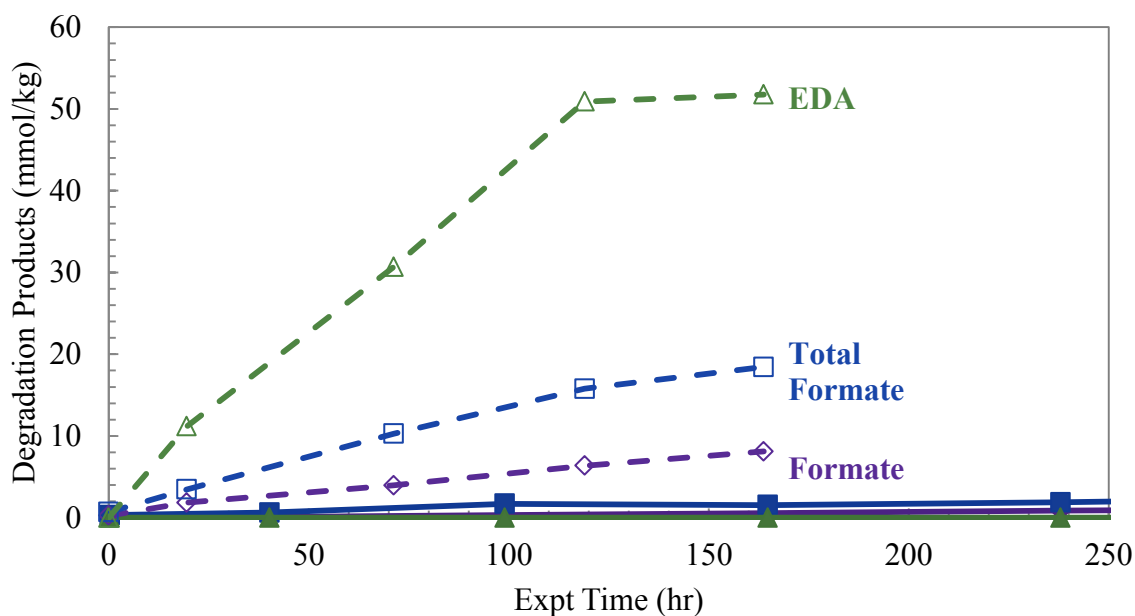


Figure 9.29: Effect of 30 mM Inhibitor C on generation of formate (♦), total formate (■), and EDA (▲) either uninhibited (solid) or inhibited (open) (8 m PZ, 55 °C, 1400 rpm, 100 mL/min 98% O₂/2% CO₂, 1 mM Fe²⁺)

9.4 COMPREHENSIVE OXIDATION RATE ANALYSIS FOR CONCENTRATED PZ

A comprehensive analysis of the oxidation rate of concentrated PZ can be performed using the loss rate of PZ and generation rate for the marker degradation products. In all of the oxidation experiments, the loss rate of PZ (R_{PZ}) and generation rate of formate (R_{formate}), total formate (R_{TF}), and EDA (R_{EDA}) have been calculated from the raw data. Linear rates were used except for data from OE2, OE23, OE25 and OE27 where very fast oxidation rates were measured that leveled out over time. In these four experiments, a linear rate was determined using the first three time points in order to estimate initial rates of oxidation. A summary of the calculated rates is provided in Table 9.3 along with the pertinent experimental conditions. All rates are calculated in units of mmole per kg per hr per kPa O_2 . The slope of the raw experimental data is divided by the partial pressure of O_2 in the experiment to normalize the effect of O_2 partial pressure and to match previous analyses. In two cases, OE6 and OE15, the PZ concentration increased with time giving a positive slope, so these rates were assumed to be zero.

The effect of process parameters on PZ oxidation can be well understood by comparing the overall oxidation rates. In the following analysis, all oxidation data is used except for OE7, OE8, OE20, and OE21, which were spiked with Inhibitor B, Inhibitor C, formate, or formaldehyde, respectively. For the remaining experiments, R_{formate} , R_{TF} , or R_{EDA} are compared to R_{PZ} in Figure 9.30, Figure 9.31, and Figure 9.32, respectively. In all of the figures, the different catalysts and inhibitor conditions are indicated with different data shapes, but no distinction is made for experiments at 55 and 70 °C. All three graphs are plotted with log-log coordinates in order to spread the data because rates extend over four orders of magnitude. A linear regression is shown that fits all of the data and a coefficient of determination (r^2) is indicated for each regression.

Analyzing the oxidation rates with this approach will highlight the oxidation behavior of PZ. As expected, all three degradation products are generated as PZ is lost to oxidation, as indicated by the increasing slope of the data. The catalytic effect of Cu^{2+} on PZ oxidation is also emphasized in these figures. For all three degradation products, the Cu^{2+} experiments have the highest product generation rates and PZ loss rates. These data points heavily influence the data regressions because they are one to two orders of magnitude higher than most of the data. The baseline, SSM, SSM with Inhibitor A, Fe, and Fe with Inhibitor A experiments all have PZ loss rates and product generation rates that are in the very low ranges of each graph. Although the log-log coordinates highlight this data by stretching it out across multiple orders of magnitude, the highest rate of PZ loss seen in any condition without Cu^{2+} is below all of the Cu^{2+} data. The same can be said for all product generation rates in the absence of Cu^{2+} . The slopes of the linear regressions shown in the Figure 9.30, Figure 9.31, and Figure 9.32 suggest the interactions between PZ and the degradation products. The slopes indicate that for each mole of PZ oxidized, 0.03 mole formate, 0.11 mole total formate, and 0.18 mole EDA are produced.

The degradation product generation rates are of particular interest in this project because, on a whole, they were more accurately quantified than PZ loss rates. The rates of production of formate and total formate are correlated in Figure 9.33. The same type of correlation is done for formate and EDA in Figure 9.34 and total formate and EDA in Figure 9.35. In each of these three figures, a linear regression has been performed with all of the oxidation data and for only the non- Cu^{2+} data. In this way, any differences in the generation of products in Cu^{2+} -catalyzed degradation can be assessed since the regression for all of the data is essentially only heavily influenced by the copper data because of its magnitude.

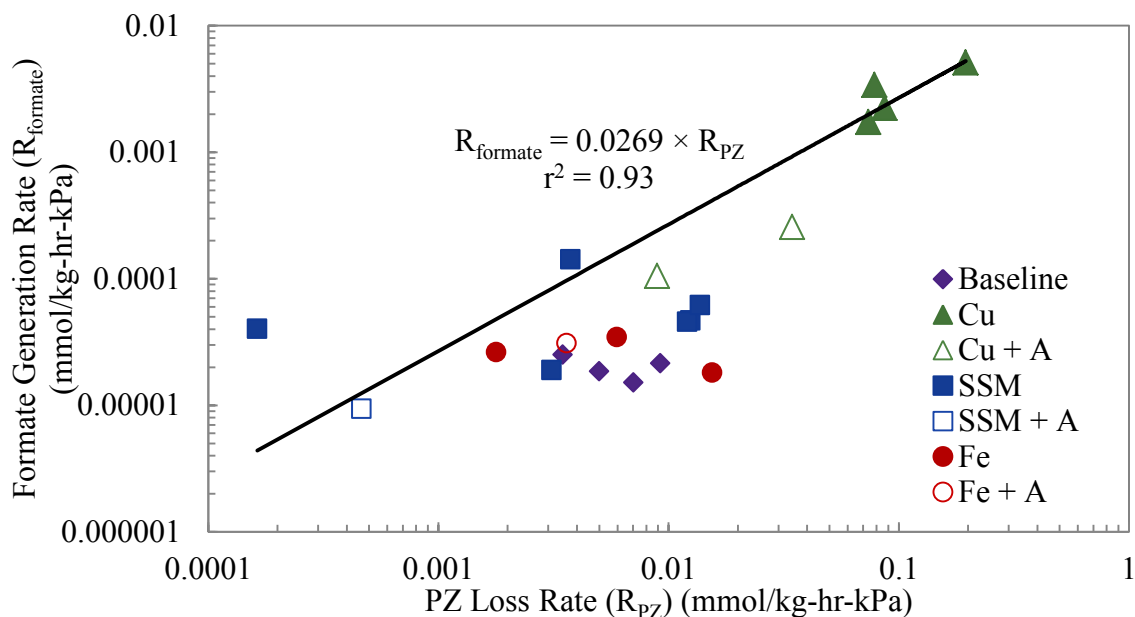


Figure 9.30: Correlation of R_{PZ} and R_{formate} for all PZ oxidation experiments with a linear regression

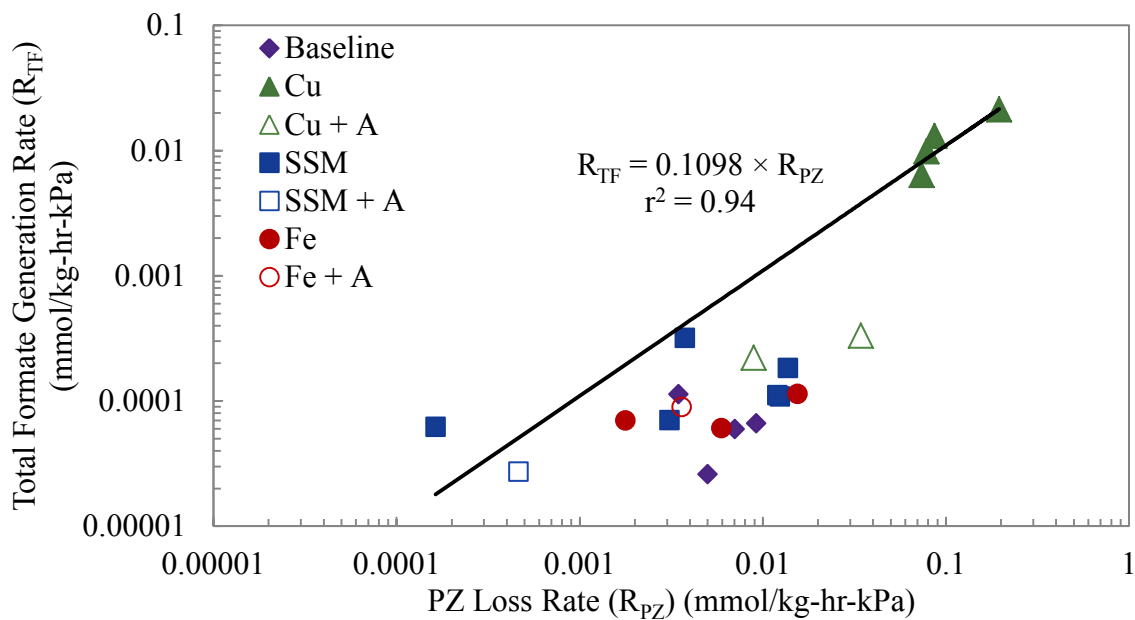


Figure 9.31: Correlation of R_{PZ} and R_{TF} for all PZ oxidation experiments with a linear regression

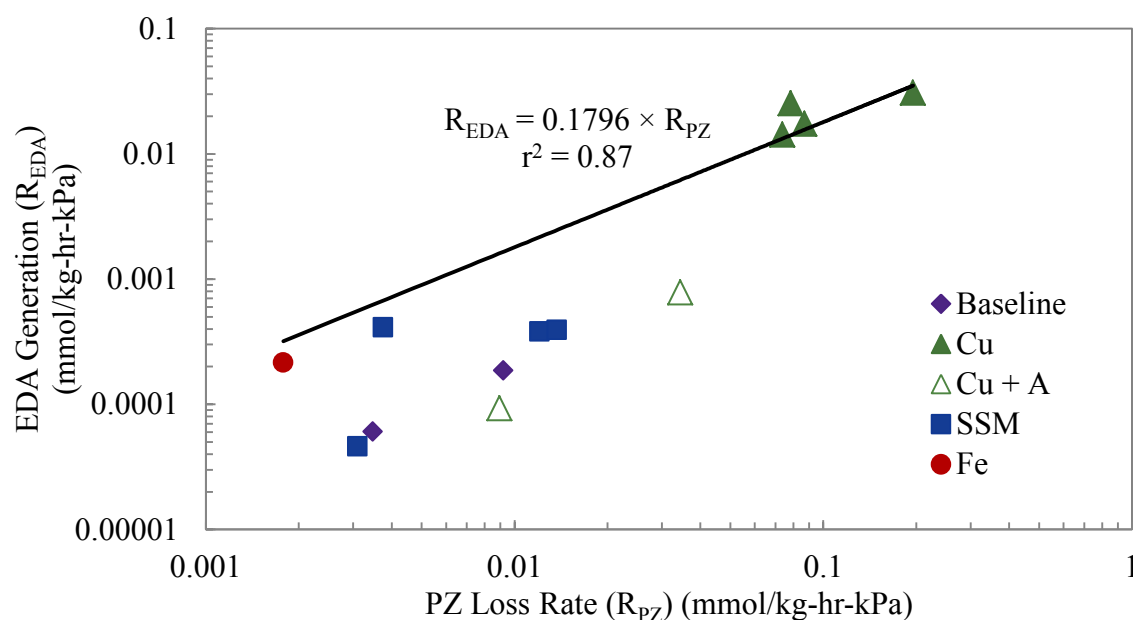


Figure 9.32: Correlation of R_{PZ} and R_{EDA} for all PZ oxidation experiments with a linear regression

The slopes of the correlation between formate and total formate suggest that there is an appreciable difference between the apparent equilibrium of formate and formyl amides in the presence of Cu^{2+} -catalyzed degradation (Figure 9.33). In more heavily oxidized solutions (i.e. with Cu^{2+} present), the equilibrium of formate and formyl amides favors amides and only a quarter of the total formate is usually in the form of free formate. In poorly oxidized solutions (i.e. in the absence of Cu^{2+}), the equilibrium shifts toward producing more formate where roughly 40% of the total formate in is the form of free formate.

The slopes of the correlation between total formate and EDA are also enlightening (Figure 9.35). The correlation based on the Cu^{2+} data or the non- Cu^{2+} data yielded the same slope of 1.6, within expected error. This indicates that regardless of the rate of oxidation or the strength of the catalyst, total formate and EDA will be generated in approximately the same ratio in all cases. There will always 1.6 moles of EDA generated

for every mole of total formate. This conclusion suggests that EDA and total formate are generated either at the same time or with mechanisms that are interdependent on each other and not influenced by the type of catalyst.

The slopes of the correlation of formate and EDA reflect the conclusions made in the two previous paragraphs (Figure 9.34). Since EDA and TF are produced at a constant ratio, the relationship between formate and EDA is dependent on the relationship or equilibrium between formate and formyl amides. In the presence of Cu^{2+} , 6.7 moles of EDA will be generated for each mole of formate. Without Cu^{2+} , 4.0 moles of EDA will be generated for each mole of formate.

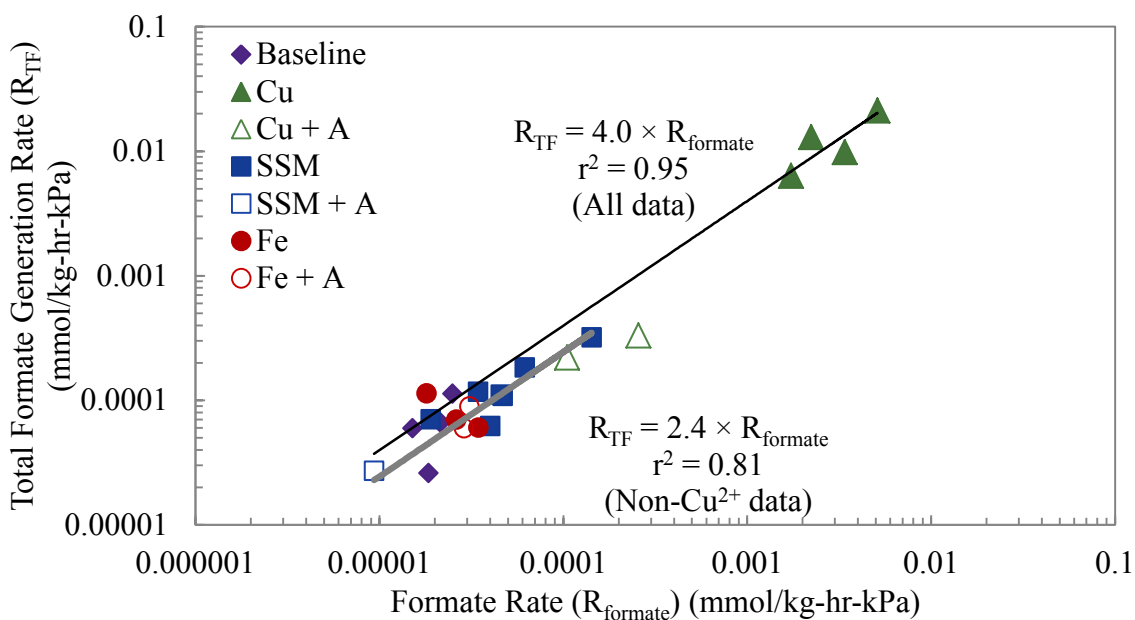


Figure 9.33: Correlation of R_{formate} and R_{TF} including linear regressions for all data (thin, black line) and only non- Cu^{2+} data (thick, gray line)

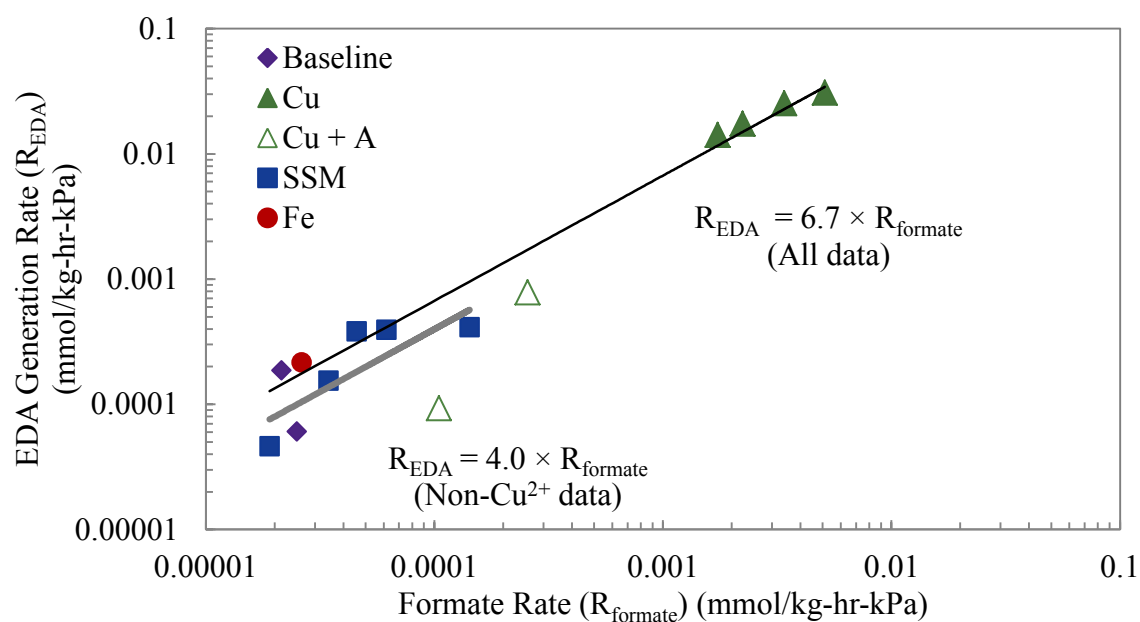


Figure 9.34: Correlation of R_{formate} and R_{EDA} including linear regressions for all data (thin, black line) and only non- Cu^{2+} data (thick, gray line)

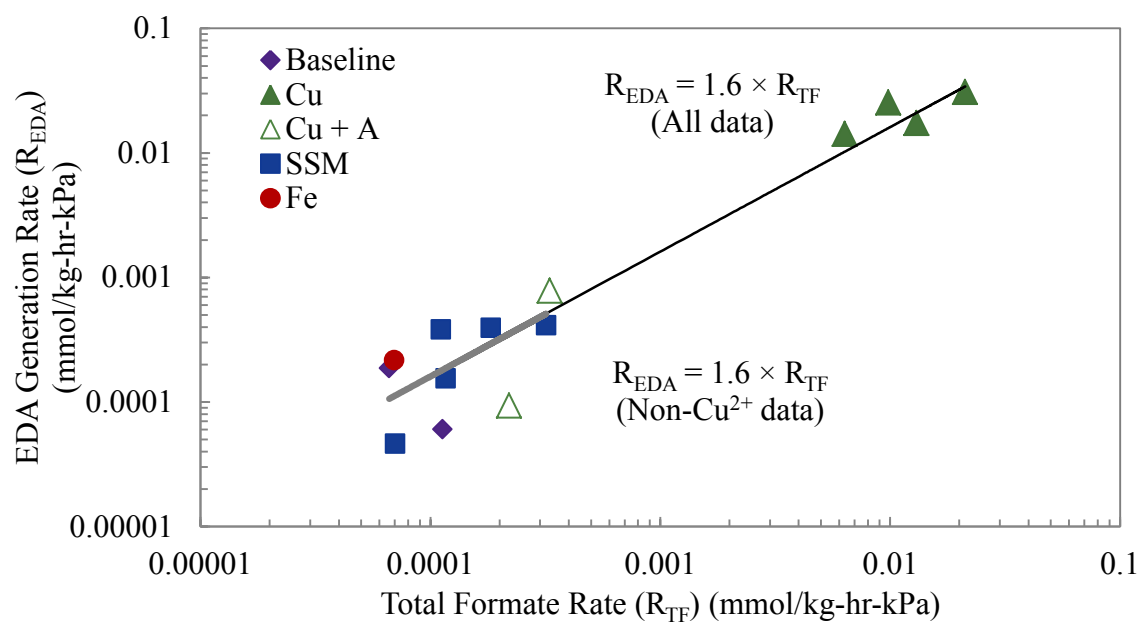


Figure 9.35: Correlation of R_{TF} and R_{EDA} including linear regressions for all data (thin, black line) and only non- Cu^{2+} data (thick, gray line)

Given the inconsistency and unreliability of PZ measurements, an estimation of the PZ loss rate based on the generation of degradation products can be performed. This will allow further understanding of the influence of metal catalysts on oxidation and allow estimation of PZ loss rates when rates based on cation IC showed significant error or positive slopes. Since total formate is consistently generated with EDA, it serves as a good marker for overall PZ oxidation. Using the R_{TF} data for all experiments and the slope of the correlation in Figure 9.31, an estimated PZ loss rate ($R_{PZ,est}$) can be calculated. This procedure essentially removes the scatter and places all data on the regressed correlation.

The $R_{PZ,est}$ based on the R_{TF} is compared to the R_{TF} in Figure 9.36. This figure is comparable to Figure 9.31, but with scatter in the PZ rate removed. From this figure, a few important new conclusions can be made. First of all, SSM have a slightly higher catalytic impact than Fe^{2+} based on the higher rates of SSM-catalyzed oxidation. There is scatter in both sets of data, and this may just be due to a lack of data for Fe^{2+} -catalyzed oxidation at higher temperature. Secondly, inhibitor is highly effective at decreasing SSM-catalyzed degradation. The experiment with both SSM and inhibitor A has the lowest PZ loss rate except for a baseline experiment. Finally, Inhibitor A is not effective at decreasing Fe^{2+} -catalyzed degradation. The experiment including both Fe^{2+} and Inhibitor A is in the middle of all of the Fe^{2+} experiments. Neither SSM or Fe^{2+} are strong catalysts for oxidation of PZ, but inhibitor A is able to decrease oxidation to extremely low levels in the SSM experiment. The same conclusions can be made when R_{PZ} is estimated from formate or EDA data. The estimation of a R_{PZ} allows for more information to be mined from degradation product data. Since that is obtained with more confidence than PZ data, conclusions can be drawn that are not apparent when looking at the raw concentration curves for each experiment.

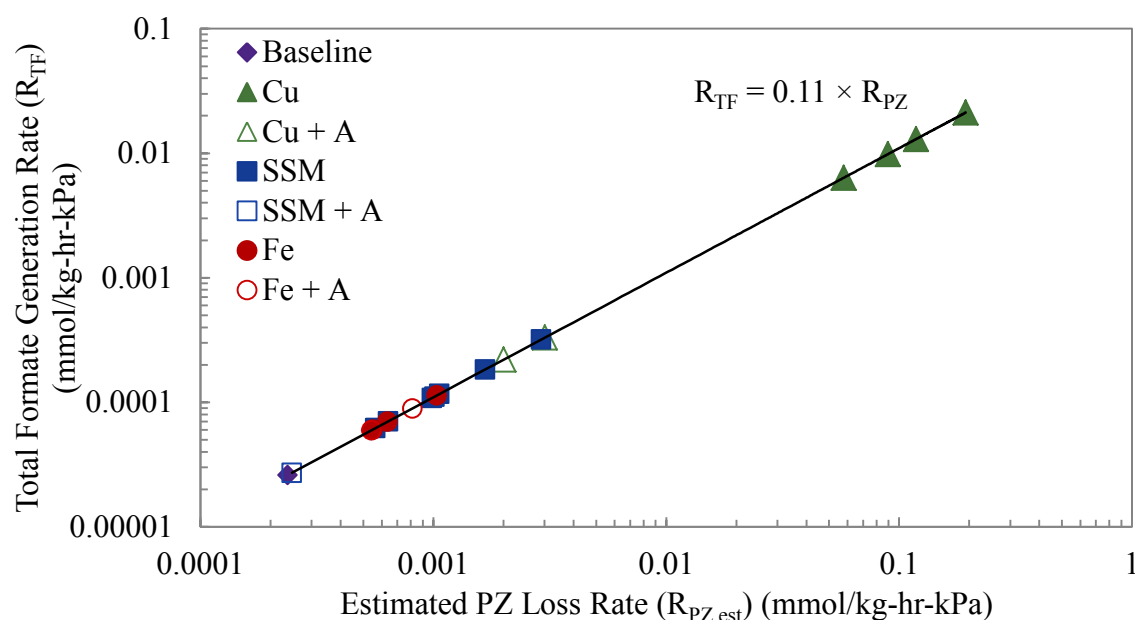


Figure 9.36: Correlation of the estimated PZ loss rate ($R_{PZ,est}$) with R_{TF}

A summary of the average rates in the presence of varying catalysts for the four species of interest is provided in Table 9.2. For the six experiments performed at 70 °C, each rate was extrapolated to the expected rate at 55 °C using the activation energy for each condition and species calculated in sections 8.5.2, 8.5.4, and 9.3.3.2. With the Cu^{2+} + Inhibitor A experiments, there was only one experiment at each temperature so the activation energy predicted exactly the conditions found in the 55 °C, so there is no standard deviation for the rates. Only one experiment was performed in the presence of SSM and 10 mM Inhibitor A, so there is also no standard deviation for this condition. The estimated PZ rate in the final column of Table 9.2 is an average rate based on the analysis shown in Figure 9.36 with the 70 °C adjusted to 55 °C using the activation energy for total formate for each catalyst condition. The total formate activation energy was used, rather than the PZ activation energy because this analysis is based on the idea that the total formate data is more reliable and indicates true PZ oxidation.

The rates from Table 9.2 for all of the catalysts conditions are also compared using a log scale in Figure 9.37, with just the formate compared in Figure 9.38. This analysis shows that although PZ oxidation is occurring in the presence of Fe^{2+} and SSM, the rate of PZ loss is likely below 0.0077 mmole PZ loss per kg per hr per kPa, well below levels seen with Cu^{2+} . The difficulty in accurately measuring the PZ loss rate, as detailed in Chapter 8, is evident by the standard deviation error bars in Figure 9.37 and Figure 9.38 and the difference between the raw PZ loss rate and the estimated PZ rate. In every case except Cu^{2+} , the estimated rate based on total formate production was lower than the raw PZ loss rate, indicating the error associated with accurately quantifying PZ oxidation. At low overall rates of oxidation, the quantification of degradation products is also subject to large standard deviations, as shown in Table 9.2. The large standard deviation of the PZ loss rate in the presence of Cu^{2+} is due to the influence of O_2 concentration, despite the normalization by O_2 partial pressure. The estimated PZ loss rates also indicate that Inhibitor A is not effective at reducing Fe^{2+} -catalyzed oxidation as the PZ loss rates and product rates are nearly the same.

Table 9.2: Average loss or generation rates for each catalyst condition during PZ oxidation with 70 °C data adjusted to 55 °C rates

Catalyst or Inhibitor (mM) ^a	Loss or Generation Rate $\times 10^3$ (mmol/kg-hr-kPa O_2)				
	PZ	Formate	Total Formate	EDA	PZ (est) ^b
4 Cu^{2+}	84.4 $\pm$ 31	2.0 $\pm$ 0.39	9.7 $\pm$ 4.0	15.8 $\pm$ 1.8	107 $\pm$ 65
4 Cu^{2+} + 100 A	8.9	0.11	0.22	0.09	2.0
SSM	3.1 $\pm$ 4.3	0.03 $\pm$ 0.02	0.09 $\pm$ 0.03	0.07 $\pm$ 0.06	1.2 $\pm$ 0.9
SSM + 10 A	0.46	0.01	0.03	0	0.2
1 Fe^{2+}	7.7 $\pm$ 7.0	0.03 $\pm$ 0.01	0.08 $\pm$ 0.03	0.07 $\pm$ 0.12	0.7 $\pm$ 0.3
1 Fe^{2+} + 100 A	1.8 $\pm$ 2.6	0.03 $\pm$ 0.001	0.07 $\pm$ 0.02	0	0.7 $\pm$ 0.2
Baseline	6.2 $\pm$ 2.5	0.02 $\pm$ 0.004	0.07 $\pm$ 0.04	0.06 $\pm$ 0.09	0.6 $\pm$ 0.3

^a SSM = stainless steel metal mixture, 0.4 mM Fe^{2+} , 0.1 mM Cr^{3+} , 0.05 mM Ni^{2+} ;

Baseline indicates no added metal catalysts

^b PZ (est) = the average PZ loss rate estimated from the total formate generation rate as shown in Figure 9.36

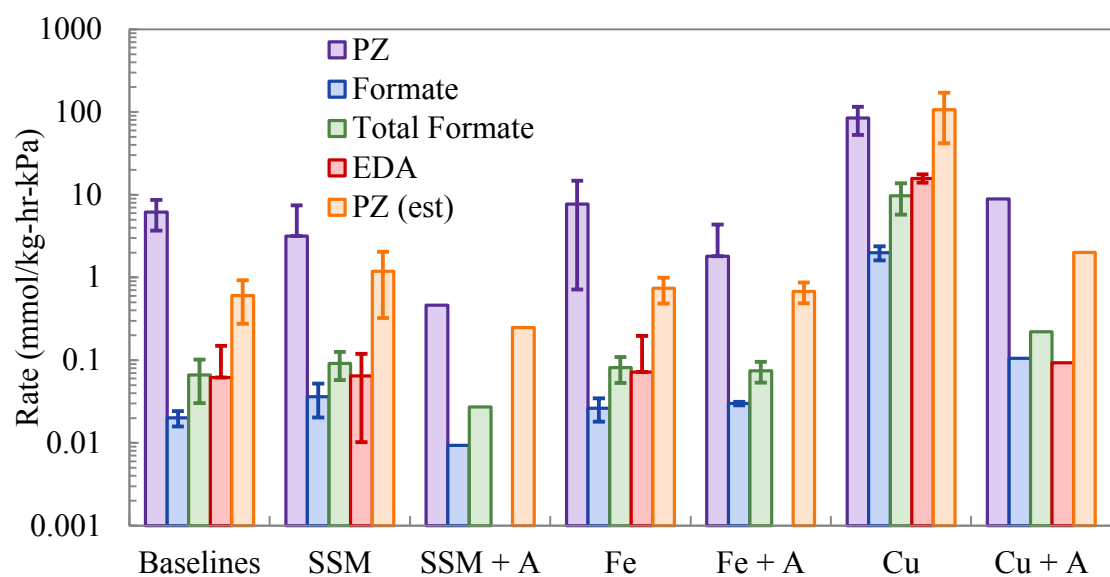


Figure 9.37: Comparison of PZ loss and product generation rates for catalysts systems tested

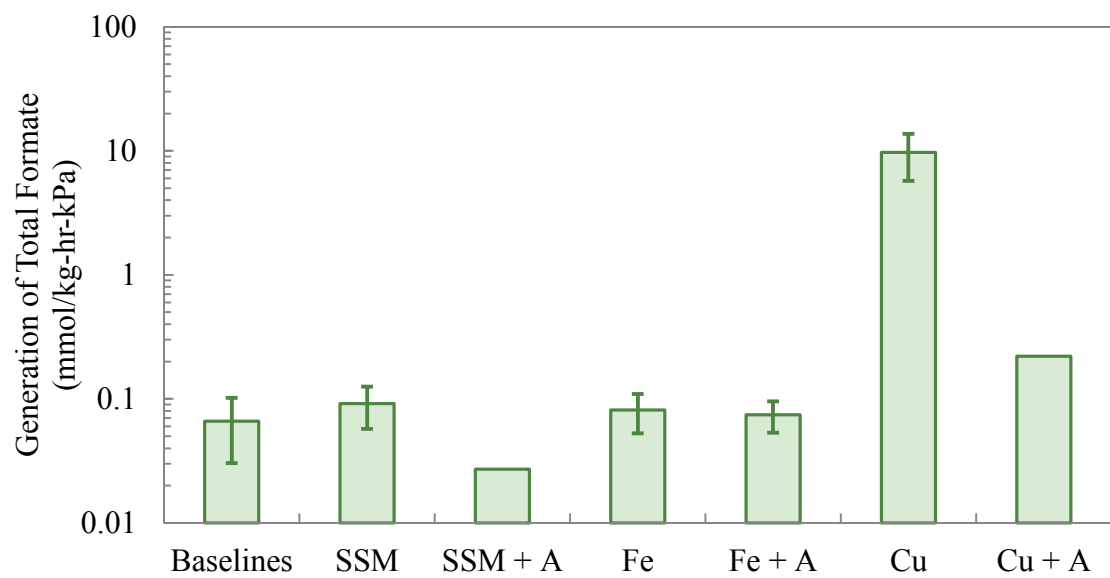


Figure 9.38: Comparison of total formate generation rates for catalysts systems tested

As an estimate of what may be expected in a real system, a rate of PZ loss and product generation can be calculated based on the expected conditions. With an inlet partial pressure of 5 kPa O₂ and absorber operation at 55 °C, the loss rate of PZ for Fe²⁺ or SSM conditions would be 0.0226 mmole per kg per hr. This estimate is based on the average rate, 0.0045 mmole per kg per hr per kPa, seen with either Fe²⁺ or SSM conditions at 55 °C, or 70 °C rates extrapolated to 55 °C. A residence time can be assumed where the solution spends only one third of its time exposed to O₂ in the absorber, absorber sump, and piping. If this rate is extrapolated, including the residence time, a loss of 66 mmole PZ per kg, or 0.066 mole PZ per kg, would be expected in one year of operation. This loss rate is likely an overestimate which provides a reasonable design specification for PZ-based absorber-stripper designs. Using the maximum rate seen in any Fe²⁺ or SSM experiment predicts roughly 0.23 mole PZ per kg loss in one year of operation. A better estimate of the residence time of the solvent when exposed to O₂ would make the estimate more accurate. This rate was based on PZ loss measurements, which may overestimate PZ loss due to the reasons discussed in this chapter and the previous one.

Performing the same estimate using the average PZ loss rate when 5 mM Cu²⁺-based corrosion inhibitor is present (5 kPa O₂, 55 °C absorber, solution exposed to O₂ one third of residence time), the loss rate of PZ is predicted to be 0.14 mmole per kg per hr or 1.23 mole PZ per kg in one year of operation. This is approximately 19 times more oxidation than seen in a Fe²⁺ or SSM system. With the addition of 100 mM of inhibitor A, the data suggest that this rate could be decreased to 0.015 mmole per kg per hr or 0.13 mole PZ per kg in one year of operation. This level of oxidation is 2 times higher than when only Fe²⁺ or SSM are present, but represent a workable level of oxidation if Cu²⁺ corrosion inhibitors are required based on the material of construction.

Table 9.3: Summary of PZ Loss and generation of degradation products in oxidation experiments on concentrated PZ

Expt.	PZ	Temp.	P _{CO2}	CO ₂ Ldg	P _{O2}	Additives	Loss or generation rate × 10 ³ (mmol/kg-hr-kPa O ₂)			
							PZ Loss	Formate	T. Formate	EDA
	m	°C	Pa	mol/mol alk	Pa	mM				
OE1	10	55	2	0.3	98	Fe (0.23), Cr (1.6), Ni (0.2)	12.44	0.047	0.108	0
OE2	10	55	2	0.3	98	Cu (4)	86.89	2.234	13.011	17.385
OE3	8	55	2	0.3	98	Fe (0.1), V (0.1)	4.49	0.065	0.194	0
OE4	8	55	2	0.3	98	Fe (0.1), Cu (5), A (100)	8.93	0.105	0.220	0.093
OE5	8	55	2	0.3	98	Fe (1)	15.46	0.018	0.113	0
OE6	8	55	2	0.3	98	Fe (1), A (100)	0	0.029	0.060	0
OE7	8	55	2	0.3	98	Fe (1), B (20)	8.63	0.004	0.003	0
OE8	8	55	2	0.3	98	Fe (1), C (30)	15.64	0.479	1.136	3.382
OE9	8	55	2	0.3	0	-	5.00	0.019	0.026	0
OE10	8	55	2	0.3	0	-	3.47	0.025	0.113	0.060
OE11	8	55	2	0.3	98	-	9.20	0.021	0.066	0.186
OE12	8	55	2	0.3	98	-	7.03	0.015	0.059	0
OE13	8	55	2	0.3	98	Fe (1)	5.95	0.035	0.060	0
OE14	8	55	2	0.3	98	Fe (1), A (100)	3.61	0.031	0.089	0
OE15	8	55	2	0.3	98	SSM	0	0.034	0.117	0.154
OE16	8	55	2	0.3	98	SSM, A (10)	0.46	0.009	0.027	0
OE17	8	55	2	0.3	98	Fe (1)	1.78	0.026	0.070	0.216
OE18	8	55	2	0.3	98	SSM	0.16	0.040	0.062	0
OE19	8	70	2	0.2	98	SSM	3.75	0.143	0.319	0.412
OE20	8	70	2	0.2	98	SSM, Formate (500)	4.99	NA	NA	0
OE21	8	70	2	0.2	98	SSM, Formaldehyde (500)	9.52	0.098	0.276	0.233
OE22	8	70	60	0.4	40	SSM	12.04	0.046	0.111	0.381
OE23	8	70	6	0.3	40	Cu (4)	78.46	3.401	9.830	25.295
OE24	8	70	6	0.3	40	Cu (4), A (100)	34.44	0.256	0.331	0.782

**Table 9.3: Summary of PZ Loss and generation of degradation products in oxidation experiments on concentrated PZ
(Continued)**

Expt.	PZ m	Temp. °C	P _{CO2} Pa	CO ₂ Ldg mol/mol alk	P _{O2} Pa	Additives mM	Loss or generation rate × 10 ³ (mmol/kg-hr-kPa O ₂)			
							PZ Loss	Formate	T. Formate	EDA
OE25	8	70	6	0.3	94	Cu (4)	195.30	5.109	21.210	30.778
OE26	8	70	6	0.3	94	SSM	13.71	0.062	0.183	0.394
OE27	8	55	2	0.3	40	Cu (4)	73.70	1.735	6.348	14.203
OE28	8	55	2	0.3	40	SSM	3.10	0.019	0.070	0.046

9.5 CONCLUSIONS

The a system with Fe^{2+} or SSM, 5 kPa O_2 in the inlet glue gas, an absorber operated at 55 °C, and with the solution exposed to O_2 approximately one third of the total residence time of the system, the maximum loss rate of PZ is expected to be 0.026 mmole per kg per hr or 0.23 mole PZ per kg solvent in one year of operation. This represents a maximum rate that is a reasonable estimate for design purposes and oxidation may occur even slower in real systems. Based on an average rate of PZ loss in the presence of Fe^{2+} or SSM, the expected rate of PZ loss is only 0.066 mole PZ per kg solvent in one year of operation.

In a similar system with 5 mM Cu^{2+} -based corrosion inhibitor, 5 kPa O_2 inlet gas, 55 °C absorber, and the same residence time, the loss rate of PZ is predicted to be 0.14 mmole per kg per hr or 1.23 mole PZ per kg solvent in one year of operation. With 100 mM of inhibitor A, this rate could be decreased to 0.015 mmole per kg per hr or 0.13 mole PZ per kg solvent in one year of operation. Oxidation in a system with a Cu^{2+} -based corrosion inhibitor could be controlled with an effective oxidation inhibitor like Inhibitor A.

Aqueous iron (Fe^{2+}) is only a weak catalyst for concentrated PZ oxidation up to a concentration of 5 mM. The rate of PZ loss in the presence of Fe^{2+} was found to be only 0.0077 ± 0.007 mmole PZ per kg per hr per kPa O_2 . For the generation of formate, total formate and EDA, average rates of only 0.00003 ± 0.000008 mmole formate, 0.00008 ± 0.00003 mmole total formate, and 0.0007 ± 0.0001 mmole EDA per kg per hr per kPa O_2 , respectively, were observed. V^{5+} is also a weak catalyst that cannot increase oxidation above the baseline experimental levels.

PZ is resistant to Fe^{2+} -catalyzed degradation in comparison with other well-known amines used for CO_2 capture processes. Only DGA oxidized noticeably slower than PZ while EDA, MEA and DEA degraded more rapidly in the presence of Fe^{2+} . Concentrated PZ was roughly 5.5 times more resistant to oxidation than 7 m MEA.

The combination of stainless steel metals (SSM), Fe^{2+} , Cr^{3+} , and Ni^{2+} , is only a weak catalyst for concentrated PZ oxidation. In the presence of SSM, the average rate of PZ loss was calculated to be only 0.0065 ± 0.006 mmole PZ per kg per hr per kPa O_2 . For the generation of formate, total formate and EDA, average rates of only 0.00006 ± 0.00004 mmole formate, 0.0001 ± 0.00009 mmole total formate, and 0.0002 ± 0.0002 mmole EDA per kg per hr per kPa O_2 , respectively, were observed.

PZ has enhanced resistance to SSM-catalyzed oxidation compared to 7 m MEA and 9 m MAPA. After 350 hours of oxidation, no PZ loss was observed compared to a loss of 35% for a comparable 7 m MEA experiment and complete oxidation of MAPA.

Cu^{2+} is a robust and effective catalyst for oxidation of concentrated PZ at both 55 and 70 °C. In the presence of Cu^{2+} , oxidation occurs rapidly with a loss rate of 0.109 ± 0.058 mmole PZ loss per kg per hr per kPa O_2 . Formate, total formate, and EDA were generated at rates of 0.0031 ± 0.001 mmole formate, 0.013 ± 0.006 mmole total formate, or 0.022 ± 0.008 mmole EDA per kg per hr per kPa O_2 , respectively. The rapid rate of Cu^{2+} -catalyzed degradation disallows the use of Cu^{2+} -based corrosion inhibitors in concentrated PZ systems without the presence of a separate oxidation inhibitor.

PZ was found to be 2.6 times more resistant to Cu^{2+} -catalyzed oxidation compared to 7 m MEA, but PZ was more easily oxidized by Cu^{2+} than both EDA and AMP.

Inhibitor A was effective at decreasing the PZ loss rate in both Fe^{2+} and SSM-catalyzed systems. Fe^{2+} and SSM cause only low levels of oxidation, as discussed above,

and Inhibitor A limits oxidation further through the decreased generation of degradation products. In systems examined with either 1 mM Fe^{2+} and 100 mM Inhibitor A or the standard SSM mixture and 10 mM Inhibitor A, almost no degradation was detected.

Inhibitor A is highly effective at inhibiting Cu^{2+} -catalyzed oxidation at 55 and 70 °C. Overall, the average PZ loss rate was decreased 10 times from 0.084 to 0.0089 mmole per kg per hr per kPa through the addition of 100 mM Inhibitor A. Oxidation was decreased to levels observed in the Fe^{2+} -catalyzed experiment.

The activation energy for PZ loss in the presence of Cu^{2+} and 100 mM Inhibitor A is 84 kJ per mole, three times higher than in the presence of Cu^{2+} alone. The activation energy for the generation of EDA is also increased 3.7 times indicating that Inhibitor A may work to inhibit the EDA generation mechanism specifically. The formate activation energy is very similar with and without Inhibitor A.

In the presence of 1 mM Fe^{2+} , Inhibitor B was effective at decreasing the concentration of degradation products formed during oxidation while Inhibitor C greatly increased degradation product concentrations. Neither Inhibitor B nor C was as effective as Inhibitor A for mitigating concentrated PZ oxidation.

Chapter 10 – Conclusions and Recommendations

The thermal degradation, oxidation, and physical properties of concentrated, aqueous PZ have been evaluated under conditions expected in industrial absorber-stripper systems for CO₂ capture from coal-fired flue gas. The conclusions developed in this thesis will be summarized with particular emphasis on what would be expected in a full scale system. Recommendations will be made for further study of the topics discussed. Additional study will be recommended where vital gaps in knowledge exist.

10.1 CONCLUSIONS

10.1.1 Thermal degradation of PZ

10.1.1.1 Expected rate of thermal degradation of PZ

At 150 °C, 8 molal (m) PZ with 0.3 mole CO₂ per mole alkalinity thermally degrades with a first order rate constant of $6.12 \times 10^{-9} \text{ s}^{-1}$, or approximately 500 mmole per kg after 30 weeks.

PZ thermal degradation can be described effectively with a first rate constant, k_1 , relating to a first order loss of PZ. For 8 m PZ with the expected lean loading of 0.3 mole CO per mole alkalinity, the fraction of PZ remaining (F_{PZ}) is provided by the following set of equations.

$$F_{PZ} = F_{PZ,0} \cdot \exp(-k_1 \cdot t) \quad (5.4)$$

$$k_1 = 2.78 \times 10^{14} \cdot \exp\left(\frac{183.5 \text{ kJ}}{\text{mole}} \cdot \frac{1}{RT}\right) \quad (5.13)$$

The activation energy of the system was determined to be 183.5 kJ per mole. At the rich loading condition, 8 m PZ with 0.4 mole CO₂ per mole alkalinity experiences slightly faster PZ loss according the following equation.

$$k_1 = 3.19 \times 10^{15} \cdot \exp\left(\frac{191.4 \text{ kJ}}{\text{mole}} \cdot \frac{1}{RT}\right) \quad (5.14)$$

The activation of the rich loaded condition was determined to be 191.1 kJ per mole.

The concentration of CO₂ generally increases the thermal degradation of concentrated PZ. At 175 °C, PZ degradation increased as a linear function of CO₂ loading up to 0.3 mole CO₂ per mole alkalinity. A maximum rate of degradation was observed between 0.3 and 0.4 mole CO₂ per mole alkalinity and then a decreased rate at

the very rich loading of 0.47 mole CO₂ per mole alkalinity. This behavior suggests that solution speciation with changes in CO₂ loading strongly affect thermal degradation. Model predictions of speciation at 175 °C do not indicate one species is solely responsible for this behavior, but it is rather a combination of H⁺PZ, PZCOO⁻, and H⁺PZCOO⁻ concentrations.

On the whole, PZ loss during thermal degradation is first order in PZ, as is the basis of the k_1 analysis. A slight effect of increasing PZ concentration was observed that increases the k_1 value approximately 30% from 4 to 12 m PZ at the same conditions (0.3 mole CO₂ per mole alkalinity, 175 °C). Highly concentrated PZ solutions do not match this behavior and degradation kinetics of more than first order was observed in 20 m PZ with 0.3 mole CO₂ per mole alkalinity.

The addition of Cu²⁺, Fe²⁺, Cr³⁺, or Ni²⁺ did not affect the rate of PZ thermal degradation. Solutions degraded in the absence of metals were found to have slightly repressed rates of generation of formate and formyl amides, indicating it is likely that the mechanisms responsible for generation of products are catalyzed by metals. Concentrated PZ has decreased tendency to corrode stainless steel metals in comparison to MEA, EDA, and MAPA based on the concentration of leached metals during thermal degradation.

The addition of 100 mM of Inhibitor A decreased PZ loss during thermal degradation by approximately 20% and decreased the production of total formate and EDA.

10.1.1.2 Degradation products of thermal degradation of PZ

The most abundant degradation products of thermally degraded 8 m PZ are N-formyl PZ (FPZ), NH₄⁺, and N-(2-aminoethyl) piperazine (AEP). These three molecules account for 57% of nitrogen and 45% of carbon lost during degradation as PZ and CO₂.

Other prominent products include, in order of decreasing impact on the nitrogen and carbon balance, 2-imidazolidone (2-Imid), N-(2-hydroxyethyl) piperazine (HEP), N-ethylpiperazine (EPZ), ethylenediamine (EDA), 1-Methylpiperazine (1-MPZ), formate, acetate, and other heat stable salts such as oxalate and glycolate.

After 20 weeks of thermal degradation at 165 °C, 74% and 63%, respectively, of the nitrogen and carbon lost in the form of PZ and CO₂ was recovered in the form of quantifiable degradation products. For the same experiment, 87% and 60% of the lost CO₂ molecules and “ethyls” were recovered.

10.1.1.3 Postulated pathways for the generation of thermal degradation products

It is postulated that thermal degradation of PZ proceeds through a variety of S_N2 type substitution reactions that result in ring opening and polymerization products. In the first step of the mechanism, 1-[2-[(2-aminoethyl) amino]ethyl] PZ (AEAEPZ) is believed to be formed from a ring opening S_N2 reaction of PZ with H⁺PZ.

The limiting rate was found to require protonated amine, but not CO₂, which agrees with the proposed production of AEAEPZ from H⁺PZ and PZ. Further reaction of AEAEPZ with CO₂ is predicted to form the internal urea of AEAEPZ.

AEAEPZ is believed to also react with PZ or other amines through S_N2 substitution to produce AEP, EDA, and NH₄⁺. Elimination reactions of AEAEPZ could produce HEP and other products. Two of the most important suspected species, AEAEPZ and the urea of AEAEPZ, have not been confirmed to be present, but are believed to represent two major, unidentified peaks on the cation IC.

Degradation of concentrated PZ in the presence of HCO₃⁻ demonstrated that PZ loss and generation of formate and EDA depend on the presence of H⁺PZ to proceed.

NMR analysis of degraded $^{13}\text{CO}_2$ -loaded PZ solutions conclusively showed that formate is generated directly from the CO_2 in solution. The mechanism is separate from the primary degradation of PZ through substitution reactions and is not clear at this point. Formate is not generated from the break-up of the PZ backbone itself. Formate is generated consistently as a major product in all oxygen-poor, CO_2 loaded amine thermal degradation where carbamate polymerization is not the major degradation mechanism.

At 150 °C, EDA is in equilibrium with 2-Imidazolidone, the cyclic urea of EDA. The equilibrium constant, K_{EQ} , tends toward a value between 0.0004 and 0.0006 kg solution per mole. EDA is produced during the thermal degradation of PZ through reactions that do not require CO_2 . In the presence of CO_2 , EDA reacts to form 2-Imid, a stable product. In the absence of CO_2 , EDA accumulates in solution.

During thermal degradation from 135 to 175 °C, and oxidation at 55 °C, formyl amides are in equilibrium with formate. Formyl amides were consistently produced at higher concentrations than formate. The ratio of formyl amides to formate produced was a strong function of PZ concentration and CO_2 concentration, but not temperature. For 8 m PZ from 55 to 175 °C, the ratio can be described as follows where the CO_2 loading, α , is in units of mole CO_2 per mole alkalinity (Equation 6.24). For 20 m PZ at 175 °C, the ratio can be described as follows (Equation 6.25).

$$\frac{C_{\text{FA}}}{C_{\text{F}}} = 5.54 \times \alpha + 0.30 \quad (6.24)$$

$$\frac{C_{\text{FA}}}{C_{\text{F}}} = 7.73 \times \alpha + 3.10 \quad (6.25)$$

The O₂ present as dissolved O₂ or in the headspace of the thermal cylinders was found to have a minimal effect that could not account for all quantified formate and formyl amides generated in typical thermal degradation experiments.

10.1.2 Oxidation of PZ

10.1.2.1 Expected oxidation rate of concentrated PZ

A system with Fe²⁺ or SSM, 5 kPa O₂ in the inlet glue gas, an absorber operated at 55 °C, and the solution exposed to O₂ approximately one third of the total residence time of the system, the maximum loss rate of PZ is expected to be 0.026 mmole per kg per hr or 0.23 mole PZ per kg solvent in one year of operation. This represents a maximum rate that is a reasonable estimate for design purposes and oxidation may occur even slower in real systems. Based on the average rate of PZ loss in the presence of Fe²⁺ or SSM, the expected rate of PZ loss is only 0.066 mole PZ per kg solvent in one year of operation.

In a similar system with 5 mM Cu²⁺-based corrosion inhibitor, 5 kPa O₂ inlet gas, 55 °C absorber, and the same residence time, the loss rate of PZ is predicted to be 0.14 mmole per kg per hr or 1.23 mole PZ per kg solvent in one year of operation. With 100 mM of inhibitor A, this rate could be decreased to 0.015 mmole per kg per hr or 0.13 mole PZ per kg solvent in one year of operation. Oxidation in a system with a Cu²⁺-based corrosion inhibitor could be controlled with an effective oxidation inhibitor like Inhibitor A.

10.1.2.2 Catalysis and inhibition of oxidation of concentrated PZ

Aqueous iron (Fe²⁺) is only a weak catalyst for concentrated PZ oxidation up to a concentration of 5 mM. The rate of PZ loss in the presence of Fe²⁺ was found to be only

0.0077 ± 0.007 mmole PZ per kg per hr per kPa O₂. V⁵⁺ is also a weak catalyst that cannot increase oxidation above the baseline experimental levels.

Concentrated PZ is 5.5 times more resistant to Fe²⁺-catalyzed degradation than 7 m MEA. DGA[®] oxidized noticeably slower than PZ while EDA and DEA degraded more rapidly in the presence of Fe²⁺.

The combination of stainless steel metals (SSM), Fe²⁺, Cr³⁺, and Ni²⁺, is only a weak catalyst for concentrated PZ oxidation. In the presence of SSM, the average rate of PZ loss was calculated to be only 0.0065 ± 0.006 mmole PZ per kg per hr per kPa O₂.

Cu²⁺ is a robust and effective catalyst for oxidation of concentrated PZ at both 55 and 70 °C. In the presence of Cu²⁺, oxidation occurs rapidly with a loss rate of 0.109 ± 0.058 mmole PZ loss per kg per hr per kPa O₂.

The rapid rate of Cu²⁺-catalyzed degradation disallows the use of Cu²⁺-based corrosion inhibitors in concentrated PZ systems without the presence of a separate oxidation inhibitor.

PZ has enhanced resistance to SSM-catalyzed oxidation compared to 7 m MEA and 9 m MAPA. After 350 hours of oxidation, no PZ loss was observed compared to a loss of 35% for a comparable 7 m MEA experiment and complete oxidation of MAPA. PZ was 2.6 times more resistant to Cu²⁺-catalyzed oxidation compared to 7 m MEA, but PZ was more easily oxidized by Cu²⁺ than both EDA and AMP.

Inhibitor A is highly effective at inhibiting Cu²⁺-catalyzed oxidation at 55 and 70 °C. Overall, the average PZ loss rate was decreased 10 times from 0.084 to 0.0089 mmole per kg per hr per kPa through the addition of 100 mM Inhibitor A. Oxidation was decreased to levels observed in the Fe²⁺-catalyzed experiment. Inhibitor A was effective at decreasing the PZ loss rate in both Fe²⁺ and SSM-catalyzed systems.

The activation energy for PZ loss in the presence of Cu^{2+} and 100 mM Inhibitor A is 84 kJ per mole, three times higher than in the presence of Cu^{2+} alone. The activation energy for the generation of EDA is also increased 3.7 times indicating that Inhibitor A may work to inhibit the EDA generation mechanism specifically. The formate activation energy is very similar with and without Inhibitor A.

10.1.2.3 Oxidation products of concentrated PZ

The identified oxidation products of PZ include EDA, carboxylate ions (formate, oxalate, acetate), amides (formyl amides, oxalyl amides, and acetyl amides of PZ or EDA), and ammonium (NH_4^+). Glycolate, nitrite and nitrate are minor products that were inconsistently generated.

TOC and TN analysis indicated the presence of unidentified liquid phase degradation products. Both a baseline experiment and a heavily oxidized solution in the presence of Cu^{2+} were found to have maintained the TOC concentration in the liquid phase during the experiment, indicating unquantified liquid phase oxidation products. Both experiments also experienced a quantifiable decrease in TN concentration, indicating the loss of volatile molecules such as ammonia, NO_x , or N_2 .

N and C mass balances on oxidized solutions were poor, especially with low rates of oxidation. In OE11, a baseline experiment, only 2.5% and 0.7% of the N and C, respectively, lost as PZ was recovered. Inclusion of an estimate of the volatile N from the TN analysis increased the N balance to 73% of the lost PZ. For OE18, an experiment with SSM, only 3.4% and 5.2% of the N and C lost as PZ was recovered in products. In OE25, the most heavily oxidized PZ solution in the study, 27% and 23% of the N and C, respectively, from the lost PZ was recovered as liquid phase products. With the inclusion

of an estimate of 2650 mmole volatile N per kg from TN, 69% of the lost PZ N was recovered.

It is suspected that aldehydes (e.g. formaldehyde, acetaldehyde, and hydroxyacetaldehyde), alcohols (e.g. methanol, ethanol, and, ethylene glycol), ureas of PZ, amino acids (e.g. N-(2-aminoethyl) glycine, N,N'-1,2-ethanediylbis-glycine), and oxidized PZ molecules (2-piperazinone, 2,5-piperazinedione, 2-piperazinol, 1,2,3,6-tetrahydro pyrazine, 1,2,3,4,-tetrahydro pyrazine, 1-piperazineaceticacid) are a significant portion of the unidentified products. Amino acid liquid chromatography indicates that this may be an important functional group in oxidation products, but no amino acids were able to be identified.

The addition of 500 mM formate to 8 m PZ eliminated the production of EDA, suggesting that PZ oxidation was significantly decreased. Formate is not oxidized to CO₂ in PZ oxidation experiments but may act as a weak oxidation inhibitor for PZ.

The addition of 500 mM formaldehyde to 8 m PZ created stable, dense, white foam that persisted through the oxidation experiment. The foam is likely a polymer of formaldehyde and PZ that was stable for over 10 months.

The foaminess coefficient is not a consistent measurement technique and does not produce repeatable results. The amount of time between the end of an experiment and the foaminess test appears to impact results, which is an unforeseen problem in the assay.

10.1.3 Thermal degradation of PZ structural analogs and other CO₂ capture amines

Calculated first order rate constants for amine thermal degradation, k_1 , were successfully translated into predicted stripper temperatures that represent a maximum acceptable degradation rate. Morpholine (Mor) was determined to be the most stable amine tested to date with a predicted stripper temperature of 170 °C. Piperidine (PD) and

piperazine (PZ) and with 0.3 mole CO₂ per mole alkalinity were the next most stable amines with estimated stripper temperatures of 166 and 163 °C, respectively. Cyclic, 6-membered amines such as PZ, Mor, and PD were determined to be exceptionally resistant to thermal degradation.

Substituted PZs such as 1-methylpiperazine (1-MPZ), 2-methylpiperazine (2-MPZ) and PZ analogs such as hexamethylenediamine (HMDA) were shown to be stable, tolerating temperatures between 148 and 160 °C. PZ structural analogs with 5- or 7-membered rings such as pyrrolidine (Pyr), hexamethyleneimine (HMI), and homopiperazine (HomoPZ), were found to have diminished stability. Methylation of the PZ structure at the 1- or 2-position also decreased stability of the PZ molecule to thermal degradation.

The most instable amines measured, such as N-(2-hydroxyethyl) ethylenediamine (HEEDA), 2-methylaminoethanol (MMEA), diethanolamine (DEA), N-methylethanolamine (MAE), diethanoltriamine (DETA), and 3-(methylamino) propylamine (MAPA), which will all degrade significantly at temperatures above 120 °C, are longer straight-chain alkyl amines with at least one secondary amino function and either hydroxyl groups, methyl groups, or multiple amino function. The estimated stripper temperature for 3.5 to 11 m MEA solutions with 0.2 to 0.5 mole CO₂ per mole alkalinity ranged from 111 to 126 °C.

A thermal equilibrium between PZ, 1-MPZ, and 1,4-DMPZ was discovered that offers the opportunity for a blended solvent that is resistant to overall thermal degradation. At 150 °C, the equilibrium constant for the disproportionation of 1-MPZ into PZ and 1,4-DMPZ with 0.3 mole CO₂ per mole alkalinity was found to be 0.28. A tertiary blend designed around this constant, 3.9 m PZ / 3.9 m 1-MPZ / 0.2 m 1,4-DMPZ

degraded with a k_1 value of $8.44 \times 10^{-9} \text{ s}^{-1}$, only 37% higher than the k_1 for 8 m PZ with 0.3 mole CO_2 per mole alkalinity.

PZ was not found to preferentially degrade in a blend of 4 m PZ + 4 m 1-MPZ since an equilibrium is being established that occurs more rapidly than thermal degradation. PZ is preferentially degraded in blends with MDEA and MEA. In the presence of MDEA, PZ thermally degrades up to 15 times faster than MDEA. The stability of PZ when blended with another amine depends heavily on the pK_a or nucleophilic strength of the amine. Blending PZ has been previously stated as inadvisable, but could be advantageous when matched with a similarly stable molecule, such as 1-MPZ or 2-MPZ.

10.1.4 Physical properties of PZ

At 0 °C, 8 m PZ will not precipitate solids between 0.32 and 0.44 mole CO_2 per mole alkalinity. At an operating temperature of 40 °C, 8 m PZ will be an aqueous solution between 0.1 and 0.45 mole CO_2 per mole alkalinity. The room temperature (20 °C) solubility of unloaded PZ is 14 weight %, or 1.9 m PZ, while the soluble loading range is approximately 0.25 to 0.4 mole CO_2 per mole alkalinity at this temperature. Transition temperatures for concentrated PZ were measured over a range of CO_2 loading and hysteresis was observed in the temperature at which crystals formed when cooled or precipitation melted when heated.

The viscosity of 8 m PZ at 40 °C with 0.4 mole CO_2 per mole alkalinity is 11.4 cP, higher than that of 9 m MEA with 0.5 mole CO_2 per mole alkalinity (3 cP). Solutions of 60wt% DGA[®] with 0.4 mole CO_2 per mole alkalinity, a commercial gas treating solvent, has a viscosity 13.7 cP, even higher than PZ. The viscosity of 8 m PZ is given

by Equation 4.9 in terms of the viscosity of water (cP), μ_{water} , concentration of CO₂ (mole per kg), C_{CO_2} , concentration of PZ (mole per kg), C_{PZ} , and temperature (K), T.

$$\ln\left(\frac{\mu}{\mu_{\text{water}}}\right) = 1.723 + 2.63 \cdot C_{\text{CO}_2} - 1.019 \cdot C_{\text{PZ}} - 0.527 \cdot C_{\text{CO}_2} \cdot C_{\text{PZ}} + \frac{-778 \cdot C_{\text{CO}_2} + 355.2 \cdot C_{\text{PZ}} + 169.3 \cdot C_{\text{CO}_2} \cdot C_{\text{PZ}}}{T} \quad (4.9)$$

Density of 5 to 12 m PZ solutions was regressed in terms of the density of water, ρ_{water} , C_{CO_2} , and C_{PZ} , and the resulting regression is shown in Equation 4.1. The effect of temperature on density was eliminated by including ρ_{water} at a given temperature.

$$\frac{\rho}{\rho_{\text{water}}} = 0.0407 \cdot C_{\text{CO}_2} + 0.008 \cdot C_{\text{PZ}} + 0.991 \quad (4.1)$$

Online measurement of density and viscosity will permit accurate on-line estimates of PZ concentration and CO₂ loading. On-line viscosity and density monitors can be employed in a pilot plant, demonstration plant, or full scale CO₂ capture application as an inexpensive, easy, and effective way to continually monitor the condition of a PZ solvent. Both PZ concentration and CO₂ loading have traditionally been offline analyses that take on the order of minutes or hours to complete. Online monitoring allows for instant feedback and constant monitoring of the solvent conditions where maintaining the solution within physical solubility windows is a crucial operational concern.

The regression for viscosity was developed with only 8 m PZ data and this limits its application. Viscosity of PZ solutions is complicated and regressions across large PZ concentration ranges generally contain unacceptable levels of error for online monitoring

applications. The density regression should be very robust in applications centering around 8 m PZ, the most likely concentration of concentrated PZ systems.

A blend of 4 m PZ / 4 m 2-MPZ, being developed for its beneficial physical solubility, has density less than 1% higher than an 8 m PZ solution with the same alkalinity. On the other hand, a blend of 5 m PZ / 2 m 1-MPZ / 1 m 1,4-DMPZ has up to a 3% lower density but 23% higher viscosity. All blends of PZ with substituted PZ molecules had very similar density values to PZ itself, but up to 30% higher viscosity. Blends can have advantageous characteristics, but can also result in unfavorable changes to density and viscosity.

10.2 RECOMMENDATIONS

Absorption-stripping with aqueous, concentrated piperazine (PZ) is a viable retrofit technology for post-combustion CO₂ capture from coal-fired power plants. The low thermal degradation and oxidation rates observed under conditions similar to those expected in industry are an important advantage of this solvent. Stability to temperature and oxidation, along with fast rates of CO₂ absorption, high CO₂ capacity, and a moderate heat of absorption recommend aqueous, concentrated PZ as the solvent of choice for absorption-stripping for CO₂ capture.

Before deployment of this solvent, there are some unanswered questions that could be investigated to understand the solvent more fully. There is further work recommended on specific lab-scale degradation experiments that will allow more rigorous explanation of the degradation seen in this dissertation. Recommendations for understanding factors important to the responsible implementation of this type of system are also discussed. The following recommendations are listed in order of importance to

indicate what must be more fully understood before full-scale implementation of a PZ system.

10.2.1 Environmental implications of PZ use at a large scale

One area where this project did not focus is the environmental implications of a full-scale PZ-based CO₂ capture system. This is a crucial issue that needs priority attention before any full-scale realization of PZ systems. One of the primary issues is the unknown environmental impact and fate of the thermal degradation and oxidation products. The issues involved with environmental impact include volatility of PZ, volatility of degradation products, reactions of these products in the atmosphere, and handling and storage of liquid and solid wastes created during reclaiming activities. The volatilities of many of the products are unknown, such as amides, or are already known to be high, such as ammonia and 1,4-dimethylpiperazine (1,4-DMPZ) (Rochelle, 2011). Reclaiming is another area where environmental concerns must be considered when designing a PZ reclaiming system. The overall degradation rate of PZ is expected to be low, but the issues surrounding the environmental impact of degradation products should be thoroughly researched before full-scale implementation of PZ.

10.2.1.1 Nitrosamine generation during PZ use

Another important topic related to the environmental impact of PZ is the generation, identification, and quantification of nitrosamines produced during PZ degradation. Nitrosamines are a class of compounds with a R₁N(-R₂)-N=O functional group. A majority of nitrosamines are carcinogenic or potentially carcinogenic to humans, demonstrating the importance of identifying any nitrosamines created during PZ degradation. During the degradation of amines like PZ, nitrite (NO₂⁻) and nitrate (NO₃⁻) can be produced in small quantities. In highly oxidative environments, significant

quantities can be created, such as in the Cu^{2+} -catalyzed oxidation of PZ. Secondary amines can react to form an amine free radical species which can react with NO to form nitrosamines (Challis and Challis 1982).

Toxicological studies on animals have shown that N-mononitrosopiperazine (MNPZ), N,N'-dinitrosopiperazine (DNPZ), N-Nitroso-3-hydroxypyrrolidine, and N-nitrosodiethanolamine can all be derived from PZ in vivo (Tricker et al. 1991). MNPZ has been reported to be mutagenic and carcinogenic in animals although this may be attributed to the rapid conversion to DNPZ which is highly mutagenic and carcinogenic (Elespuru and Lijinsky 1976; Love et al. 1977). Given these few nitrosamines as a starting point, the importance of finding nitrosamines as degradation products is crucial to fully understanding the PZ solvent system and appreciating its full safety and environmental impact.

Large concentrations of nitrosamines are not expected to be produced under standard operating conditions of a PZ-based CO_2 capture system. NO_2^- , which can produce NO in solution, is only found in trace quantities outside of heavily oxidized PZ solutions. In real systems, oxidation will not be allowed to progress this far in any case due to loss of CO_2 capture capacity and cost. Also, any nitrosamine created is not expected to be stable at high temperatures, so any reaching the stripping section of the system will not persist. A real concern though is the generation of nitrosamines either in the absorber itself, where they could volatilize and reach the atmosphere, or the photolytic reaction of volatile PZ in the atmosphere with NO_x molecules to create nitrosamines in the atmosphere, after leaving the CO_2 capture system. Any of these possibilities need to be fully understood before any application of PZ at a large scale.

10.2.2 Identification of degradation products

One of the most important recommendations of this dissertation is the need for more sophisticated analytical methods to detect unknown degradation products. In both thermal degradation and oxidation of PZ, there is significant gap in the mass balance that was determined to be liquid phase, unknown degradation products. Identifying these products is important for a variety of reasons including understanding their environmental impact, understanding the degradation mechanisms that produce them, studying the best way to reclaim them, and learning how to mitigate or prevent their production.

Important classes of compounds that have not been identified and quantified at this point are aldehydes, alcohols, and ureas. These types of molecules are suspected in both oxidation and thermal degradation of PZ and could represent significant portions of the overall degraded mass balance. Only one significant urea (2-Imid) has been positively identified and many others are suspected, such as the urea of AEAEPZ. No aldehydes or alcohols have been identified yet, but many such as formaldehyde, acetaldehyde, and methanol are strongly suspected.

10.2.3 Further investigation of thermal degradation

Although the rate of thermal degradation with respect to temperature, PZ concentration, and CO₂ concentration is fairly well understood as a result of this dissertation, the specific mechanisms responsible for degradation are not well known. More work is needed to determine exactly which mechanisms are responsible for the loss of PZ observed. In collaboration with this work will be the identification of thermal degradation products, as discussed above, and a better understanding of speciation at high temperature.

High temperature speciation of any amine system is needed to fully grasp the mechanisms that are occurring during degradation. High temperature speciation can be predicted based on current models, but are mostly extrapolations of low temperature NMR speciation results. Medium or high temperature experimental data (80-175 °C) for PZ speciation would make the speciation predicted by the thermodynamic models more robust and could add insight into the mechanisms responsible for thermal degradation.

More thermal degradation experiments are also recommended to determine the details of the dominant mechanisms. Some experiments were performed with the express intention of learning about the mechanisms, but more would be needed to solidify the hypothesized reactions. Work focused on speciation, such as the acidified experiments in section 6.3, could be extended to investigate the role of specific species during degradation. Also, more spiked experiments, like those performed with EDA and 2-Imid, could be done with other degradation products to determine their behavior.

10.2.4 Further investigation of oxidation

There are many effects related to PZ oxidation that were not fully explored in this project due to time or equipment constraints. First, differences in the generation of degradation products due to various metal catalysts should be further explored. With the application of novel techniques to identify and quantify degradation products, the products expected in each particular system can be identified. This will allow a more directed analysis of systems in the field using each catalyst set based on knowledge of what is expected to be the most dominant product or which indicates overall oxidation rates.

If inhibition is needed, further tests should be performed that isolate the exact concentration of Inhibitor A, for example, which is needed to see inhibition. The use of

100 mM Inhibitor A is likely more concentrated than needed and an optimization should be performed based on the catalyst system expected to be present.

The catalytic effect of Fe^{2+} and SSM should be further investigated. Significant error and poor repeatability were observed in these experiments due to very low rates of PZ oxidation. If an experiment was developed to accurately measure low rates of PZ oxidation, the effect of each catalyst could be determined with better accuracy. This is an important point since the use of stainless steel as a material of construction is the most likely choice of CO_2 capture systems.

The effect of CO_2 concentration on PZ oxidation was not fully understood during the course of this project. Additional experiments could determine if a large difference in oxidation rate is expected across the absorber and absorber sump due to differences in CO_2 concentration.

10.2.5 Monitoring of PZ degradation in pilot, demonstration, or full-scale plants

When PZ is used in pilot or demonstration plants, a number of monitoring tools are recommended to fully track the progress of PZ as a solvent. First, the PZ and CO_2 concentrations should be monitored regularly to maintain alkalinity and the appropriate CO_2 loading range. This can be achieved through online density and viscosity measuring, as discussed in Chapter 4. This is also important in order to maintain an aqueous solution to avoid solubility issues with PZ. This represents the very minimal level of monitoring needed to use PZ. Other techniques such as acid titration or total inorganic carbon (TIC) should also be employed offline to ensure the accuracy of the online measurements.

A second level of monitoring for degradation is suggested for longer term pilot plant tests, demonstration plants, and full-scale application. With longer term tests, the

rate of degradation, either from oxidation or thermal degradation, is very useful in order to understand changes in CO₂ capacity or shifts in the loading range that can be seen in degraded solution. This project has identified some of the major degradation products that can be quantified through chromatographic techniques. A basic level of monitoring for degradation products would include a dual IC system (or two separate systems) that can test for liquid phase concentrations of anions and cations. This will allow quantification of heat stable salts (formate, oxalate, acetate, glycolate), potential nitrosamine precursors (nitrate and nitrite), ammonium, amine based degradation products (EDA, AEP, and others), and quantify the parent amine itself. The methods employed in this project, as detailed in Appendix C, could be replicated on any ion chromatography system and would allow monitoring of some of the important liquid phase products.

A third level of monitoring should be used for very long-term experiments where the effect of degradation of PZ would be the most pronounced. This implies the use of high performance liquid chromatography (HPLC), nuclear magnetic resonance (NMR) or other advanced techniques to extend the quantification of degradation products. HPLC techniques were only used in this project to quantify 2-imidazolidone, but can be extended to include more amine products and amino acids. Developments in the quantification of amides, ureas, aldehydes, and alcohols will hopefully lead to chromatographic techniques that can monitor these important species in solution.

Appendix A – Nomenclature, Abbreviations, and Glossary of Degradation Products

The first two tables in this appendix detail the nomenclature and abbreviations used throughout this thesis. This includes symbols used for variables (rate constants, μ , ρ), symbols representing units (g, kg, m), abbreviations for molecules (PZ, EDA, CO₂), and abbreviations for equipment and materials (LGF, TOR). The final table in this appendix is a summary of the degradation products discussed frequently in chapters 5 through 9. This summary includes identified and quantified products as well as suspected products and includes pertinent identifying data. A more detailed list of the chemicals used including their purity, source, and synonyms is given in Appendix B.

Table A.1: List of Abbreviations

Symbol	Units	Definition
1-EPZ	-	1-Ethyl piperazine
1-MPZ	-	1-Methyl piperazine
1-PA	-	1-Piperazineacetic acid
1,4-DMPZ	-	1,4-Dimethyl piperazine
1,4-DEPZ	-	1,4-Diethyl piperazine
2-MPZ	-	2-Methyl piperazine
2-PE	-	2-Piperidineethanol
2-PM	-	2-Piperidinemethanol
2,5-PZdione	-	2,5-Piperazinedione
3a1p	-	3-Amino-1-propanol
4a1b	-	4-Amino-1-butanol
5a1p	-	5-Amino-1-propanol
6a1h	-	6-Amino-1-hexanol
AEAEPZ	-	1-[2-[(2-aminoethyl) amino]ethyl] piperazine
AEI	-	1-(2-Aminoethyl)-2-imidazolidone
AEP	-	1-(2-Aminoethyl) piperazine
AMP	-	2-Amino-2-methyl-1-propanol
AP	-	3-Aminopropanol
bHEP	-	N,N'-bis(2-hydroxyethyl) piperazine
C	-	Carbon; a carbon atom within a molecule
CO ₂	-	Carbon dioxide
Cr or Cr ³⁺	-	Chromium, chromic (usually in aqueous solution)
Cu or Cu ²⁺	-	Copper (usually in aqueous solution)
D ₂ O	-	Deuterium oxide: used in mass spectrometry analyses
DAEP	-	1,4-di(2-aminoethyl) piperazine
DEA	-	Diethanolamine
DETA	-	Diethylenetriamine
DGA [®]	-	Diglycolamine
DOF	-	Degrees of freedom, statistically
diPZ urea	-	1,1'-carbonylbis-PZ
DMAE	-	N,N-Dimethylethanolamine
DMMEA	-	N,N-Dimethylethanolamine
EDA	-	Ethylenediamine
Fe or Fe ²⁺	-	Iron, ferrous (usually in aqueous solution)
FPZ	-	N-Formyl Piperazine
g	gram	Mass in units of gram
GC-MS	-	Gas chromatography coupled with mass spectroscopy
HEEDA	-	N-(2-hydroxyethyl) ethylenediamine
HEIA	-	1-(2-Hydroxyethyl)-2-Imidazolidone
HEOD	-	3-(2-Hydroxyethyl)-2-Oxazolidone

Table A.1: List of Abbreviations (Continued)

Symbol	Units	Definition
HEP	-	N-(2-Hydroxyethyl) Piperazine
HMDA	-	Hexamethylenediamine
HMI	-	Hexamethyleneimine
HomoPZ	-	Homopiperazine
IC	-	Ion chromatography, anion or cation
IC-MS	-	Cation IC coupled with mass spectroscopy
k ₁	-	First order rate constant for amine loss during thermal degradation
KOH	-	Potassium hydroxide: eluent for anion IC analysis
kg	kilogram	Mass in units of kilogram
LGF	-	Low Gas Flow Reactor
m	Mole·(kg H ₂ O) ⁻¹	Molal, concentration unit based on kg H ₂ O
m/z	-	Mass to charge ratio of ions detected during mass spectroscopy
MAPA	-	3-(Methylamino)propylamine
MDEA	-	N-Methyldiethanolamine
MEA	-	Monoethanolamine
MIPA	-	DL-2-Amino-1-propanol
mM	mmol·L ⁻¹	Millimolar, concentration unit
MMEA	-	2-Methylaminoethanol
Mor	-	Morpholine
MS	-	Mass spectrometry: analytical technique to determine the molecular weight of a molecule of interest
MSA	-	Methanesulfonic acid: eluent for cation IC analysis
N	-	Nitrogen; a nitrogen atom within a molecule
Ni or Ni ²⁺	-	Nickel (usually in aqueous solution)
N,N'-	-	N,N'-Dimethylethylenediamine
diMEDA	-	N,N-Dimethylethylenediamine
N,N-diMEDA	-	N,N-Dimethylethylenediamine
O ₂	-	Oxygen
OOR	-	Original oxidation reactor
PD	-	Piperidine
PMDETA	-	N,N,N',N',N''-pentamethyldiethylenetriamine
PMDPTA	-	N,N,N',N',N''-pentamethyldipropylenetriamine
PEP	-	1,1'-(1,2-ethanediyl)bis-PZ
Pyr	-	Pyrrolidine
PZ	-	Piperazine
t2,5-DMPZ	-	<i>trans</i> -2,5-Dimethyl piperazine
TEDA	-	Triethylenediamine

Table A.1: List of Abbreviations (Continued)

Symbol	Units	Definition
TEPA	-	Tetraethylenediamine
TIC	-	Total Inorganic Carbon: assay to measure CO ₂ concentration
TIC	-	Total Ion Current: raw signal output of mass spectrometer
TMBDA	-	N,N,N',N'-tetramethylbutylenediamine
TMEDA	-	N,N,N',N'-Tetramethylethylenediamine
TMPDA	-	N,N,N',N'-Tetramethypropylenediamine
TriMEDA	-	N,N,N'-Trimethylethylenediamine
TOR	-	Teflon oxidative reactor

Table A.2: List of Greek Symbols

Symbol	Units	Definition
α	mole CO ₂ /mole alkalinity	CO ₂ loading in terms of moles of CO ₂ per mole alkalinity (equivalent to mole CO ₂ per mole amine functions)
α -	-	The first carbon or other molecule away from a dominant atom (i.e. nitrogen). The α -carbon is the carbon nearest to the nitrogen in a PZ molecule
ρ	g mL ⁻¹	Density of a solution
μ	mPa-s	Viscosity of a solution

The following table (Table A.3) is a summary of the degradation products identified or suspected for either thermal degradation or oxidation. The table is sorted alphabetically by abbreviation and then chemical name. Those molecules that have been positively identified and can be quantified readily with techniques described in this dissertation are indicated with a “Q”. Those that are suspected and not yet confirmed due to a lack of a commercial standard or an appropriate method to identify them are indicated with an “S”.

Table A.3: Glossary of Degradation Products

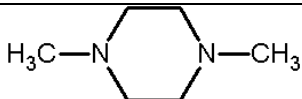
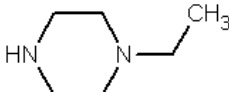
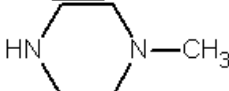
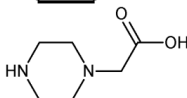
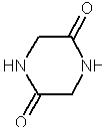
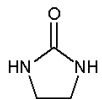
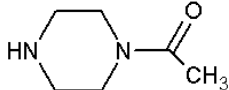
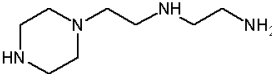
Chemical Name	Abbreviation	Structure	CAS Number	MW (g/mol)	Status*	Deg. Type ⁺
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1-Ethylpiperazine	1-EPZ		5308-25-8	114.2	Q	T
1-Methylpiperazine	1-MPZ		109-01-3	100.2	Q	T
1-Piperazineacetic acid	1-PA		37478-58-3	144.17	S	O, T
2,5-Piperazinedione	2,5dione		106-57-0	114.10	S	O
2-Imidazolidone	2-Imid		120-93-4	86.09	Q	T
1-Acetylpiperazine	AcPZ		13889-98-0	128.17	S	O, T
1-[2-[(2-Aminoethyl)amino] ethyl] piperazine	AEAEPZ		24028-46-4	172.27	S	T

Table A.3: Glossary of Degradation Products (Continued)

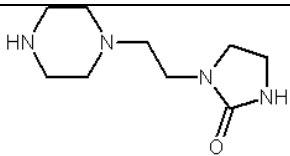
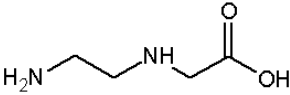
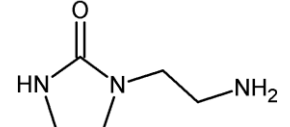
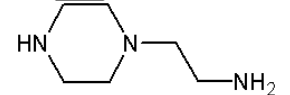
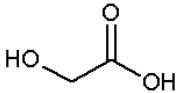
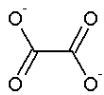
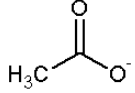
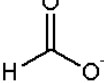
Chemical Name	Abbreviation	Structure	CAS Number	MW (g/mol)	Status*	Deg. Type ⁺
1-[2-(Piperazinyl)ethyl]-2-imidazolidinone	AEAEPZ Urea		104087-61-8	198.27	S	T
1-(2-Aminoethyl)glycine	AEG		24123-14-6	118.13	S	O
1-(2-Aminoethyl)-2-imidazolidone	AEI		6281-42-1	129.16	S	T
1-(2-Aminoethyl)piperazine	AEP		140-31-8	129.2	Q	T
Glycolate	C ₂ H ₄ O ₃		79-14-1	75.1	Q	O, T
Oxalate	C ₂ O ₄ ²⁻		NA	88.0	Q	O, T
Acetate	CH ₃ COO		NA	59.1	Q	O, T
Formaldehyde	CHO		50-00-0	30.03	S	O, T
Formate	CHO ₂		NA	45.0	Q	O, T

Table A.3: Glossary of Degradation Products (Continued)

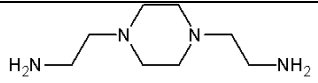
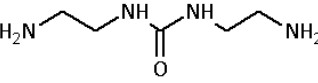
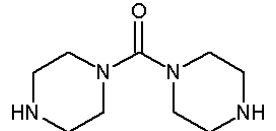
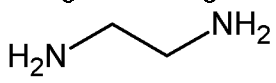
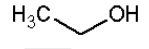
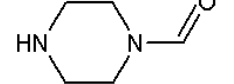
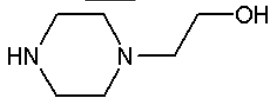
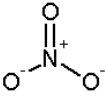
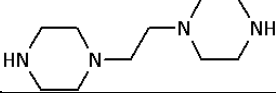
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N,N'-bis(2-aminoethyl)-urea (diEDA urea)	diEDA urea		940866-61-5	146.19	S	T
1,1'-carbonylbis-piperazine	diPZ urea		17159-16-9	198.2654	S	T
Ethylenediamine	EDA		107-15-3	60.1	Q	O, T
Ethanol	EtOH		64-17-5	46.07	S	O
1-Formylpiperazine	FPZ		7755-92-2	114.2	Q	O, T
1-(2-Hydroxyethyl)piperazine	HEP		103-76-4	130.19	Q	T
Methanol	MeOH		67-56-1	32.04	S	O
Nitrite	NO ₂ ⁻		NA	46.0	Q	O
Nitrate	NO ₃ ⁻		NA	62.0	Q	O
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Table A.3: Glossary of Degradation Products (Continued)

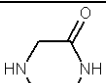
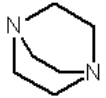
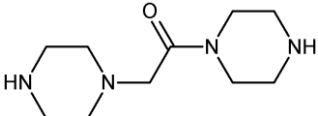
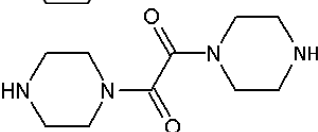
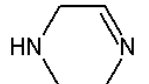
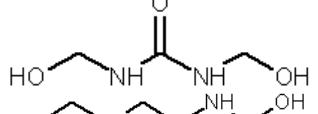
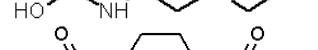
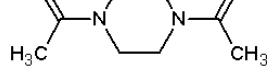
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Triethylenediamine	TEDA		280-57-9	112.17	S	T
1-(1-Piperazinylacetyl)-piperazine (Amide of 1-PZ)			69253-90-3	212.29	S	T
1,1'-(1,2-dioxo-1,2-ethanediyl)bis-piperazine (diPZ oxalyl amide)			105807-56-5	226.28	S	O, T
1,2,3,4-tetrahydro pyrazine (enamine of PZ)			5194-05-8	84.12	S	O
1,2,3,6-tetrahydro pyrazine (imine of PZ)			77253-83-9	84.12	S	O
1,3-bis(N-hydroxymethyl) urea			140-95-4	120.11	S	T
1,4-di(2-hydroxymethyl) EDA			70495-38-4	120.15	S	T
1,4-Diacetylpiperazine			18940-57-3	170.21	S	O, T

Table A.3: Glossary of Degradation Products (Continued)

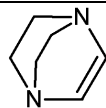
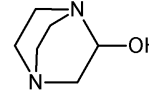
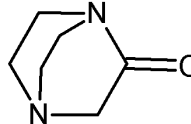
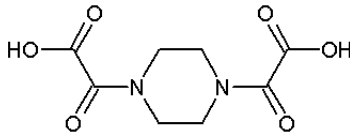
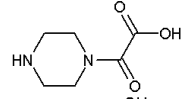
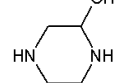
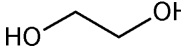
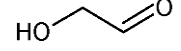
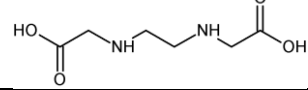
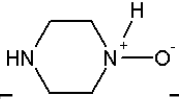
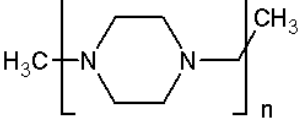
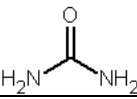
Chemical Name	Abbreviation	Structure	CAS Number	MW (g/mol)	Status*	Deg. Type ⁺
1,4-Diazabicyclo[2.2.2]oct-2-ene (TEDA enamine)			122883-12-9	110.16	S	O, T
1,4-Diazabicyclo[2.2.2]octan-2-ol (TEDA hemiaminal)			146562-84-7	128.17	S	O, T
1,4-Diazabicyclo[2.2.2]octan-2-one (Amide of 1-PA)			146562-83-6	126.16	S	O, T
1,4-Dioxalylpiperazine			None	230.17	S	O, T
1-Oxalylpiperazine (α -oxo-1-piperazineacetic acid)			691394-09-9	158.16	S	O, T
2-piperazinol (hemiaminal of PZ)			1104858-53-8	102.14	S	O
Acetaldehyde			75-07-0	44.05	S	O, T
Ethylene glycol			107-21-1	62.07	S	O
Hydroxyacetaldehyde			141-46-8	60.05	S	O, T
N,N'-1,2-ethanediylbis-glycine			5657-17-0	176.17	S	O

Table A.3: Glossary of Degradation Products (Continued)

Chemical Name	Abbreviation	Structure	CAS Number	MW (g/mol)	Status*	Deg. Type ⁺
N-oxidepiperazine			NA	102.1	S	O
Poly(methylene)piperazine			NA	NA	S	T
Urea			57-13-6	60.06	S	T

* S: Suspected; Q: positively identified and quantified

⁺ O: Oxidation; T: thermal degradation

Appendix B – List of Chemicals

All chemicals used for experimentation or analytical techniques were laboratory grade or purer. Details of the materials used in this thesis are included in Table B.1.

Table B.1: Details of All Chemicals Used

Chemical Name [Synonyms]	Abbreviation	Manufacturer*	CAS No.^	Purity ⁺	MW (g/mol)
1-(2-Aminoethyl) piperazine [N-(2-Aminoethyl) piperazine]	AEP	Acros	140-31-8	99%	129.2
1-(2-Hydroxyethyl)-2-Imidazolidone [N-(2-Hydroxyethyl) imidazolidinone]	HEI	Aldrich	3699-54-5	75% Soln.	130.2
1-(2-Hydroxyethyl)-4-methyl piperazine [N-(2-Hydroxyethyl)-N'-methyl piperazine]	HEMP	Acros	5464-12-0	98%	144.2
1-(2-Hydroxyethyl) ethylenediamine [N-(2-Hydroxyethyl) ethylenediamine] [2-(2-Aminoethylamino) ethanol]	HEEDA	Acros	111-41-1	>99%	104.2
1-(2-Hydroxyethyl) piperazine [N-(2-Hydroxyethyl) piperazine] [1-piperazineethanol]	HEP	TCI	103-76-4	>99.0%	130.19
1,4-bis(β-hydroxyethyl)piperazine [N,N'-bis(2-hydroxyethyl) piperazine] [1,4-piperazinediethanol]	bHEP	Aldrich	122-96-3	99%	174.24
1,4-Diethyl piperazine [N,N'-Diethyl PZ]	DEPZ	Acros	229-341-5	98%	142.24
1,4-Diformyl piperazine [N,N'-Diformyl PZ]	DFPZ	TCI	4164-39-0	>98.0%	142.2
1,4-Dimethyl piperazine [N,N'-Dimethyl PZ]	1,4-DMPZ	Acros	106-58-1	98.5%	114.2
1,4-Dioxane, stabilized	Dioxane	Acros	123-91-1	99+%	88.11
1-Acetyl piperazine [N-Acetyl piperazine]	AcPZ	TCI	13889-98-0	>98.0%	128.2

Table B.1: Details of All Chemicals Used (Continued)

Chemical Name [Synonyms]	Abbreviation	Manufacturer*	CAS No.^	Purity ⁺	MW (g/mol)
1-Amino-4-methyl piperazine [N-Amino-N'-methyl piperazine]	AMPZ	Acros	6928-85-4	99%	115.2
1-Ethyl piperazine [N-Ethyl piperazine]	EPZ	TCI	5308-25-8	99	114.2
1-Formyl piperazine [N-Formyl piperazine]	FPZ	TCI	7755-92-2	>98.0%	114.2
1-Formyl piperazine [N-Formyl piperazine]	FPZ	Acros Organics	7755-92-2	98%	114.2
1-Methyl piperazine [N-Methyl piperazine]	1-MPZ	Acros	109-01-3	>99%	100.2
2,5-Dimethyl piperazine [<i>trans</i> -2,5-Dimethyl piperazine]	t2,5-DMPZ	AK Scientific	3815-34-1	99%	114.19
2,5-Piperazinedione [Glycine anhydride]	2,5-PZdione	Acros	106-57-0	98%	114.1
2-Imidazolidone	2-Imid	Aldrich	120-93-4	96%	86.09
2-Imidazolidone Hemihydrate		Acros	121325-67-5	>99%	86.1
2-Methyl-2-imidazoline		TCI	534-26-9	>97.0%	84.16
2-Methyl piperazine	2-MPZ	Acros	109-07-9		100.16
3-(2-Hydroxyethyl)-2-Oxazolidone	HEOD	MP	3356-88-5		131.1
3-(Trimethylsilyl)-1-propanesulfonic acid, sodium salt [Sodium 2,2-dimethyl-2-silapentane-5- sulfonate]	DDS	Aldrich	2039-96-5	97%	218.3
Acetic Acid, glacial	CH ₃ COOH	Fisher	64-19-7	100%	60.1

Table B.1: Details of All Chemicals Used (Continued)

Chemical Name [Synonyms]	Abbreviation	Manufacturer*	CAS No.^	Purity ⁺	MW (g/mol)
Ammonium Chloride	NH ₄ Cl	Fisher	12125-02-9	99.6%	53.49
Ammonium Sulfate	(NH ₄) ₂ SO ₄	EM	7783-20-2	99.0%	132.15
Carbon, Inorganic Standard (Na ₂ CO ₃ /NaHCO ₃)	NA	Ricca	None	1000 ppm	NA
Carbon Dioxide	CO ₂	Matheson	124-38-9	99.5%	44.01
Carbon Dioxide (2%)/Oxygen (98%)	CO ₂ /O ₂	Matheson	None	NA	NA
Chromic (III) Sulfate Hydrate	Cr ₂ (SO ₄) ₃ xH ₂ O	Pfaltz & Bauer	15244-38-9	NA	392.16
Chromium in 3% Nitric Acid	Cr	Ricca	NA	1000 ppm	NA
Chromium Potassium Sulfate Dodecahydrate	CrK(SO ₄) ₂ ·1 2H ₂ O	Acros	7788-99-0	99%	499.25
Copper in 3% Nitric Acid	Cu	Ricca	NA	1000 ppm	NA
Cupric (II) Sulfate Pentahydrate	CuSO ₄ ·5H ₂ O	Mallinckrodt	7758-99-8	99.5%	249.68
Deuterium oxide	D ₂ O	Cambridge	7789-20-0	99.9%	20.04
Ethylenediamine	EDA	Strem	107-15-3	99%	60.10
Ferric (III) Chloride	FeCl ₃ ·6H ₂ O	Fisher	10025-77-1	99.4%	270.3
Ferrous (II) Sulfate Heptahydrate	FeSO ₄ ·7H ₂ O	Spectrum	7782-63-0	99.0%	278.05
Formaldehyde	CH ₂ O	Fisher	50-00-0	37 wt%	30.0
Formic Acid	CH ₂ O ₂	Fisher	None	90.4%	46.03
Glycolic Acid, 67% solution in water	C ₂ H ₄ O ₃	Acros	79-14-1	67%	76.05
Homopiperazine [1,4-Diazacycloheptane] [Hexahydro-1H-1,4-Diazepine]	HomoPZ	Acros	505-66-8	98%	100.16
Hexamethylenediamine [1,6-Hexanediamine]	HMDA	Sigma Aldrich	124-09-4	98%	100.16

Table B.1: Details of All Chemicals Used (Continued)

Chemical Name [Synonyms]	Abbreviation	Manufacturer*	CAS No.^	Purity ⁺	MW (g/mol)
Hexamethyleneimine [Azacycloheptane] [Azepane] [Perhydroazepine]	HMI	Acros	111-49-9	99%	99.15
Iodine (Iodide/Iodine)	I ₂	Ricca	NA	0.1 N	NA
Inhibitor A	-	-	-	99%	-
Inhibitor B	-	-	-	-	-
Inhibitor C	-	-	-	-	-
Iron in 3% Nitric Acid	Fe	Ricca	NA	1000 ppm Fe	NA
Methanesulfonic Acid	MSA	Acros	75-75-2	99%	96.1
Morpholine	Mor	Aldrich	110-91-8	99.5+%	87.12
Nickel (II) Sulfate Hexahydrate	NiSO ₄ ·6H ₂ O	Alfa Aesar	10101-97-0	>98.0%	237.72
Nitric Acid	HNO ₃	Fisher	7697-37-2	68-71%	63.01
Nitric Acid	HNO ₃	Fisher	NA	6M	NA
Nitrogen	N ₂	Praxair	7727-37-9	97	28.01
Oxygen	O ₂	Matheson	7782-44-7	99.9	32.00
Piperazine, anhydrous [1,4-diazacyclohexane]	PZ	Fluka	110-85-0	>99.0%	86.14
Piperazine, anhydrous [1,4-diazacyclohexane]	PZ	Sigma Aldrich	110-85-0	99%	86.14
Piperidine [Azacyclohexane] [Pentamethyleneimine]	PD	Sigma Aldrich	110-89-4	99%	85.15
Phosphoric Acid	H ₃ PO ₄	Acros	7664-38-2	85%	98.00

Table B.1: Details of All Chemicals Used (Continued)

Chemical Name [Synonyms]	Abbreviation	Manufacturer*	CAS No.^	Purity ⁺	MW (g/mol)
Potassium Formate	KCHO ₂	Alfa Aesar	590-29-4	99%	84.12
Potassium Iodate	KIO ₃	Acros	758-05-6	-	214.0
Pyrazine	C ₄ H ₄ N ₂	Acros	290-37-9	99+%	80.09
Pyrrolidine [Azacyclopentane] [Tetramethyleneimine]	Pyr	Fluka	123-75-1	>99%	71.12
Sodium Chloride	NaCl	EM Science	7647-14-5	99.0%	58.44
Sodium Hydroxide Solution	NaOH	Fisher	None	5 N	40.00
Sodium Metavanadate	NaVO ₃	Acros	13718-26-8	96.%	121.93
Sodium Nitrate	NaNO ₃	Fisher	7631-99-4	>99%	84.99
Sodium Nitrite	NaNO ₂	Fisher	7632-00-0	97.0%	69.00
Sodium Oxalate	Na ₂ C ₂ O ₄	JT Baker	62-76-0	99.9%	134.0
Sodium Sulfate	NaSO ₄	Spectrum	7757-82-6	>99%	142.04
Sodium Sulfide Nonahydrate	Na ₂ S · 9H ₂ O	Ricca	1313-84-4	5% (m/v)	240.18
Sulfuric Acid, Concentrated	H ₂ SO ₄	Fisher	None	36 N	98.07
Sulfuric Acid Solution	H ₂ SO ₄	Fisher	None	0.2 N	98.07
Triethylenediamine [1,4-Diazabicyclo[2.2.2]octane]	TEDA	Acros	280-57-9	97%	112.17

* Manufacturer abbreviations are as follows:

Acros: Acros Organics N.V., Geel, Belgium

AK Scientific: AK Scientific Incorporated, Mountain View, CA

Alfa Aesar: Alfa Aesar, Ward Hill, MA

Cambridge: Cambridge Isotope Laboratories, Andover, MA

EM Science: Division of EM Industries, Gibbstown, NJ

Fisher: Fisher Scientific Worldwide, Hampton, NH

Fluka: Sigma-Aldrich Corporation, St. Louis, MO
JT Baker: Mallinkrodt Baker Inc., Phillipsburg, NJ
Matheson: Matheson Tri-Gas Inc., Basking Ridge, NJ
Mallinckrodt: Mallinkrodt Baker Inc., Phillipsburg, NJ
MP: MP Biomedicals LLC, Solon, OH
Pfaltz & Bauer: Pfaltz & Bauer, Waterbury, CT
Praxair: Praxair, Inc., Danbury, CT
Ricca: Ricca Chemical Company, Pequannock, NJ
Sigma-Aldrich: Sigma-Aldrich Corporation, St. Louis, MO
Spectrum: Spectrum Chemical Manufacturing Company, Gardena, CA
Strem Chemicals: Strem Chemicals, Inc., Newburyport, MA
TCI: Tokyo Chemical Industry (TCI) America, Portland, OR

[^] CAS Number: “none” is listed for items that do not have a CAS number because it is a mixture of more than one chemical or because it is a specialty item

⁺ Purity: The concentration is listed for chemical solutions; NA is listed when chemical purity is not available from supplier

Appendix C – Details of Analytical Methods Used

The details of the analytical techniques methods used throughout this dissertation are included in this appendix. The program methods that were used on the anion IC, cation IC, cation IC-MS, HPLC, and amino acid liquid chromatography (AA-LC) are described in this chapter.

C.1 ANION IC

The anion IC was used to quantify the concentration of formate, acetate, glycolate, oxalate, sulfate, chlorine, nitrite, and nitrate in experimental samples. The 35 minute method used a gradient ranging from 2 to 45 mM KOH and a 6 minute equilibration time at the start of the program. The program used, “Anions.pgm”, was as follows:

Anions.pgm

```
Sampler.AcquireExclusiveAccess
Sampler_DiverterValve.Position_2
Column_TC.AcquireExclusiveAccess
Compartment_TC.AcquireExclusiveAccess
Pressure.LowerLimit = 200 [psi]
Pressure.UpperLimit = 3000 [psi]
MaximumFlowRamp = 6.00 [ml/min²]
%A.Equate = "%A"
CR_TC = On
Flush Volume = 250
Wait FlushState
NeedleHeight = 2 [mm]
CutSegmentVolume = 10 [µl]
SyringeSpeed = 2
CycleTime = 0 [min]
WaitForTemperature = False
Data_Collection_Rate = 5.0 [Hz]
Temperature_Compensation = 1.7 [%/°C]
CellHeater.Mode = On
CellHeater.TemperatureSet = 35.00 [°C]
Column_TC.Mode = On
Column_TC.TemperatureSet = 30.00 [°C]
Compartment_TC.Mode = On
Compartment_TC.TemperatureSet = 30.00 [°C]
Suppressor2.Type = ASRS_4mm
Suppressor2.CurrentSet = 179 [mA]
Flow = 1.600 [ml/min]
Pump_2.Curve = 5
Wait SampleReady

-6.10 Concentration = 45.00 [mM]
      EGC_1.Curve = 5

-6.00 Concentration = 2.00 [mM]
      EGC_1.Curve = 5

0.00  CDet1.Autozero
      Load
      Wait CycleTimeState
      Inject
      Wait InjectState
```



```

CD_1.AcqOn
CD_1_Total.AcqOn
Sampler.ReleaseExclusiveAccess
Compartment_TC.ReleaseExclusiveAccess
Column_TC.ReleaseExclusiveAccess

17.00 Concentration = 2.00 [mM]
EGC_1.Curve = 5

25.00 Concentration = 45.00 [mM]
EGC_1.Curve = 5

35.00 Concentration = 45.00 [mM]
CD_1.AcqOff
CD_1_Total.AcqOff
EGC_1.Curve = 5

End

```

C.2 CATION IC

Two different methods were used for cation IC analysis. The first method used was a short method that was used to quantify the concentration of PZ, EDA, FPZ, other amines, Na⁺, and K⁺ in experimental samples. The 20 minute method used a gradient ranging from 5.5 to 38.5 mM MSA and a 3 minute equilibration time at the start of the program. The gradient was delivered by assigning a percentage of the eluent that was either analytical grade water (Channel B) or 55 mM MSA (Channel C). The program used, “Jason3Auto.pgm”, was as follows:

Jason3Auto.pgm

```

Pressure.LowerLimit = 200
Pressure.UpperLimit = 4000
%A.Equate = "6"
%B.Equate = "8"
%C.Equate = "55"
%D.Equate = "%D"
Pump_InjectValve.LoadPosition
Data_Collection_Rate = 2.0

```

Temperature_Compensation = 1.7
 Oven_Temperature = 40
 Suppressor_Type = CSRS_4mm
 Suppressor_Current = 136

-3.00 Flow = 1.20
 %B = 90.0
 %C = 10.0
 %D = 0.0
 Curve = 5

-2.40 Pump_relay_1.open

-2.30 Pump_Relay_1.Closed duration = 120
 Flow = 1.20
 %B = 90.0
 %C = 10.0
 %D = 0.0
 Curve = 5

0.00 Autozero
 Flow = 1.20
 %B = 90.0
 %C = 10.0
 %D = 0.0
 Curve = 5
 ECD_1.AcqOn
 Pump_InjectValve.InjectPosition Duration= 30
 Flow = 1.20
 %B = 90.0
 %C = 10.0
 %D = 0.0
 Curve = 5

7.00 Flow = 1.20
 %B = 90.0
 %C = 10.0
 %D = 0.0
 Curve = 5

7.001 Flow = 1.20
 %B = 80.0
 %C = 20.0

```

%D = 0.0
Curve = 5

12.0  Flow = 1.20
      %B = 80.0
      %C = 20.0
      %D = 0.0
      Curve = 5

17.0  Flow = 1.20
      %B = 30.0
      %C = 70.0
      %D = 0.0
      Curve = 5

20.0  ECD_1.AcqOff
      Flow = 1.20
      %B = 30.0
      %C = 70.0
      %D = 0.0
      Curve = 5

End

```

A second, longer method was used to quantify complex, degraded amine mixtures. It mimicked the method used for cation IC-MS (detailed in the next section), but was performed on the IC not connected to the MS. The flow rate was lower than “Jason3Auto.pgm” to enhance separation. The details of the “Stephanie3Auto.pgm” method are as follows:

Stephanie3Auto.pgm

```

Pressure.LowerLimit = 200 [psi]
Pressure.UpperLimit = 3000 [psi]
%A.Equate = "%A"
CR_TC = On
DeliverSpeed = 4.0 [ml/min]
DelayVolume = 125 [μl]
FlushFactor = 10
Sampler.LoadPosition
DeliverSampleVolume=1666

```

```

EndSamplePrep
Data_Collection_Rate =      5.0 [Hz]
CellTemperature.Nominal =  30.0 [°C]
ColumnTemperature.Nominal =    30.0 [°C]
Suppressor_Type =   CSRS_4mm
Suppressor_Current =      77 [mA]
Channel_Pressure.Average = On
Flow =                0.50 [ml/min]

0.000 Autozero
      Concentration =      5.50 [mM]
      Curve =          5
      Wait CycleTimeState
      Inject
      ECD_1.AcqOn
      Channel_Pressure.AcqOn
      Concentration =      5.50 [mM]
      Curve =            5

0.500 BeginOverlap

16.400 Concentration =      5.50 [mM]
      Curve =            5

16.501 Concentration =     11.00 [mM]
      Curve =            5

26.400 Concentration =     11.00 [mM]
      Curve =            5

36.400 Concentration =     38.50 [mM]
      Curve =            5

47.400 Concentration =     38.50 [mM]
      Curve =            5

47.500 Concentration =      5.50 [mM]
      Curve =            5

50.000 ECD_1.AcqOff
      Concentration =      5.50 [mM]
      Curve =            5
      Channel_Pressure.AcqOff

```

End

C.3 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

The HPLC was used to quantify organic molecules that were not easily quantified using anion or cation IC. A 30 minute method, PA2-MeOH-CAN-2.pgm, was used that contained a gradient of water, methanol, and acetonitrile. It was developed for the Polar Advantage 2 analytical separation column (Dionex Corporation) as described in section 3.1.12. It is important to note that in the HPLC set-up, eluent A was a buffer, eluent B was acetonitrile, eluent C was methanol, and eluent D was water. The details of PA2-MeOH-CAN-2.pgm are as follows:

PA2-MeOH-ACN-2.pgm

```
Column_A.ActiveColumn = No
TempCtrl = On
Temperature.Nominal = 30.0 [°C]
Column_B.ActiveColumn = No
Pressure.LowerLimit = 5 [bar]
Pressure.UpperLimit = 300 [bar]
MaximumFlowRampDown = Infinite
MaximumFlowRampUp = Infinite
%A.Equate = "%A"
%B.Equate = "%B"
%C.Equate = "%C"
%D.Equate = "%D"
DrawSpeed = 5.000 [µl/s]
DrawDelay = 3000 [ms]
DispSpeed = 20.000 [µl/s]
DispenseDelay = 0 [ms]
WasteSpeed = 32.000 [µl/s]
SampleHeight = 2.000 [mm]
InjectWash = NoWash
LoopWashFactor = 2.000
PunctureOffset = 0.0 [mm]
PumpDevice = "Pump"
InjectMode = Normal
SyncWithPump = On
```

```

Data_Collection_Rate =    2.5 [Hz]
TimeConstant =    0.60 [s]
ELS_1.Step = 0.10 [s]
ELS_1.Average =    Off
UV_VIS_1.Wavelength =    210 [nm]
EvaporatorTemperature.Nominal =    50 [°C]
NebuliserTemperature =    90 [°C]
LightSourceIntensity =    85 [%]
CarrierFlow.Nominal =    1.60 [slm]
SmoothWidth =    20
PMTGain =    1.0
UV.LeakSensorMode =    Disabled

-4.000 Flow =    1.000 [ml/min]
      %B = 0.0 [%]
      %C = 0.0 [%]
      %D = 100.0 [%]

0.000
      UV.Autozero
      ELSD.Autozero
      Wait  AZ_Done
      Wait  UV.Ready and ELSD.Ready
      Inject
      ELS_1.AcqOn
      UV_VIS_1.AcqOn

3.000 Flow =    1.000 [ml/min]
      %B = 0.0 [%]
      %C = 0.0 [%]
      %D = 100.0 [%]

10.000 Flow =    1.000 [ml/min]
      %B = 0.0 [%]
      %C = 5.0 [%]
      %D = 95.0 [%]

20.000 Flow =    1.000 [ml/min]
      %B = 0.0 [%]
      %C = 50.0 [%]
      %D = 50.0 [%]

30.000 Flow =    1.000 [ml/min]

```

```
%B = 20.0 [%]  
%C = 50.0 [%]  
%D = 30.0 [%]  
  
ELS_1.AcqOff  
UV_VIS_1.AcqOff  
End
```

NOTE:

A=NH₄Ac

B=Acetonitrile

C=Methanol

D=Water

C.4 CATION IC-MS

The cation IC-MS was used to identify unknown peaks observed on the cation IC. The method used was essentially the same as “Jason3Auto.pgm” described above, except the timing was stretched out to accommodate a lower flowrate required for the MS. The 50 minute method used a gradient ranging from 5.5 to 38.5 mM MSA and a 2.4 minute equilibration and injection time at the start of the program. The Xcalibur® program which operates the IC-MS cannot accept negative time, so the equilibration and injection time are in positive time with the injection of the sample at 2.4 minutes. The gradient was delivered by an eluent generator for MSA. The program used, “Jason3Auto-HalfmL_min.pgm”, was as follows:

Jason3Auto-HalfmL_min.pgm:

```
Pressure.LowerLimit = 200 [psi]  
Pressure.UpperLimit = 3000 [psi]  
%A.Equate = "%A"  
CR_TC = On  
WaitForTemperature = False  
Data_Collection_Rate = 5.0 [Hz]  
CellTemperature.Nominal = 30.0 [°C]  
ColumnTemperature.Nominal = 30.0 [°C]  
Suppressor_Type = CSRS_4mm  
Suppressor_Current = 77 [mA]
```

```

ECD_Total.Step = 0.20 [s]
ECD_Total.Average = Off
Pump_InjectValve.LoadPosition
Flow = 0.50 [ml/min]

0.000 Concentration = 5.50 [mM]
      Autozero
      Inject
      ECD_1.AcqOn
      ECD_Total.AcqOn
      Concentration = 5.50 [mM]
      Pump_ECD_Relay_2.Closed Duration=10.00

0.100 Pump_ECD_Relay_1.State   Closed

1.000 Pump_ECD_Relay_1.State   Open

2.300 Pump_InjectValve.InjectPosition   Duration=60.00

16.400 Concentration = 5.50 [mM]

16.501 Concentration = 11.00 [mM]

26.400 Concentration = 11.00 [mM]

36.400 Concentration = 38.50 [mM]

47.400 Concentration = 38.50 [mM]

47.500 Concentration = 5.50 [mM]

50.000 ECD_1.AcqOff
      ECD_Total.AcqOff
      Concentration = 5.50 [mM]

End

```

C.5 AA-LC

The amino acid liquid chromatography (AA-LC) analysis was used to identify amino acid-based degradation products. The 50 minute method used a gradient ranging from 5.5 to 38.5 mM MSA and a 2.4 minute equilibration and injection time at the start

of the program. The Xcalibur® program which operates the IC-MS cannot accept negative time, so the equilibration and injection time are in positive time with the injection of the sample at 2.4 minutes. The gradient was delivered by an eluent generator for MSA. The program used, “Voice-1.pgm”, was as follows:

“Voice-1.pgm”

```

Sampler.AcquireExclusiveAccess
Sampler_DiverterValve.Position_1
Column_TC.AcquireExclusiveAccess
Compartment_TC.AcquireExclusiveAccess
Pressure.LowerLimit =      200 [psi]
Pressure.UpperLimit =      3900 [psi]
MaximumFlowRamp =      1.00 [ml/min²]
%A.Equate = "%A"
%B.Equate = "%B"
%C.Equate = "%C"
%D.Equate = "%D"
Flush Volume = 250
Wait FlushState
NeedleHeight =      2 [mm]
CutSegmentVolume =      10 [µl]
SyringeSpeed =      4
CycleTime = 0 [min]
WaitForTemperature =      False
EDet1.Mode =      IntAmp
EDet1.CellControl = On
Data_Collection_Rate =      1.00 [Hz]
pH.UpperLimit =      13.00
pH.LowerLimit =      10.00
WaveformName = "amino acids (ph,ag,agcl reference)"
WaveformDescription = "Amino Acids (pH/Ag/AgCl Ref.)"
Electrode = pH
Waveform Time = 0.000, Potential = 0.130, GainRegion = Off, Ramp = On,
Integration = Off
Waveform Time = 0.040, Potential = 0.130, GainRegion = Off, Ramp = On,
Integration = Off
Waveform Time = 0.050, Potential = 0.330, GainRegion = Off, Ramp = On,
Integration = Off
Waveform Time = 0.210, Potential = 0.330, GainRegion = On, Ramp = On,

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        Integration = On
Waveform Time = 0.220, Potential = 0.550, GainRegion = On, Ramp = On,
        Integration = On
Waveform Time = 0.460, Potential = 0.550, GainRegion = On, Ramp = On,
        Integration = On
Waveform Time = 0.470, Potential = 0.330, GainRegion = On, Ramp = On,
        Integration = On
Waveform Time = 0.560, Potential = 0.330, GainRegion = Off, Ramp = On,
        Integration = Off
Waveform Time = 0.570, Potential = -1.670, GainRegion = Off, Ramp = On,
        Integration = Off
Waveform Time = 0.580, Potential = -1.670, GainRegion = Off, Ramp = On,
        Integration = Off
Waveform Time = 0.590, Potential = 0.930, GainRegion = Off, Ramp = On,
        Integration = Off
Waveform Time = 0.600, Potential = 0.130, GainRegion = Off, Ramp = On,
        Integration = Off, LastStep = On
Column_TC.Mode = On
Column_TC.TemperatureSet =      30.00 [°C]
Compartment_TC.Mode = On
Compartment_TC.TemperatureSet = 30.00 [°C]
Wait SampleReady

-1.000 Flow =      0.250 [ml/min]
      %B = 24.0 [%]
      %C = 0.0 [%]
      %D = 0.0 [%]
      Curve =      5

0.000 Load
      Inject
      InjectValve_1.InjectPosition Duration=120.00
      ED_1.AcqOn
      ED_1_Total.AcqOn
      Sampler.ReleaseExclusiveAccess
      Compartment_TC.ReleaseExclusiveAccess
      Column_TC.ReleaseExclusiveAccess

8.000 Flow =      0.250 [ml/min]
      %B = 36.0 [%]
      %C = 0.0 [%]
      %D = 0.0 [%]
      Curve =      8

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11.000 Flow = 0.250 [ml/min]
%B = 36.0 [%]
%C = 0.0 [%]
%D = 0.0 [%]
Curve = 8

18.000 Flow = 0.250 [ml/min]
%B = 20.0 [%]
%C = 40.0 [%]
%D = 0.0 [%]
Curve = 8

21.000 Flow = 0.250 [ml/min]
%B = 16.0 [%]
%C = 44.0 [%]
%D = 0.0 [%]
Curve = 5

23.000 Flow = 0.250 [ml/min]
%B = 16.0 [%]
%C = 70.0 [%]
%D = 0.0 [%]
Curve = 8

42.000 Flow = 0.250 [ml/min]
%B = 16.0 [%]
%C = 70.0 [%]
%D = 0.0 [%]
Curve = 8

42.100 Flow = 0.250 [ml/min]
%B = 80.0 [%]
%C = 0.0 [%]
%D = 0.0 [%]
Curve = 5

44.100 Flow = 0.250 [ml/min]
%B = 80.0 [%]
%C = 0.0 [%]
%D = 0.0 [%]
Curve = 5

44.200 ED_1.AcqOff
ED_1_Total.AcqOff
Flow = 0.250 [ml/min]
%B = 24.0 [%]
%C = 0.0 [%]
%D = 0.0 [%]
Curve = 5

75.000 Flow = 0.250 [ml/min]
%B = 24.0 [%]
%C = 0.0 [%]
%D = 0.0 [%]
Curve = 5
End

Note:

A: Water

B: 250 mM sodium hydroxide

C: 1.0 M sodium acetate

Appendix D – Tabulated From Thermal Degradation Experiments

All tabulated experimental data that follows maintains the same format. Original sample data are the experimental sample while the base hydrolyzed data is the post-NaOH treatment data. Nitrite (NO_2^-) and nitrate (NO_3^-) were not found in thermally degraded PZ solutions. Abbreviations are as follows:

Gly, Glycolate (Anion IC)
Ace, Acetate (Anion IC)
Form, Formate (Anion IC)
Oxa, Oxalate (Anion IC)
Sulf, Sulfate (Anion IC)
 Cl^- , Chloride (Anion IC)
 NH_4^+ , ammonium (Cation IC)
FPZ, N-formyl PZ (Cation IC)
EDA, Ethylenediamine (Cation IC)
PZ, Piperazine (Cation IC)
HEP, N-(2-Hydroxyethyl) piperazine (Cation IC)

1-MPZ, N-Methylpiperazine (Cation IC)
1-EPZ, N-Ethylpiperazine (Cation IC)
1,4-DMPZ, N,N'-dimethylpiperazine (Cation IC)
AEP, N-(2-Aminoethyl)piperazine (Cation IC)
CO₂, Carbon Dioxide (TIC)
SD_{CO2}, standard deviation of three CO₂ measurements
Alk, total alkalinity (Acid Titration), calculation assumes diamine is present, raw alkalinity would be twice this number
SD_{Alk}, standard deviation of two total alkalinity titrations
Fe²⁺, aqueous iron (ICP-OES)
Cr³⁺, aqueous chromium (ICP-OES)
Ni²⁺, aqueous nickel (ICP-OES)
NT, value not tested
NA, not applicable; when only one measurement was made, calculation of standard deviation was not possible

Table D.1A: Tabulated Experimental Data for TE1A (10 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 135 °C)

Time (wk)		0	499	1008	2008
Original Samples (mmol/kg)	Gly	0.013	0.039	0.072	0.021
	Ace	0.051	0.115	0.480	0.298
	Form	0.113	2.790	3.474	1.937
	Oxa	0	0	0.244	0.019
	EDA	0	0	0	0
	PZ	4901.1	4727.7	4829.4	4733.5
	CO ₂	NT	NT	NT	NT
	SD _{CO2}	NT	NT	NT	NT
	Alk	4682.8	4629.4	4706.8	4710.1
	SD _{Alk}	32.9	NT	NT	14.2
Hydrolyzed Samples (mmol/kg)	Gly	0	0.472	0.225	0.134
	Ace	0	0.340	1.087	0.486
	Form	0.462	13.709	11.404	10.326
	Oxa	0.057	0.124	0.048	0.026
	EDA	NT	7.3	0	0
	PZ	NT	4668.2	4947.1	4701.6

Table D.1B: Tabulated Experimental Data for TE1B (10 m PZ, 0.4 mole CO₂ per mole alkalinity initially, 135 °C)

Time (wk)		499	1008	1504.5	2008	2521
Original Samples (mmol/kg)	Gly	0	0.019	0.052	0.017	0.013
	Ace	0.105	0.052	0.086	0.030	0.064
	Form	0.223	3.710	4.567	2.742	3.472
	Oxa	0	0	0.203	0.010	0.005
	EDA	0	0	0	0	0
	PZ	4577.7	4366.2	4431.1	4596.7	4130.7
	CO ₂	NT	NT	NT	NT	NT
	SD _{CO2}	NT	NT	NT	NT	NT
	Alk	4446.1	4223.7	NT	NT	4390.2
	SD _{Alk}	20.7	NT	NT	NT	16.2
Hydrolyzed Samples (mmol/kg)	Gly	NT	0.108	NT	0.048	0.024
	Ace	NT	0.184	NT	0.117	0.168
	Form	NT	20.360	NT	17.248	21.157
	Oxa	NT	0.018	NT	0.009	0.008
	EDA	NT	6.0	NT	0	0
	PZ	NT	4021.5	NT	4772.4	4431.5

Table D.2A: Tabulated Experimental Data for TE2A (10 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 150 °C)

Time (wk)		0.0	1.0	2.0	3.0	3.8	5.2
Original Samples (mmol/kg)	Gly	0.01	0.06	0.03	0.05	0	0.02
	Ace	0.05	0.15	0.11	0.70	0.58	0.10
	Form	0.11	1.11	1.88	2.65	3.54	8.41
	Oxa	0	0.09	0	0.03	0.03	0.23
	EDA	0	0	0	0	10.41	0
	PZ	4901.2	4723.2	4760.5	4755.0	4721.4	4716.2
	CO ₂	NT	NT	NT	NT	NT	NT
	SD _{CO2}	NT	NT	NT	NT	NT	NT
	Alk	4659.6	4758.4	4659.3	4653.2	4597.3	4887.0
	SD _{Alk}	32.90	NA	11.87	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0.11	0.13
	Ace	0	0.33	0	1.32	1.03	0.20
	Form	0.46	3.08	4.68	4.84	23.76	22.17
	Oxa	0.06	0.18	0	0.09	0.04	0.11
	EDA	NT	NT	NT	NT	NT	NT
	PZ	NT	NT	NT	NT	NT	NT

Table D.2B: Tabulated Experimental Data for TE2B (10 m PZ, 0.4 mole CO₂ per mole alkalinity initially, 150 °C)

Time (wk)		0.0	1.0	2.0	3.8	5.2
Original Samples (mmol/kg)	Gly	0.0	0.0	0.1	0.0	0.0
	Ace	0.10	0.13	0.14	0.20	0.12
	Form	0.22	1.45	3.72	4.12	13.70
	Oxa	0	0	0	0.03	0.23
	EDA	0	0	0	9.34	0
	PZ	4577.7	4614.3	4310.0	4555.8	4500.6
	CO ₂	NT	NT	NT	NT	NT
	SD _{CO2}	NT	NT	NT	NT	NT
	Alk	4431.5	4414.2	4402.5	4468.9	4679.8
	SD _{Alk}	32.90	NA	11.87	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	NT	0	0	0.05	0.05
	Ace	NT	0.12	0.29	0.16	0.17
	Form	NT	3.58	9.95	30.60	38.81
	Oxa	NT	0	0.09	0.07	0.04
	EDA	NT	NT	NT	NT	NT
	PZ	NT	NT	NT	NT	NT

Table D.3A: Tabulated Experimental Data for TE3A (15 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 150 °C)

Time (wk)		0.0	1.0	2.0	3.0	4.0	4.8
Original Samples (mmol/kg)	Gly	0	0.01	0.01	0.01	0.02	0.02
	Ace	0.32	0.03	0.02	0.07	0.07	0.11
	Form	0.37	0.44	0.98	5.73	8.06	8.09
	Oxa	0	0.02	0.02	0.39	0.25	0.19
	EDA	0	0	0	0	0	0
	PZ	5560.9	5626.0	5568.7	5721.9	5796.4	5699.4
	CO ₂	NT	NT	NT	NT	NT	NT
	SD _{CO2}	NT	NT	NT	NT	NT	NT
	Alk	5478.4	5455.0	5416.2	5839.0	5668.8	5652.9
	SD _{Alk}	27.10	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	0.17	0	0.05	0.05	0.04	0.06
	Ace	0.29	0.10	0.17	0.18	0.15	0.17
	Form	0.57	3.78	14.81	19.00	25.72	29.29
	Oxa	0.03	0	0.05	0.02	0.02	0.04
	EDA	NT	NT	NT	NT	NT	NT
	PZ	NT	NT	NT	NT	NT	NT

Table D.3B: Tabulated Experimental Data for TE3B (20 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 150 °C)

Time (wk)		0.0	1.0	2.0	3.0	4.0	4.8
Original Samples (mmol/kg)	Gly	0	0.01	0.01	0	0.03	0.02
	Ace	0.14	0.03	0.03	0.10	0.11	0.09
	Form	0.17	0.29	0.64	5.55	6.04	9.28
	Oxa	0	0.03	0.02	0.27	0.22	0.21
	EDA	0	0	0	0	0	0
	PZ	6232.4	7140.2	6122.8	6337.1	6018.2	6246.7
	CO ₂	NT	NT	NT	NT	NT	NT
	SD _{CO2}	NT	NT	NT	NT	NT	NT
	Alk	6065.6	6116.5	6124.9	6491.9	NT	6369.0
	SD _{Alk}	59.37	NA	NA	NA	NT	NA
Hydrolyzed Samples (mmol/kg)	Gly	0.37	0	0.06	0.06	NT	0.08
	Ace	0.10	0.24	0.09	0.29	NT	0.18
	Form	0.67	3.53	16.00	27.39	NT	45.30
	Oxa	0.03	0	0.05	0.07	NT	0.04
	EDA	NT	NT	NT	NT	NT	NT
	PZ	NT	NT	NT	NT	NT	NT

Table D.4: Tabulated Experimental Data for TE4 (8 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 175 °C)

Time (wk)		0	0.4	1.0	2.0	3.0	4.0
Original Samples (mmol/kg)	Gly	0	0.02	0.02	0	0.02	0.02
	Ace	0.02	0.33	1.19	3.45	6.60	9.72
	Form	0.06	10.65	23.60	46.25	58.68	70.43
	Oxa	0	0.01	0.01	0.00	0.00	0.00
	Sulf	0.18	0.18	1.85	0.52	0.20	0.15
	EDA	0	0	4.88	22.64	35.77	46.54
	PZ	4307.5	4020.6	3985.4	3523.9	3236.3	3085.2
	CO ₂	2831.5	2710.8	2691.8	2483.2	2227.2	2289.8
	SD _{CO2}	12.56	32.13	5.45	18.87	37.60	5.71
	Alk	4126.2	4045.8	3951.9	3771.5	3627.7	3615.1
Hydrolyzed Samples (mmol/kg)	SD _{Alk}	NA	NA	NA	NA	NA	NA
	Gly	0.06	0.21	2.07	0.41	2.22	3.11
	Ace	0.46	0.83	2.28	6.39	12.46	15.72
	Form	0.52	46.34	82.04	197.19	231.92	238.18
	Oxa	0.03	0.01	0.07	0.02	0.10	0.06
	Sulf	0.34	0.22	1.11	0.34	2.16	0.19
	EDA	7.81	3.21	3.63	38.72	42.54	50.03
	PZ	4151.9	4081.1	4000.2	3652.5	3405.0	3297.0

Table D.5: Tabulated Experimental Data for TE5 (8 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 175 °C, 5.0 mM Cu²⁺, 1.0 mM Fe²⁺)

	Time (wk)	0	0.4	1.0	2.0	3.0	4.0
Original Samples (mmol/kg)	Gly	0.35	0.04	0.04	0.05	0.02	0.04
	Ace	0	0.38	1.30	3.22	6.67	10.84
	Form	0.12	11.63	24.52	45.24	58.12	75.31
	Oxa	0	0.01	0.00	0	0.00	0
	Sulf	8.43	8.00	10.35	8.19	7.77	7.72
	EDA	0	0	4.94	17.54	37.53	41.89
	PZ	4140.9	3876.7	3877.3	3439.6	3237.0	2948.1
	CO ₂	2767.5	2619.3	2619.0	2396.8	2222.3	2083.1
	SD _{CO2}	41.93	37.48	7.30	23.80	23.99	21.14
	Alk	4005.3	3915.3	3852.6	3676.8	3573.7	3387.7
	SD _{Alk}	NA	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	0.85	0.27	2.11	0.70	3.51	4.19
	Ace	0.38	0.85	3.04	5.51	12.25	22.07
	Form	3.04	43.69	86.62	189.16	214.48	284.24
	Oxa	0.86	0.03	0.05	0.04	0.06	0.07
	Sulf	7.89	8.21	9.69	6.80	7.62	8.07
	EDA	27.46	3.45	4.23	38.29	41.76	46.12
	PZ	3909.2	3875.3	3983.9	3647.5	3384.5	3115.4

Table D.6: Tabulated Experimental Data for TE6 (8 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 175 °C, 5.0 mM Cu²⁺, 1.0 mM Fe²⁺, 100 mM Inhibitor A)

	Time (wk)	0	0.4	1.0	2.0	3.0	4.0	5.0
Original Samples (mmol/kg)	Gly	0	0.03	0.06	0	0.03	0.04	NT
	Ace	0	0.31	1.28	2.50	5.29	7.28	NT
	Form	0.06	9.22	22.15	35.38	47.94	57.12	NT
	Oxa	0	0.01	0.01	0	0.00	0	NT
	Sulf	8.17	8.11	9.89	7.81	7.41	6.33	NT
	EDA	0	0	2.64	15.72	28.77	30.62	NT
	PZ	4075.4	3802.3	3746.9	3472.6	3226.4	2673.1	NT
	CO ₂	2714.2	2536.6	2533.6	2409.4	2202.3	1882.1	2165.1
	SD _{CO2}	19.04	47.26	16.44	20.84	29.79	16.67	16.15
	Alk	3934.8	3849.5	3761.1	3665.2	3523.0	2986.0	3394.2
	SD _{Alk}	NA	NA	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	0.04	0.24	2.37	0.87	2.82	3.99	NT
	Ace	0.34	1.05	2.83	4.46	8.74	13.00	NT
	Form	0.76	37.27	83.91	131.52	171.96	168.69	NT
	Oxa	0.01	0.02	0.06	0.01	0.06	0.05	NT
	Sulf	8.22	7.93	9.13	6.84	7.35	6.52	NT
	EDA	25.53	7.86	1.70	32.90	34.50	31.17	NT
	PZ	4041.1	3899.2	3826.2	3628.9	3333.8	2736.5	NT

Table D.7: Tabulated Experimental Data for TE7 (8 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 175 °C, 1000 mM formate, 100 mM oxalate, 150 mM EDA)

Time (wk)		0	0.4	1.0	2.0	4.0
Original Samples (mmol/kg)	Gly	0.02	0	0.00	0	0
	Ace	8.12	5.39	7.21	7.44	9.86
	Form	1342.7	396.7	429.3	358.6	628.0
	Oxa	66.29	0.07	0.07	0.03	0.02
	Sulf	0.19	0.26	1.56	0.22	0.34
	EDA	125.76	36.48	32.45	33.37	35.27
	PZ	3965.6	2773.8	2904.0	2589.4	1938.3
	CO ₂	2380.5	2209.0	2264.2	2146.8	1704.1
	SD _{CO2}	11.49	25.99	6.58	20.86	14.67
	Alk	3442.5	3185.3	3243.6	3106.8	2442.5
	SD _{Alk}	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	0.03	0	0.13	0.18	3.12
	Ace	9.80	8.85	10.86	12.16	17.37
	Form	1343.1	1397.0	1417.5	1475.4	1233.8
	Oxa	101.69	0.08	0.13	0.07	0.11
	Sulf	0.25	0.27	0.92	0.20	0.47
	EDA	111.46	34.62	32.84	51.79	42.24
	PZ	3968.7	3721.3	3747.5	3584.3	2618.3

Table D.8: Tabulated Experimental Data for TE8 (8 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 175 °C, 0.1 Fe²⁺, 0.6 mM Cr³⁺, 0.1 mM Ni²⁺)

	Time (wk)	0	0.4	1.0	2.0	3.0	4.0	5.0
Original Samples (mmol/kg)	Gly	0.01	0.02	0.02	0	0.03	0.02	NT
	Ace	0.03	0.26	0.91	2.31	5.56	8.29	NT
	Form	0.59	7.35	21.14	37.05	49.99	65.28	NT
	Oxa	0	0.01	0.01	0.00	0.00	0	NT
	Sulf	1.30	1.64	2.69	1.37	1.51	1.63	NT
	EDA	0	0	3.48	18.32	32.01	39.91	NT
	PZ	4223.3	4062.0	3927.7	3641.8	3318.1	3139.7	NT
	CO ₂	2722.5	2674.1	2598.7	2468.6	2345.9	2250.3	2150.1
	SD _{CO2}	19.90	17.60	8.64	17.44	31.24	8.71	1.80
	Alk	4070.7	3998.3	3911.5	3823.6	3749.1	3542.2	3442.2
	SD _{Alk}	NA	NA	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	0	0.24	1.79	1.21	3.56	3.96	NT
	Ace	0	1.30	2.72	4.89	7.18	16.99	NT
	Form	0.83	29.37	81.36	148.78	186.22	258.34	NT
	Oxa	0.02	0.02	0.07	0.03	0.05	0.06	NT
	Sulf	1.46	1.68	2.31	1.26	1.52	1.78	NT
	EDA	5.87	6.27	2.16	36.32	37.12	41.08	NT
	PZ	4206.7	4018.4	3968.5	3837.4	3585.1	3344.9	NT

Table D.9: Tabulated Experimental Data for TE9 (8 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 150 °C)

	Time (wk)	0	1.0	2.0	3.0	4.1	5.0	6.0	6.0	6.0	7.6	9.4	12.3	13.3	16.0	17.2	18.0
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0	0	0	0	0	0	2.82	1.30	0	0	0	0	0	0.47	0	0
	Form	0	3.09	4.02	4.07	5.85	5.96	11.84	9.02	11.99	15.20	15.45	21.86	20.58	18.90	18.94	17.05
	Oxa	0	0	0	0	0	0.01	0.07	0.05	0	0	0.01	0.01	0	0.00	0.01	0
	Sulf	0	0.80	0.79	0.69	0.61	0.24	0.97	0.20	0.52	0.26	0.16	0.18	0.85	0.20	0.13	1.46
	Cl ⁻	0	1.69	1.87	1.82	1.23	0.04	1.58	0.03	1.46	0.04	0.04	0.03	2.12	0.02	0.02	3.84
	EDA	0	4.33	4.50	5.03	6.93	7.21	9.23	10.39	10.03	15.68	17.13	20.23	19.53	20.40	21.55	22.63
	PZ	4400.0	4378.1	4327.7	4348.3	4329.8	4326.5	4285.8	4282.2	4202.9	4216.4	4206.9	4113.0	4072.5	4037.3	4037.3	4028.5
	CO ₂	2626.7	2798.2	2715.8	2620.8	2634.8	2424.7	2635.9	2692.9	2659.2	2639.1	2627.2	2549.1	2602.4	2587.5	2573.5	2550.9
	SD _{CO2}	29.73	22.53	16.48	81.97	16.29	130.45	41.19	34.31	23.94	12.01	13.77	45.98	9.64	9.89	6.69	29.36
	Alk	4163.7	4151.9	4160.0	4124.5	4114.9	4143.7	4101.4	4096.2	4079.5	4069.3	4071.4	4033.6	4016.7	4025.1	4010.2	4022.5
	SD _{Alk}	2.85	2.29	30.70	7.25	1.48	41.72	2.37	9.76	2.74	26.96	11.10	28.33	7.88	22.40	9.29	3.94
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0	0	0	0	0	0	0	0	0.28	0	0.18	0.31	0.36	0	0.20	0.34
	Form	0	7.13	8.82	12.93	18.07	17.88	24.68	27.24	34.08	43.95	44.01	65.94	62.74	62.53	65.61	58.57
	Oxa	0	0.01	0.00	0.00	0.01	0.00	0	0.00	0.01	0.00	0.01	0.01	0.01	0.01	0.04	0.02
	Sulf	0	0.28	0.27	0.28	0.26	0.25	0.26	0.24	0.16	0.25	0.26	0.22	0.25	0.23	0.18	0.42
	Cl ⁻	0	0.28	0.22	0.45	0.05	0.23	0.18	0.10	0.02	0.17	0.17	0.12	0.09	0.14	0.08	0.08
	EDA	0	4.72	5.11	6.85	6.81	7.75	9.48	9.84	10.84	13.35	14.27	18.06	19.02	21.20	21.61	22.12
	PZ	4400.0	4409.1	4387.3	4371.5	4199.2	4328.6	4330.8	4283.4	4303.0	4269.9	4280.5	4212.3	4185.6	4176.5	4197.2	4185.5

Table D.10: Tabulated Experimental Data for TE10 (8 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 135 °C)

	Time (wk)	0	2.0	4.0	8.0	12.0	16.0	24.0	32.1	39.0	39.0	39.0	39.0	48.1	56.0	64.0	72.0
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0.42	0.43	0.44	0.42	0.42	0.42	0.41	0.39	0.39	0.40	0.35	0.39	0.39	0.40	0.38	0.38
	Ace	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Form	0.17	0.84	1.34	1.68	3.12	4.32	5.31	7.69	7.39	8.62	9.09	7.40	8.12	9.30	10.62	10.02
	Oxa	0	0.01	0.02	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01
	Sulf	0.11	0.21	0.19	0.12	0.25	1.15	0.41	0.14	0.09	0.09	0.10	0.15	0.09	0.15	0.19	0.14
	Cl ⁻	0	0.04	0.03	0.04	0.12	0.04	0.07	0.04	0.04	0.02	0.05	0.04	0.04	0.04	0.05	0.05
	NH ₄ ⁺	0	0	1.51	0	0	18.76	3.07	0	3.71	0	4.32	0.88	4.67	3.67	10.11	20.45
	FPZ	0	2.07	3.89	4.06	6.85	12.65	14.91	20.35	20.04	23.12	22.56	20.50	24.19	25.91	30.79	36.84
	EDA	0	0	0	0	0.67	1.49	1.86	2.56	2.62	3.62	3.85	2.29	3.55	3.72	4.43	5.42
	PZ	4087.8	4122.0	4241.1	4092.9	4072.6	4099.1	4075.9	4124.6	4056.4	4089.0	4072.6	4051.6	4101.4	4022.5	3991.9	3894.9
	1-EPZ	0	0	0	0	0	0.15	0.23	0.43	0.41	0.42	0.54	0.24	0.55	0.75	0.84	1.11
	AEP	0	0	0	0	0	0.22	0.17	0.34	0.51	0.72	0.72	0.54	0.84	1.03	1.10	1.55
	CO ₂	2394.0	2379.8	2350.2	2315.1	2272.6	2275.9	2271.5	2223.7	2219.7	2215.4	2190.5	2199.4	2183.8	2197.8	2207.1	2280.8
	SD _{CO2}	3.46	63.67	6.59	13.05	8.15	22.80	10.80	12.52	3.75	28.00	14.53	20.90	2.55	3.42	22.22	27.10
	Alk	4166.1	4152.3	4255.8	4153.5	4134.6	4142.9	4154.6	4115.0	4102.4	4093.7	4100.9	4100.1	4087.0	4093.1	4072.7	4055.3
	SD _{Alk}	23.57	12.44	57.05	15.37	8.64	11.59	11.24	1.09	2.00	6.45	15.51	3.06	5.05	10.59	8.51	1.47
	Fe ²⁺	0.13	10.21	3.07	21.56	28.19	24.17	10.49	19.79	8.83	8.58	9.94	9.45	16.05	14.21	10.23	8.79
	Ni ²⁺	0.06	17.65	14.87	15.36	20.65	29.68	39.40	40.94	40.86	43.49	46.36	42.14	41.75	57.80	60.18	67.76
	Cr ³⁺	0.07	7.52	10.20	14.60	12.27	8.07	5.30	7.29	6.08	7.14	6.23	6.63	6.56	6.23	5.21	5.07
Hydrolyzed Samples (mmol/kg)	Gly	0.26	0.29	0.32	0.32	0.29	0.30	0.34	0.28	0.35	0.36	0.33	0.35	0.34	0.42	0.38	0.53
	Ace	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	Form	0.40	1.92	3.30	4.37	7.70	10.88	13.26	18.43	18.45	21.23	22.23	17.56	19.58	22.61	26.46	31.33
	Oxa	0.00	0.02	0.04	0.19	0.03	0.04	0.03	0.03	0.03	0.02	0.03	0.02	0.02	0.01	0.02	0.02
	Sulf	0.16	0.48	0.40	0.28	0.18	1.21	0.50	0.18	0.25	0.18	0.16	0.16	0.28	0.16	0.37	0.12
	Cl ⁻	0.05	0.59	0.48	0.37	0.16	0.04	0.09	0.06	0.13	0.05	0.06	0.11	0.34	0.08	0.53	0.07
	NH ₄ ⁺	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	FPZ	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	EDA	0	2.25	2.50	3.24	4.67	6.13	6.98	8.53	7.11	9.25	10.89	8.19	9.44	10.28	20.74	13.37
	PZ	4150.7	4134.3	4177.6	4112.8	4108.6	4116.3	4114.5	4036.8	3356.2	4017.5	4187.5	4092.2	3932.4	4007.9	7197.7	3924.3
	1-EPZ	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
	AEP	0	0	0.43	0.53	1.32	1.82	2.55	3.34	2.81	4.05	4.57	3.32	3.87	4.53	10.22	7.16

Table D.11: Tabulated Experimental Data for TE11 (8 m PZ, 0.4 mole CO₂ per mole alkalinity initially, 135 °C)

Time (wk)	0	2.0	4.0	8.0	16.0	24.0	32.1	39.0	39.0	39.0	48.1	56.0	64.0	72.0
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0.47	0.46	0.46	0.46	0.44	0.51	0.42	0.41	0.42	0.37	0.34	0.39	0.37
	Ace	0	0	0	0	0	0	0	0	0	0	0	0	0
	Form	0.09	0.88	1.52	2.67	5.96	8.43	7.08	8.75	9.39	8.01	11.52	12.91	14.34
	Oxa	0	0	0.01	0.01	0.02	0.03	0	0.02	0.01	0.02	0.01	0.01	0.01
	Sulf	0.09	0.33	0.10	0.19	0.10	0.11	0.29	0.22	0.14	0.10	0.11	0.12	0.15
	Cl ⁻	0	0.37	0.06	0.03	0.04	0.05	0.05	0.03	0.04	0.04	0.04	0.03	0.03
	NH ₄ ⁺	0	0	0.27	0	0	0	8.00	6.50	0	0.37	2.65	1.42	9.95
	FPZ	0	1.47	7.09	13.07	25.73	40.61	40.34	46.51	41.85	37.54	51.56	48.07	67.81
	EDA	0	0	0	1.00	1.42	3.99	1.99	3.00	3.12	2.58	5.31	5.07	6.04
	PZ	3922.4	3908.3	3940.9	3884.2	3872.1	4587.1	3898.3	3884.3	3864.2	3848.0	3857.7	3844.5	3846.5
	1-EPZ	0	0	0	0	0	0.40	0.48	0.61	0.49	0.55	0.67	0.61	1.09
	AEP	0	0	0	0	0	0.56	0.38	0.62	0.52	0.53	0.91	1.43	1.40
	CO ₂	3463.4	3478.6	3447.7	3411.2	3362.3	3056.5	3532.1	3511.6	3403.6	3440.4	3209.8	3340.7	3064.4
	SD _{CO2}	48.21	14.47	9.73	17.90	17.28	26.54	25.94	61.59	10.00	5.10	12.71	9.89	23.40
	Alk	3973.1	3974.5	3974.4	3977.9	3967.0	3973.5	3969.9	3955.6	3966.0	3934.1	3908.4	3915.6	3903.6
	SD _{Alk}	7.83	7.94	17.85	17.84	22.63	39.88	19.58	0.15	17.27	0.68	3.79	1.93	13.71
	Fe ²⁺	0.22	5.83	4.22	3.80	16.77	14.30	9.46	10.58	10.42	12.66	51.22	48.83	30.69
	Ni ²⁺	0.05	21.30	21.99	20.82	38.06	70.33	88.51	75.96	77.91	67.33	59.73	77.98	101.42
	Cr ³⁺	0.14	34.15	33.65	34.81	56.10	60.26	30.47	43.10	62.38	44.70	83.86	60.36	54.01
Hydrolyzed Samples (mmol/kg)	Gly	0.52	0.50	0.48	0.47	0.48	0.54	0.47	0.46	0.47	0.48	0.46	0.47	0.51
	Ace	0	0	0	0	0	0	0	0	0	0	0	0	0
	Form	0.31	2.68	5.46	9.72	19.97	26.87	27.33	30.55	30.84	28.00	36.84	37.42	48.32
	Oxa	0	0.02	0.02	0.02	0.03	0.08	0.06	0.03	0.02	0.04	0.01	0.02	0.02
	Sulf	0.28	0.24	0.46	0.38	0.18	0.22	0.30	0.30	0.21	0.19	0.15	0.22	0.25
	Cl ⁻	0.25	0.36	1.18	0.49	0.22	0.31	0.12	0.08	0.16	0.09	0.04	0.13	0.31
	NH ₄ ⁺	0	0	0	0	0	0	0	0	0	0	0	0	0
	FPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	EDA	0	1.83	2.58	3.96	51.88	9.39	8.93	9.87	9.42	9.17	12.26	14.76	14.85
	PZ	3991.5	3855.0	3917.4	3929.3	12941	4625.0	3872.5	3859.5	3859.6	3836.6	3798.5	3806.1	3800.4
	1-EPZ	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
	AEP	0	0.31	0.38	0.70	1.30	2.41	3.14	3.75	3.37	3.28	4.63	4.99	6.25

Table D.12: Tabulated Experimental Data for TE12 (8 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 175 °C)

	Time (wk)	0	0.6	0.6	1.0	2.1	4.0	5.0	5.0	9.3	13.2	14.1	14.8
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0	0.93	1.08	1.93	6.00	9.20	15.64	13.48	33.14	46.32	45.74	48.70
	Form	0.34	39.23	42.67	62.04	137.74	163.51	152.70	179.85	294.95	362.56	389.05	377.75
	Oxa	0	0.14	0.06	0.10	0.15	0.16	0.34	0.21	0.17	0.33	0.21	0.19
	Sulf	0	0	0.04	0.24	0	0.21	0.60	0.19	0	0.08	0	0
	Cl ⁻	0.17	0.14	0.42	0.17	0.17	0.95	0.34	0.12	0.13	0.73	0.09	0.74
	NH ₄ ⁺	94.61	53.78	54.71	79.80	147.09	66.98	332.83	130.36	542.82	667.69	754.24	651.80
	FPZ	0	51.09	53.80	76.84	153.36	54.21	186.40	112.42	201.17	182.72	183.22	185.44
	EDA	0	14.20	14.07	23.30	41.43	17.94	49.24	30.07	55.38	42.45	45.67	45.83
	PZ	4204.4	3594.5	3652.7	3465.0	3017.0	898.99	2419.6	1640.5	1899.8	1361.5	1354.5	1342.7
	HEP	0	0	0	0	19.57	49.75	72.80	57.67	72.77	81.12	84.66	83.32
	1-MPZ	0	0	0	0	13.02	0	19.35	8.09	17.18	21.21	22.39	18.59
	AEP	0	7.65	8.71	15.20	45.92	18.83	72.86	44.08	106.63	101.89	105.78	114.26
	CO ₂	2501.9	2614.4	2144.8	2409.0	2148.7	1994.9	2369.5	1897.3	1489.3	1280.0	1188.4	1216.6
	SD _{CO2}	186.48	10.02	9.90	40.08	12.00	5.51	8.27	1.32	12.65	4.53	23.64	4.32
	Alk	4130.8	3921.1	3989.3	3803.1	3725.5	3495.0	3280.4	3361.4	2818.9	2580.6	2511.1	2529.1
	SD _{Alk}	2.08	63.65	5.93	142.61	173.66	14.08	30.15	24.55	131.48	102.08	3.69	40.32
	Fe ²⁺	0	57.28	46.02	84.82	120.66	82.35	133.12	121.55	133.70	84.48	105.20	86.21
	Ni ²⁺	0	84.99	32.98	74.44	132.89	429.69	148.18	419.30	240.22	312.14	439.57	380.21
	Cr ³⁺	0	9.30	13.54	19.39	22.97	0	22.90	4.54	11.83	6.18	4.12	0
Hydrolyzed Samples (mmol/kg)	Gly	0.22	0.87	1.45	1.94	2.19	2.35	3.14	2.41	3.69	3.04	4.28	2.96
	Ace	0	3.24	2.14	2.90	8.81	14.95	25.80	19.45	47.40	70.42	72.56	73.31
	Form	0.96	83.97	89.25	129.67	278.49	347.69	348.90	361.07	569.57	688.20	735.20	752.48
	Oxa	0	0.55	0.32	0.43	0.47	0.60	2.14	0.83	0.77	2.31	1.49	1.26
	Sulf	0.70	0.85	1.98	0.69	0.69	1.09	0.51	0.53	0.54	0.44	3.02	1.20
	Cl ⁻	0.16	1.31	0.26	0.44	0.18	0.25	0.27	0.20	0.30	0.13	0.34	1.52
	NH ₄ ⁺	0	88.93	69.62	101.04	199.35	302.37	359.75	374.51	584.99	747.82	804.47	792.42
	FPZ	0	0	0	0	0	0	0	0	0	0	0	0
	EDA	0	21.40	18.66	27.85	50.10	60.85	56.15	59.77	71.08	59.00	62.49	65.38
	PZ	4027.8	3871.3	3897.2	3370.1	3056.4	2755.1	2548.5	2907.3	2224.0	1656.1	1625.6	1757.6
	HEP	0	0	0	51.36	60.27	68.16	70.57	66.51	84.78	90.22	90.99	95.51
	1-MPZ	0	0	0	7.50	12.28	13.46	16.75	12.72	16.95	20.04	20.52	23.33
	AEP	0	7.36	8.22	13.03	43.36	69.31	75.99	79.17	126.59	127.64	129.83	150.66

Table D.13: Tabulated Experimental Data for TE13 (8 m PZ, 0.4 mole CO₂ per mole alkalinity initially, 175 °C)

Time (wk)	0	0.5	1.0	2.1	3.0	4.0	5.0	5.0	9.3	14.1	14.8
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0	0	0	0	0	0	0	0	0
	Ace	0	1.17	1.00	3.34	6.63	6.71	9.06	7.60	31.69	43.50
	Form	0.52	36.14	56.28	62.59	136.81	148.63	164.12	126.73	268.20	281.49
	Oxa	0	0.09	0.10	0.34	0.14	0.18	0.15	0.40	0.19	0.38
	Sulf	0.67	0.57	0.70	0.80	0.44	0.56	0.80	0.56	0.53	0.65
	Cl ⁻	0.52	0.36	0.43	1.07	0.15	0.15	0.26	0.24	0.13	0.26
	NH ₄ ⁺	0.00	26.75	50.04	131.59	180.96	225.61	282.25	277.17	521.19	859.50
	FPZ	0	59.30	89.15	127.22	184.54	182.84	210.97	199.21	241.20	247.02
	EDA	0	20.82	27.47	38.72	52.20	52.22	58.96	55.83	59.43	49.30
	PZ	4012.9	3743.9	3552.4	3148.3	2826.1	2406.4	2577.7	2719.3	1814.4	1328.6
	HEP	0	0	51.51	54.88	48.94	58.63	59.75	61.08	61.61	75.03
	1-MPZ	0	0	7.92	8.61	9.11	15.32	14.90	12.20	17.97	20.34
	AEP	0	6.33	12.51	30.34	50.55	58.53	72.99	69.88	97.10	103.52
	CO ₂	3171.7	3044.2	2993.6	3256.9	2598.9	2636.2	2441.0	2290.9	2209.5	2378.9
	SD _{CO2}	15.94	18.08	2.86	28.05	16.11	40.42	75.50	12.60	16.10	5.15
	Alk	3952.5	3817.7	3730.0	3478.1	3344.9	3224.8	3164.6	3205.6	2705.3	2332.9
	SD _{Alk}	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Fe ²⁺	0	23.63	44.80	81.82	124.23	153.55	128.07	110.95	141.96	71.12
	Ni ²⁺	0	25.50	39.05	162.52	104.80	190.20	157.31	208.41	274.03	765.10
	Cr ³⁺	0	40.61	62.03	15.13	118.41	73.33	48.82	26.24	48.24	0
Hydrolyzed Samples (mmol/kg)	Gly	0	0.38	0.40	0.23	0.37	0.26	0.21	0.13	0.36	0.31
	Ace	0	1.44	2.96	4.78	13.86	20.08	22.26	16.88	50.47	68.26
	Form	1.96	98.12	152.15	196.55	354.76	397.30	426.16	368.12	653.46	709.43
	Oxa	0.02	0.14	0.19	0.45	0.27	0.69	0.38	0.63	0.59	1.46
	Sulf	0.76	0.51	0.62	0.82	0.40	0.77	0.72	0.53	0.72	0.59
	Cl ⁻	0.31	0.12	0.52	0.57	0.28	0.52	0.24	0.88	0.50	0.21
	NH ₄ ⁺	0.00	68.64	68.27	161.37	262.65	325.85	347.15	260.31	585.61	873.83
	FPZ	0	0	0	0	0	0	0	0	0	0
	EDA	0	19.04	30.09	42.25	56.49	59.89	60.73	41.01	68.14	58.58
	PZ	4276.4	3707.7	3710.6	3362.9	3184.3	3085.1	2837.6	2177.1	2202.1	1591.7
	HEP	0	0	42.46	49.68	57.98	59.56	64.42	56.25	70.21	85.01
	1-MPZ	0	0	4.68	10.21	14.24	16.41	16.99	8.80	18.42	22.82
	AEP	0	6.26	14.42	31.94	56.30	71.97	79.27	55.28	115.93	119.95

Table D.14: Tabulated Experimental Data for TE14 (8 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 150 °C)

Time (wk)		0	1.1	2.0	4.0	6.0	10.0	14.0	14.0	14.0	18.1	22.2	26.0	30.0
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0	0	0	0	0.08	0.16	0.18	0.15	0.18	0.20	0.27	1.11	1.37
	Form	0.16	0.76	1.44	2.95	8.01	9.99	13.70	12.89	14.10	15.54	18.32	32.61	34.62
	Oxa	0.06	0.05	0.05	0.06	0	0.05	0.05	0.06	0.05	0.05	0.05	0.02	0.02
	Sulf	0.32	0.35	0.34	0.33	0.29	0.40	0.35	0.34	0.33	0.33	0.32	0.15	0.16
	Cl ⁻	0.14	0.09	0.04	0.08	0.07	0.05	0.07	0.05	0	0.06	0	0.06	0.04
	EDA	0	0	0	1.95	5.59	12.35	14.34	12.39	14.36	14.28	17.78	20.96	22.58
	PZ	4300.9	4311.7	4287.8	4258.0	4281.1	4193.9	4146.2	4153.6	4199.5	4049.9	4002.2	3969.2	3817.8
	CO ₂	2632.9	2602.2	2600.2	2573.9	2516.5	2456.1	2434.0	2521.8	2485.6	2456.7	2417.6	2400.9	2368.1
	SD _{CO2}	14.37	7.46	62.05	26.40	23.33	26.56	18.75	8.11	10.53	11.67	25.43	32.89	28.99
	Alk	4117.3	4132.7	4118.8	4093.9	4136.2	4041.8	4021.6	4038.2	4017.3	3990.1	3994.1	4004.6	3882.8
	SD _{Alk}	1.10	11.58	12.69	14.53	32.27	7.10	35.61	26.92	15.23	21.75	4.52	13.49	6.02
	Fe ²⁺	0.53	5.79	17.12	25.80	24.91	28.81	35.16	33.94	25.15	32.84	29.81	35.52	57.52
	Ni ²⁺	0.93	13.87	21.48	21.03	34.91	48.38	59.50	52.92	60.89	60.14	66.74	82.66	76.39
	Cr ³⁺	1.54	6.59	26.66	23.84	15.57	14.38	14.82	17.13	15.41	15.94	12.94	12.95	13.97
Hydrolyzed Samples (mmol/kg)	Gly	0	0.17	0.08	0.12	0.18	0.23	0.22	0.22	0.49	0.38	1.03	0.42	0.43
	Ace	0.06	0.08	0.09	0.11	0.15	0.22	0.38	0.34	0.20	0.48	0.65	0.87	0.63
	Form	0.06	2.23	4.59	7.99	13.98	27.89	38.62	36.62	27.78	46.88	56.54	68.79	59.34
	Oxa	0.04	0.06	0.07	0.06	0.08	0.09	0.11	0.10	0.13	0.10	0.12	0.12	0.12
	Sulf	0.34	0.41	0.41	0.34	0.49	0.46	0.43	0.40	0.40	0.38	0.42	0.43	0.41
	Cl ⁻	0.07	0.21	0.12	0.11	0.13	0.18	0.16	0.15	0.11	0.12	0.12	0.14	0.13
	EDA	0	0	2.41	2.65	5.90	10.24	11.39	9.94	14.08	15.95	20.32	20.18	12.19
	PZ	4311.6	4314.3	4280.5	4269.6	4222.4	4154.2	4109.6	4141.6	4154.6	4044.4	3999.8	3916.9	3159.3

Table D.15: Tabulated Experimental Data for TE15 (8 m PZ, 0.4 mole CO₂ per mole alkalinity initially, 150 °C)

Time (wk)		0	1.1	2.0	4.0	6.0	10.0	14.0	14.0	14.0	18.1	22.2	26.0	30.0
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0.63	0.04	0.05	0.09	0.10	0.13	0.23	0.20	0.18	0.29	0.48	1.56	2.05
	Form	0.30	1.76	5.66	7.20	10.61	17.60	18.72	19.65	15.88	22.22	23.47	39.82	44.18
	Oxa	0.02	0.04	0.03	0.03	0.03	0.02	0.03	0.06	0.03	0.03	0.03	0.03	0.03
	Sulf	0.26	0.28	0.27	0.26	0.28	0.25	0.25	0.30	0.25	0.27	0.25	0.17	0.12
	Cl ⁻	0.16	0.06	0.04	0.05	0.06	0.03	0.04	0.05	0.04	0.05	0.02	0.12	0.08
	EDA	0	0	2.93	8.39	11.41	16.01	17.80	17.31	16.69	18.29	24.61	25.48	32.80
	PZ	4174.7	4166.6	4087.7	4061.8	3997.8	3913.6	3879.9	3886.2	3928.9	3832.4	3813.7	3516.7	3538.2
	CO ₂	3203.3	3177.5	3224.8	3148.3	3080.8	3249.5	3213.3	3180.8	3260.4	3157.3	3158.5	3121.8	2992.7
	SD _{CO2}	15.64	10.27	69.48	54.60	15.74	33.01	12.77	39.51	20.19	31.91	31.55	5.50	4.25
	Alk	3961.3	3961.9	3933.7	3914.5	3945.1	3919.3	3910.8	3998.9	3884.1	3796.0	3900.7	3778.6	3904.2
	SD _{Alk}	24.05	5.30	8.39	20.46	112.32	51.25	30.86	14.60	17.67	31.93	136.98	21.01	86.15
	Fe ²⁺	0.31	14.74	45.41	41.12	37.77	72.15	82.14	43.38	36.93	59.61	79.18	113.05	72.01
	Ni ²⁺	0.74	18.68	51.87	35.41	47.39	80.86	77.30	85.87	93.85	104.70	107.21	119.22	123.98
	Cr ³⁺	1.23	31.66	79.05	53.70	70.00	109.48	111.39	70.34	73.33	109.31	131.78	150.36	132.18
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0.38	0.07	0.05	0.08	0.04	0.05	0.08
	Ace	0	0.08	0.11	0.17	0.22	0.44	0.56	0.55	0.59	0.70	0.99	1.21	1.80
	Form	0.08	8.19	22.22	30.16	41.98	67.46	72.56	75.36	79.99	88.43	104.63	115.30	140.73
	Oxa	0.02	0.05	0.07	0.05	0.05	0.07	0.10	0.10	0.08	0.09	0.09	0.09	0.09
	Sulf	0.34	0.37	0.39	0.39	0.39	0.35	0.39	0.35	0.29	0.41	0.36	0.38	0.38
	Cl ⁻	0.15	0.08	0.12	0.13	0.11	0.08	0.10	0.11	0.13	0.13	0.12	0.11	0.09
	EDA	0	1.97	4.75	9.94	11.56	15.28	16.59	17.01	15.63	20.96	23.96	31.86	33.72
	PZ	4101.4	4098.3	4104.9	4040.0	4030.1	3899.5	3892.7	3874.7	3877.6	3840.9	3821.5	3796.5	3692.9

Table D.16: Tabulated Experimental Data for TE16 (8 m 2-Methylpiperazine, 0.3 mole CO₂ per mole alkalinity initially, 150 °C)

Time (wk)		0	1.0	2.5	4.0	5.9	9.9	13.9	13.9	13.9	17.6	21.8	26.5	29.9
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0	1.11	2.04	3.09	3.15	4.10	5.54	5.53	5.81	6.52	20.95	24.41	25.61
	Form	0.19	10.36	22.77	32.19	32.33	36.09	44.43	43.77	43.98	44.26	112.77	121.23	117.50
	Oxa	0.33	0.13	0.12	0.10	0.21	0.12	0.11	0.09	0.10	0.10	0.15	0.14	0.14
	Sulf	0.24	0.24	0.27	0.24	0.38	0.38	0.39	0.37	0.42	1.03	0.19	0.18	0.19
	Cl ⁻	0.13	0.09	0.08	0.07	0.09	0.03	0.06	0.08	0.02	0.03	0.03	0.08	0.02
	EDA	32.88	15.17	16.45	19.24	24.55	37.20	51.21	49.58	51.31	53.69	65.83	64.77	54.46
	2-MPZ	3908.1	3728.4	3647.3	3665.8	3182.6	3161.4	3084.3	3032.5	3044.9	2946.8	2575.7	2585.9	2454.4
	CO ₂	2345.6	2424.9	2383.1	2388.7	2352.4	2316.2	2280.2	2277.2	2170.0	2077.7	1987.1	1889.3	1891.9
	SD _{CO2}	16.39	25.99	18.92	10.86	17.96	17.29	0.41	30.10	7.89	9.18	15.46	26.81	10.95
	Alk	3865.9	3832.0	3780.0	3772.3	3692.8	3636.0	3603.9	3569.3	3571.8	3472.0	3431.6	3352.7	3347.9
	SD _{Alk}	0.76	8.33	0.89	58.03	28.03	3.69	31.10	12.90	14.34	6.82	0.86	83.13	15.64
	Fe ²⁺	1.82	30.45	24.13	26.05	31.35	26.68	29.36	29.62	29.12	32.22	31.64	35.20	34.85
	Ni ²⁺	0	75.11	95.89	120.65	139.45	157.36	185.00	177.47	175.31	189.77	197.26	199.35	198.11
	Cr ³⁺	0	69.41	38.75	34.12	32.50	24.81	23.88	19.68	16.32	16.52	14.85	16.41	16.65
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0.45	4.12	3.68	5.11	5.78	6.31	8.25	8.41	8.54	9.29	31.25	33.17	36.31
	Form	2.23	66.27	71.96	102.28	76.06	83.69	108.69	109.76	110.47	126.47	199.62	201.21	213.10
	Oxa	0.28	0.22	0.12	0.14	0.11	0.10	0.11	0.11	0.13	0.14	0.25	0.24	0.27
	Sulf	0.25	0.77	0.34	0.31	0.39	0.39	0.44	0.42	0.52	0.41	0.19	0.21	0.28
	Cl ⁻	0	0.40	0.18	0.17	0.12	0.06	0.17	0.06	0.18	0.09	0.15	0.12	0.31
	EDA	29.15	15.35	14.77	20.32	26.73	32.59	42.33	35.55	40.07	50.34	60.87	57.16	56.06
	2-MPZ	3788.1	3772.5	3641.9	3629.1	3401.2	3232.1	3146.7	3098.0	3103.1	3102.3	2736.3	2577.5	2550.1

Table D.17: Tabulated Experimental Data for TE17 (4 m PZ + 4 m 2-Methylpiperazine, 0.3 mole CO₂ per mole alkalinity initially, 150 °C)

Time (wk)		0	1.0	2.5	4.0	5.9	9.9	13.9	13.9	13.9	17.6	21.8	26.5	29.9
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0	0.52	1.11	1.01	1.55	1.89	1.99	2.40	3.51	3.37	13.63	15.50	16.43
	Form	0	6.98	15.47	18.20	18.65	22.08	25.31	21.18	32.53	24.82	86.04	89.25	84.40
	Oxa	0	0.03	0.04	0.10	0.12	0.10	0.10	0.10	0.09	0.10	0.09	0.10	0.10
	Sulf	0.27	0.23	0.20	0.28	0.40	0.36	0.37	0.37	0.38	0.37	0.19	0.36	0.17
	Cl ⁻	0.04	0.03	0.02	0.57	0.08	0.04	0.09	0.09	0.07	0.02	0.03	0.15	0
	EDA	13.03	8.35	8.60	10.43	14.63	14.21	23.07	19.45	27.07	24.45	21.84	26.63	30.11
	PZ + 2-MPZ	4205.6	4148.9	4108.1	3565.7	3824.7	3777.5	3407.5	3847.4	3573.1	3556.0	3295.3	3184.2	3047.8
	CO ₂	2380.4	2321.8	2315.0	2234.0	2533.0	2477.6	2352.7	2469.6	2341.5	2755.2	2312.3	2224.8	2197.4
	SD _{CO2}	18.17	1.73	9.54	29.26	22.33	32.60	23.61	10.20	4.50	57.26	77.42	54.98	13.20
	Alk	4007.0	4028.9	3943.8	3835.2	3860.3	3853.8	3761.3	3978.6	3750.4	3755.6	3726.0	3667.6	3641.3
	SD _{Alk}	6.30	99.09	11.49	20.12	0.83	7.56	19.14	7.92	22.59	4.36	13.43	6.59	5.38
	Fe ²⁺	0.20	84.83	70.52	103.55	49.48	60.16	99.51	58.84	55.09	56.04	56.77	64.77	71.61
	Ni ²⁺	0	69.48	123.25	119.54	197.91	189.40	219.63	184.05	242.27	190.25	216.00	245.10	346.97
	Cr ³⁺	0	87.27	47.43	18.96	16.43	26.16	22.66	20.25	13.98	16.76	14.18	19.60	15.98
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0	0	0.70	0.73	0.69
	Ace	0.29	1.11	2.25	2.40	3.21	3.33	3.92	4.00	5.26	5.39	21.31	23.98	24.85
	Form	1.01	23.76	54.97	77.48	43.62	50.32	70.26	59.75	78.55	76.75	152.69	165.77	169.77
	Oxa	0.12	0.05	0.09	0.12	0.14	0.16	0.11	0.11	0.12	0.08	0.16	0.17	0.15
	Sulf	0.35	0.33	0.37	0.36	0.48	0.47	0.54	0.44	0.41	0.46	0.23	0.26	0.23
	Cl ⁻	0	0	0.09	0.63	0.14	0.18	0.27	0.13	0.09	0.18	0.18	0.22	0.09
	EDA	13.89	7.54	8.83	7.99	13.62	16.38	22.93	18.32	26.05	25.79	19.63	28.20	23.94
	PZ	4096.7	4161.7	3866.7	3656.9	3962.3	3894.8	3550.5	3822.7	3663.3	3669.4	3264.2	3132.7	3274.6

Table D.18: Tabulated Experimental Data for TE18 (8 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 175 °C)

	Time (wk)	0	0.6	1.0	1.5	2.4	2.9	2.9	2.9	3.4	5.0	6.0
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0.07	0.11	0.16	0.07	0.24	0.27	0.24	0.25	0.08	0.12	0.25
	Ace	0.07	0.29	1.26	1.48	3.16	5.68	5.34	5.11	4.44	12.42	9.79
	Form	0.35	22.13	28.87	43.59	66.23	82.71	77.67	75.20	53.07	126.35	104.47
	Oxa	0.08	0.07	0.10	0.06	0.06	0.08	0.07	0.07	0.08	0.13	0.09
	Sulf	0.17	0.16	0.16	0.18	0.20	0.16	0.16	0.16	0.19	0.17	0.16
	Cl ⁻	0.13	0.18	0.16	0.11	0.19	0.18	0.13	0.09	0.12	0.10	0.17
	EDA	0	10.81	17.61	29.15	33.94	39.52	41.67	41.34	37.45	54.22	44.95
	PZ	3352.8	4312.8	4197.2	4015.5	3706.7	3509.7	3577.0	3578.3	3272.7	2527.8	2737.4
	CO ₂	2497.3	2386.7	2317.7	2269.5	2103.7	2102.7	2177.9	2186.4	2977.8	2427.6	1863.3
	SD _{CO2}	17.67	4.78	5.81	10.33	1.42	63.84	15.74	13.88	29.05	33.29	14.30
	Alk	4129.1	4024.9	3966.8	3884.6	3813.7	3630.4	3650.7	3729.1	3419.7	3037.2	3347.9
	SD _{Alk}	13.39	0.85	0.23	13.91	85.21	10.40	2.69	83.50	18.20	37.78	6.66
	Fe ²⁺	0	27.89	72.41	91.55	74.18	110.23	109.62	127.41	96.68	222.06	126.69
	Ni ²⁺	0	54.10	40.24	65.55	91.20	103.58	94.38	91.41	305.54	199.41	205.86
	Cr ³⁺	0.67	38.54	35.63	31.54	12.03	24.24	25.54	39.79	10.16	174.49	24.19
Hydrolyzed Samples (mmol/kg)	Gly	0.17	0.28	0.32	0.70	0.72	0.75	0.58	0.44	1.61	0.30	0.30
	Ace	0.13	0.61	1.62	2.99	5.21	6.99	6.45	6.40	7.86	19.07	18.92
	Form	0.45	62.18	71.28	121.23	181.32	233.05	217.43	210.52	202.68	541.41	550.08
	Oxa	0.04	0.10	0.08	0.09	0.10	0.11	0.10	0.13	0.40	0.15	0.15
	Sulf	0.30	0.31	0.28	0.25	0.31	0.32	0.31	0.33	0.45	0.27	0.32
	Cl ⁻	0.43	0.48	0.39	0.17	0.23	0.40	0.55	0.59	0.42	0.42	0.66
	EDA	0	8.41	19.64	22.06	39.58	44.97	44.27	42.64	42.73	68.83	64.99
	PZ	4472.0	4295.8	4031.3	4041.8	3839.6	3708.7	3704.2	3725.6	3588.9	2924.7	2917.0

Table D.19: Tabulated Experimental Data for TE19 (8 m PZ, 0.4 mole CO₂ per mole alkalinity initially, 175 °C)

	Time (wk)	0	0.6	1.0	1.5	2.4	2.9	2.9	2.9	3.4	5.0	6.0
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0.09	0.12	0.11	0.11	0.11	0.12	0.08	0.10	0.13	0.08	0.15
	Ace	0.04	1.78	2.69	3.99	7.09	8.44	7.75	7.17	9.58	8.07	15.01
	Form	0.19	32.09	48.34	72.84	88.98	102.15	93.59	89.00	108.66	99.49	143.15
	Oxa	0.01	0.06	0.07	0.10	0.11	0.11	0.10	0.10	0.10	0.08	0.14
	Sulf	0.13	0.15	0.13	0.16	0.15	0.15	0.14	0.14	0.15	0.14	0.13
	Cl ⁻	0.29	0.14	0.13	0.29	0.11	0.30	0.13	0.11	0.12	0.05	0.07
	EDA	0	21.72	30.08	44.06	53.03	56.29	51.86	51.94	56.05	57.56	61.05
	PZ	4332.9	3880.1	3802.9	3464.3	3235.0	3072.8	3164.1	3092.4	2869.7	3147.5	2273.4
	CO ₂	3245.0	3048.2	2930.7	2903.5	2670.5	2656.3	2752.9	2789.8	2653.6	1965.2	1829.7
	SD _{CO2}	5.93	15.84	15.06	236.90	30.47	18.77	11.06	6.38	10.63	5.34	17.44
	Alk	3960.7	3761.0	3649.7	3477.5	3343.3	3372.6	3389.6	3329.4	3145.3	3222.4	2811.2
	SD _{Alk}	3.27	28.14	10.30	19.16	13.76	167.76	118.64	5.73	6.48	317.87	3.72
	Fe ²⁺	0	72.56	94.12	123.15	156.45	128.98	135.62	154.74	175.07	142.15	192.94
	Ni ²⁺	0	34.79	54.25	69.18	92.41	152.70	115.78	113.24	203.89	153.48	299.46
	Cr ³⁺	0	46.11	74.66	89.36	111.11	74.72	78.74	115.42	75.08	34.89	144.34
Hydrolyzed Samples (mmol/kg)	Gly	0.18	0.20	0.19	0.22	0.20	0.41	0.36	0.26	0.39	1.02	0.49
	Ace	0.12	2.06	3.68	6.66	9.47	12.43	11.22	9.99	15.02	11.51	25.13
	Form	0.31	122.82	183.49	272.14	341.50	405.06	364.09	344.05	448.48	309.93	705.08
	Oxa	0.02	0.08	0.09	0.17	0.11	0.14	0.14	0.11	0.16	0.14	0.20
	Sulf	0.31	0.33	0.38	0.38	0.38	0.36	0.37	0.36	0.32	0.36	0.40
	Cl ⁻	0.22	0.27	0.73	0.55	0.52	0.57	0.31	0.35	0.47	0.30	0.39
	EDA	0	23.30	30.02	48.23	50.83	56.33	57.74	56.86	65.36	57.93	66.01
	PZ	4313.9	4003.0	3892.8	3623.7	3452.8	3316.9	3333.2	3422.8	3187.3	3372.6	2637.7

Table D.20: Tabulated Experimental Data for TE20 (8 m 1-Methylpiperazine, 0.3 mole CO₂ per mole alkalinity initially, 150 °C)

	Time (wk)	0	1.0	2.4	3.8	6.1	10.4	14.7	17.9	22.4	26.0	30.0
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0	0	0	0	0	0	0	0	0	0
	Ace	0.64	0	0.28	0.43	0.71	1.11	1.09	0.06	0.26	3.52	4.82
	Form	3.63	7.73	16.08	24.85	36.86	48.08	50.11	4.13	18.08	72.44	90.12
	Oxa	0.05	0.04	0.04	0.05	0.04	0.04	0	0.02	0.02	0	0
	Sulf	0.14	0.12	0.14	0.14	0.12	0.13	0.12	0.18	0.13	0.10	0.10
	Cl ⁻	0.27	0.04	0.05	0.05	0.04	0.05	0.02	0.02	0.07	0.02	0.04
	FPZ	0	0	0	0	0	0	0	0	17.39	102.10	126.26
	EDA	0	0	0	0	0	0	0	0.32	0.66	1.53	1.69
	PZ	0	90.68	194.33	321.83	437.19	559.20	648.09	284.03	719.01	790.14	748.42
	1-MPZ	3899.5	3771.5	3384.3	3115.3	2790.9	2491.0	2284.5	4672.9	3165.5	1907.4	1723.8
	1,4-DMPZ	0	77.98	276.78	405.88	481.76	647.85	686.34	317.64	689.12	815.32	797.18
	CO ₂	2189.8	2104.5	2153.7	1802.6	2069.1	1895.9	1666.4	157.5	575.61	1664.3	1633.6
	SD _{CO2}	5.42	10.41	17.12	4.25	2.24	19.14	3.95	1.62	3.47	5.61	7.65
	Alk	3947.7	3959.0	3901.4	4041.9	3804.5	3752.7	3727.1	4631.3	4251.7	3583.0	3359.0
	SD _{Alk}	7.33	2.54	8.79	5.55	24.92	9.78	29.03	17.97	19.31	45.35	1.36
	Fe ²⁺	0	10.08	9.33	10.99	13.85	13.10	9.51	0	2.67	11.41	13.49
	Ni ²⁺	0	21.79	14.71	27.28	41.19	54.18	55.99	6.96	36.52	98.46	110.34
	Cr ³⁺	0	35.81	14.54	13.35	25.20	16.55	7.07	0	0	9.23	14.95
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0.29	0.18	0.29	0.39	0	0	1.00	1.00
	Ace	0	0.51	1.55	1.88	2.42	3.34	3.36	0.24	1.42	6.72	9.31
	Form	1.02	29.34	59.99	93.28	136.05	186.86	183.14	11.76	59.17	322.99	464.04
	Oxa	0.03	0.11	0.12	0.21	0.10	0.15	0.08	0.11	0.07	0.10	0.07
	Sulf	0.11	0.12	0.16	0.16	0.14	0.14	0.15	0.21	0.31	0.29	0.14
	Cl ⁻	0.06	0.18	0.10	0.09	0.10	0.08	0.05	0.05	0.11	0.40	0.08
	FPZ	0	0	0	0	0	0	0	0	0	0	0
	EDA	0	0	0	0	0	0	0	0.44	0.80	2.15	2.37
	PZ	0	70.38	178.85	332.86	448.59	470.39	644.85	285.10	730.72	857.71	746.12
	1-MPZ	4081.2	3628.7	3299.3	3058.4	2792.6	2281.3	2211.0	4447.9	3157.3	1951.7	1628.7
	1,4-DMPZ	0	70.05	231.27	305.28	434.51	470.93	586.89	292.84	689.26	781.34	707.57

Table D.21: Tabulated Experimental Data for TE21 (8 m PZ, unloaded, 175 °C)

Time (wk)		0	1.0	2.0	3.7	4.3	5.1	5.1	5.1	7.3	9.1	11.1	12.9	14.9
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0.17	0.12	0.20	0.13	0.15	0.17	0.15	0.22	0.16	0.10	0.16	0.12
	Ace	0	0.12	0.14	0.26	0.26	0.18	0.22	0.44	0.32	0.72	1.61	0.83	1.07
	Form	0.44	1.98	4.44	7.35	6.71	7.24	7.33	10.30	9.86	14.02	14.58	12.81	14.40
	Oxa	0.05	0.05	0.06	0.05	0.08	0.04	0.08	0.07	0.06	0.07	0.06	0.09	0.07
	Sulf	0.19	0.21	0.12	0.14	0.20	0.19	0.22	0.20	0.20	0.18	0.19	0.16	0.14
	Cl ⁻	0.15	0.11	0.05	0.05	0.06	0.05	0.16	0.11	0.04	0.08	0	0.04	0.10
	EDA	0	0	0	0	4.88	0	5.50	8.92	10.41	22.80	34.93	18.42	33.43
	PZ	4826.8	4852.8	4801.8	4793.6	4776.8	4941.3	4784.0	4790.9	4669.0	4641.1	4500.1	4700.0	4593.6
	Alk	4715.2	4688.0	4685.0	4661.0	4655.2	4671.7	4655.0	4680.0	4660.8	4667.1	4629.7	4653.3	4626.1
	SD _{Alk}	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Fe ²⁺	0	0	1.15	0.11	1.31	0.09	0.47	0.77	4.50	2.66	1.77	0	7.68
	Ni ²⁺	0	0	1.57	0	0.14	0	0	0.28	1.40	1.09	2.91	1.08	1.66
	Cr ³⁺	0	0	0.12	0	0	0	0	0	0.16	0.12	0.04	0	1.43
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0.16	0.25	0.26	0.54	0.41	0.51	0.44	0.85	0.88	1.91	3.22	1.46	1.50
	Form	0.76	2.56	4.94	8.02	8.04	8.91	7.66	11.60	11.54	15.65	17.46	15.85	18.28
	Oxa	0.13	0.06	0.06	0.07	0.23	0.06	0.09	0.14	0.08	0.10	0.12	0.10	0.08
	Sulf	0.20	0.19	0.22	0.21	0.23	0.23	0.26	0.21	0.23	0.28	0.21	0.36	0.23
	Cl ⁻	0.18	0.32	0.24	0.22	0.23	0.38	0.26	0.27	0.23	0.27	0.21	0.27	0.26
	EDA	0	0	0	0	4.68	9.75	9.20	11.27	11.31	25.47	33.08	15.21	20.45
	PZ	5575.1	4962.6	4877.2	4777.9	4855.0	4721.5	4915.5	5019.1	4787.9	4716.3	4647.3	4764.5	4665.7

Table D.22: Tabulated Experimental Data for TE22 (8 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 175 °C, glass-lined cylinders)

	Time (wk)	0.0	1.0	3.7	4.3	5.1	5.1	5.1	7.3	12.9	14.9
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0	0	0	0	0	0	0	0	0
	Ace	0	0.64	6.72	4.15	10.87	8.80	9.45	13.18	19.77	23.07
	Form	0.16	6.78	79.91	46.67	141.02	110.62	119.64	180.37	304.73	373.02
	Oxa	0.04	0.09	0.10	0.08	0.14	0.10	0.10	0.12	0.12	0.04
	Sulf	0.21	0.24	0.27	0.23	0.27	0.22	0.27	0.24	0.23	0.26
	Cl ⁻	0.09	0.13	0.06	0.14	0.05	0.08	0.06	0.14	0.09	0.06
	EDA	0	20.11	36.99	42.46	53.02	35.78	27.86	48.59	41.52	46.20
	PZ	4301.1	6767.4	3750.0	4296.9	3047.9	3129.0	3106.5	2716.3	1901.4	1457.3
	CO ₂	2803.0	915.8	2175.5	1378.8	2276.9	2199.1	2107.7	2125.6	1305.0	NT
	SD _{CO2}	4.71	52.02	139.01	14.44	51.17	12.81	35.49	62.77	51.28	NT
	Alk	4.15	6.87	3.67	4.61	3.48	3.49	3.46	3.32	2.97	2.66
	SD _{Alk}	0.01	NA	0.13	0.03	0.02	0.05	0.02	0.02	0.01	0.11
	Fe ²⁺	0	0	0	NT	NT	1.19	NT	NT	0	0
	Ni ²⁺	0	0	0	NT	NT	0	NT	NT	0	0
	Cr ³⁺	0	0	0	NT	NT	0	NT	NT	0	0
Hydrolyzed Samples (mmol/kg)	Gly	0	1.78	1.24	1.48	0	0	0	0	0.66	0.25
	Ace	0.35	3.81	10.00	6.69	15.13	12.63	13.50	18.19	28.14	29.57
	Form	3.72	42.59	128.06	79.61	213.34	170.27	185.54	272.67	492.00	538.00
	Oxa	0.03	0.57	0.21	0.30	0.36	0.22	0.28	0.34	0.34	0.15
	Sulf	0.27	0.58	0.24	0.31	0.26	0.26	0.22	0.22	0.44	0.26
	Cl ⁻	0.26	0.27	0.20	0.52	0.23	0.17	0.19	0.22	0.23	0.21
	EDA	0	13.72	34.82	42.31	48.50	46.49	38.38	47.04	53.78	50.73
	PZ	4370.2	6789.7	3693.9	4355.0	3252.2	3317.7	3259.0	2960.6	2201.3	1786.9

Table D.23: Tabulated Experimental Data for TE23 (8 m PZ, 0.3 mole H+ per mole alkalinity initially, 175 °C)

Time (wk)		0	0.9	2.0	3.7	4.3	5.1	5.1	5.1	7.3	9.1	11.1	12.9	14.9
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0	0.22	0.21	1.86	0.30	0.44	0.77	0.81	1.09	1.60	2.46	3.42	3.05
	Form	0.24	1.44	1.37	6.02	1.49	1.85	2.20	2.62	2.78	2.70	3.51	4.58	2.75
	Oxa	0	0	0	0	0	0	0	0	0	0	0	0	0
	Sulf	1641.1	1685.2	1631.0	5073.7	1604.6	1564.1	1638.4	1619.2	1626.1	1624.3	1575.3	1645.4	1427.3
	Cl ⁻	0.05	0.08	0.15	0.51	0.05	0.05	0.08	0.10	0.06	0.14	0.08	0.06	0.08
	EDA	0	0	12.26	20.82	23.85	28.14	40.11	32.35	51.31	75.17	84.05	116.87	116.73
	PZ	4341.8	4133.5	3941.2	3775.8	3738.1	3707.4	3622.0	3832.4	3497.9	3282.8	2980.5	2900.6	2868.5
	CO ₂	0	0	0	0	0	0	0	0	0	0	0	0	0
	SD _{CO2}	0	0	0	0	0	0	0	0	0	0	0	0	0
	Alk	2858.0	2833.6	2710.8	2753.1	2707.6	2726.1	2702.6	2718.7	2656.3	2609.3	2491.4	2535.0	2506.0
	SD _{Alk}	5.10	13.88	3.97	11.84	25.40	2.40	11.01	16.24	29.54	12.36	1.06	37.73	17.51
	Fe ²⁺	0	16.98	31.29	55.69	63.75	51.30	60.07	74.94	65.16	177.14	221.06	243.79	374.71
	Ni ²⁺	0	9.72	18.68	52.46	19.48	25.64	28.12	65.34	76.99	106.15	131.19	243.79	151.36
	Cr ³⁺	0	0	0.01	0	0.14	0.06	0	0	0.19	0	0	0.54	0.23
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0	0.95	0.74	1.70	1.10	1.14	1.36	1.61	1.88	2.84	3.37	5.46	4.98
	Form	0.33	3.55	2.89	5.42	3.56	4.21	4.77	6.08	5.90	6.26	6.90	10.46	7.72
	Oxa	0	0	0	0	0	0	0	0	0	0	0	0	0
	Sulf	1686.0	1597.1	1492.5	917.1	1545.2	980.9	1742.0	1129.8	978.7	1618.7	1575.3	1449.7	1674.5
	Cl ⁻	0.09	0.25	0.15	0.20	0.12	0.10	0.10	0.28	0.18	0.08	0.08	0.14	0.13
	EDA	0	4.33	7.98	25.15	36.37	35.62	34.22	39.51	61.80	73.47	85.18	114.97	110.65
	PZ	4479.7	4168.4	3931.4	3958.1	3617.4	3848.3	3559.0	3801.6	3641.4	3442.5	3061.7	2995.3	2872.6

Table D.24: Tabulated Experimental Data for TE24 (8 m Homopiperazine (HomoPZ), 0.3 mole CO₂ per mole alkalinity initially, 175 °C)

Time (wk)		0	0.9	4.1	6.1	9.9
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0	0	0	0
	Ace	0	9.37	17.57	23.13	23.20
	Form	0.51	38.02	59.11	26.36	54.49
	Oxa	0	0.25	0.32	0.47	0.15
	Sulf	15.67	16.60	17.29	19.15	16.70
	Cl ⁻	0.64	0.59	0.70	1.14	0.74
	HomoPZ	3770.2	1029.7	35.37	44.26	86.94
	CO ₂	2546.0	1243.7	806.6	1274.8	483.2
	SD _{CO2}	22.03	12.73	8.26	8.18	4.46
	Alk	3933.9	2455.0	1345.1	1705.0	1380.9
	SD _{Alk}	2.84	0.98	12.61	6.91	172.74
	Fe ²⁺	0	NT	100.75	NT	35.01
	Ni ²⁺	0	NT	1136.6	NT	1628.1
	Cr ³⁺	0	NT	14.70	NT	4.72
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0.44	NT	0.34
	Ace	0	9.40	30.77	NT	43.42
	Form	12.54	293.16	175.81	NT	107.23
	Oxa	0.33	0.53	0.84	NT	0.84
	Sulf	17.07	19.59	18.25	NT	17.40
	Cl ⁻	0.77	0.60	0.63	NT	0.60
	HomoPZ	2978.9	1106.1	106.9	NT	0

Table D.25: Tabulated Experimental Data for TE25 (8 m Pyrrolidine (Pyr), 0.3 mole CO₂ per mole alkalinity initially, 175 °C)

Time (wk)		0	0.9	1.8	4.1	6.1	6.1	6.1	8.1	9.9
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0	0	0	0	0	0	0	0
	Ace	0	0.81	0	0	0	0	0	0	0
	Form	1.07	45.46	43.72	72.24	80.27	81.58	77.89	88.35	82.13
	Oxa	0.21	0.14	0	0	0.10	0.12	0.16	0.15	0.13
	Sulf	17.12	16.37	17.57	10.47	12.90	14.41	14.12	16.24	17.33
	Cl ⁻	0.38	0	0.11	0.06	0.07	0.21	0.10	0.06	0.40
	Pyr	4354.9	1945.0	1410.5	1077.3	989.58	981.07	967.15	880.55	817.47
	CO ₂	1400.7	1454.4	1413.7	1438.8	1439.3	1436.4	1414.5	1341.4	1288.3
	SD _{CO2}	10.88	1.42	4.02	11.32	7.98	49.02	12.20	13.07	30.72
	Alk	4725.2	4366.1	4316.5	3988.5	4019.6	4032.7	3972.8	4021.7	4156.0
	SD _{Alk}	24.32	97.63	375.76	18.89	64.73	26.96	28.28	33.85	59.81
	Fe ²⁺	0	NT	NT	5.92	NT	NT	NT	NT	3.69
	Ni ²⁺	0	NT	NT	5.74	NT	NT	NT	NT	7.02
	Cr ³⁺	0	NT	NT	0.96	NT	NT	NT	NT	0.29
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0
	Ace	0	1.31	0	0	0	0	0	0	0
	Form	2.00	66.22	76.55	94.71	103.69	103.26	104.59	101.88	112.63
	Oxa	0.59	0.19	0.18	0.17	0.20	0.26	0.17	0.12	0
	Sulf	29.45	17.94	17.74	18.29	18.36	29.78	15.01	13.75	13.72
	Cl ⁻	0.73	0.22	0.19	0.23	0.20	0.16	0.23	0.11	0.10
	Pyr	1501.2	2206.8	1453.2	955.71	800.70	570.09	890.41	871.87	841.00

Table D.26: Tabulated Experimental Data for TE26 (8 m Piperidine (PD), 0.3 mole CO₂ per mole alkalinity initially, 175 °C)

Time (wk)		0	0.9	1.8	4.1	6.1	6.1	6.1	8.1	9.9
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0	0	0	0	0	0	0	0
	Ace	0	0	0	0	0	0	0.25	0	0
	Form	0.46	65.44	71.31	89.69	100.09	95.54	36.57	95.06	95.83
	Oxa	0	0	0	0	0	0	0	0	0
	Sulf	6.92	5.12	7.40	7.52	7.40	3.42	2.27	2.78	2.55
	Cl ⁻	0.13	0.12	0.07	0.10	0.06	0.07	0.27	0.06	0.14
	PD	4489.3	4146.1	3685.6	3274.2	3054.3	2903.7	3382.7	2882.0	2619.5
	CO ₂	1645.7	1475.9	1483.7	1456.0	1417.1	1402.8	2323.4	1357.4	1338.1
	SD _{CO2}	11.30	6.94	7.07	12.91	26.39	14.57	8.96	5.73	3.45
	Alk	4375.7	4281.0	4261.7	4246.9	4136.2	4142.5	4476.1	4107.8	4081.7
	SD _{Alk}	17.76	6.02	1.79	57.24	108.70	14.60	NA	34.67	59.80
	Fe ²⁺	0	NT	NT	4.11	NT	NT	NT	NT	5.60
	Ni ²⁺	0	NT	NT	1.48	NT	NT	NT	NT	1.47
	Cr ³⁺	0	NT	NT	1.56	NT	NT	NT	NT	0.88
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0
	Ace	0	0	0	0	0	0	0.37	0	0.10
	Form	1.24	136.02	0	211.69	244.61	242.61	94.09	256.17	272.21
	Oxa	0.08	0.07	0	0.06	0.06	0.07	0.06	0.06	0.06
	Sulf	1.07	3.58	2.54	0.53	0.65	0.53	0.69	0.60	0.60
	Cl ⁻	0.17	0.24	0	0.24	0.24	0.23	0.52	0.22	0.22
	PD	797.36	701.34	689.18	631.66	620.89	565.34	3221.2	1203.9	1146.3

Table D.27: Tabulated Experimental Data for TE27 (8 m Hexamethyleneimine (HMI), 0.3 mole CO₂ per mole alkalinity initially, 175 °C)

Time (wk)		0	0.9	1.8	6.1	6.1	9.9
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0	0	0	0	0
	Ace	0	0	0	0	0	0
	Form	0.34	41.73	56.51	65.64	71.93	71.06
	Oxa	0	0	0.44	0.02	0.04	0.03
	Sulf	0.46	7.37	7.62	0.27	0.75	0.54
	Cl ⁻	0.17	0.70	1.13	0.14	0.10	0.04
	HMI	4282.2	143.93	416.96	299.19	270.46	231.56
	CO ₂	1355.6	1077.3	1176.1	1138.2	1210.0	1104.8
	SD _{CO2}	23.18	8.01	14.04	11.38	7.92	8.29
	Alk	4196.3	3392.9	3085.2	2668.6	2698.6	2668.1
	SD _{Alk}	37.71	30.41	31.93	46.20	24.97	49.49
	Fe ²⁺	0	NT	NT	4.93	NT	5.23
	Ni ²⁺	0	NT	NT	4.54	NT	5.27
	Cr ³⁺	0	NT	NT	0.33	NT	0.67
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0
	Ace	0	0	0	0.21	0	0.14
	Form	1.40	144.77	144.58	174.49	160.38	151.25
	Oxa	0.05	0.07	0.07	0.09	0.06	0.05
	Sulf	0.59	0.58	0.69	0.88	0.46	0.45
	Cl ⁻	0.31	0.26	0.26	0.47	0.28	0.19
	HMI	376.12	233.33	101.91	54.23	42.59	47.19

Table D.28: Tabulated Experimental Data for TE28 (4 m PZ + 4 m 1-Methylpiperazine (1-MPZ), 0.3 mole CO₂ per mole alkalinity initially, 175 °C)

	Time (wk)	0	1.0	4.2	6.3	8.6	10.0
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0	0	0	0	0
	Ace	0.12	0	0.09	0.24	0.16	1.13
	Form	0.20	4.16	14.44	16.16	17.16	28.65
	Oxa	0	0	0	0	0	0.02
	Sulf	0.22	0.17	0.17	0.25	0.19	0.21
	Cl ⁻	0	0.14	0	0	0	0.01
	FPZ	0	0	0	0	0.62	1.02
	EDA	0	0	0	9.21	0	4.92
	PZ	2027.6	2030.8	2015.6	2036.4	2145.8	2002.4
	1-MPZ	1910.6	1920.8	1662.7	1642.8	1587.3	1598.9
	1,4-DMPZ	0	36.85	111.98	165.19	175.22	187.75
	CO ₂	2575.9	2582.3	2429.7	NT	1601.7	2470.9
	SD _{CO2}	13.05	24.15	63.75	NT	9.95	23.02
	Alk	3989.8	3974.1	3966.1	NT	4145.0	3812.6
	SD _{Alk}	2.92	11.14	27.94	NT	NA	17.71
	Fe ²⁺	0	13.95	23.94	18.51	1.60	25.85
	Ni ²⁺	0	10.28	62.70	107.96	103.87	85.07
	Cr ³⁺	0	19.86	43.57	5.89	3.70	28.03
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0
	Ace	0.07	0.09	0.51	0.59	1.17	2.76
	Form	1.23	17.98	55.68	66.68	59.62	116.97
	Oxa	0	0	0	0	0.07	0.07
	Sulf	0.23	0.21	0.20	0.43	0.23	0.24
	Cl ⁻	0.08	0.06	0.04	0.42	0.04	0.04
	FPZ	0	0	0	0	0	0
	EDA	0	6.28	0	0	0	5.40
	PZ	2040.1	2027.6	2069.7	2025.7	2237.2	2200.7
	1-MPZ	1877.4	1844.2	1763.3	1680.7	1610.2	1753.3
	1,4-DMPZ	0	74.37	108.48	201.95	303.46	200.89

Table D.29: Tabulated Experimental Data for TE29 (5 m PZ + 2 m 1-Methylpiperazine (1-MPZ) + 1 m 1,4-Dimethylpiperazine (1,4-DMPZ), 0.3 mole CO₂ per mole alkalinity initially, 150 °C)

	Time (wk)	0	1.0	4.2	6.3	8.6	10.1	12.2	15.0
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0	0	0	0	0	0	0
	Ace	0	0	0	0.15	0.19	2.01	1.72	0.83
	Form	0.49	4.34	13.66	11.55	16.48	33.77	29.20	30.83
	Oxa	0	0	0	0	0	0.03	0.02	0
	Sulf	0.31	0.26	0	0.30	0.24	0.22	0.19	0.11
	Cl ⁻	0.06	0.07	0.04	0.16	0.04	0.02	0	0.02
	FPZ	0	0	0	0	0	1.52	1.43	0
	EDA	0	0	0	2.91	3.08	0	0	7.39
	PZ	2626.6	2536.8	2410.7	2282.8	2342.8	2163.7	2197.9	2152.1
	1-MPZ	988.78	1159.6	1345.4	1223.6	1257.4	1124.0	1228.4	1388.7
	1,4-DMPZ	622.97	748.35	642.64	594.15	579.76	483.01	408.11	291.18
	CO ₂	NT	NT	NT	NT	NT	NT	NT	NT
	Alk	4038.5	4043.0	3999.1	NT	3973.5	3856.8	3889.0	3849.1
	SD _{Alk}	9.57	15.80	20.03	NT	18.31	15.97	12.60	14.67
	Fe ²⁺	0	7.91	23.80	NT	9.76	24.33	17.31	NT
	Ni ²⁺	0	19.98	33.88	NT	87.01	71.36	63.06	NT
	Cr ³⁺	0	2.03	32.06	NT	0	20.86	7.39	NT
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0.79
	Ace	0	0	0	0.23	0.40	3.74	0.65	2.31
	Form	2.40	15.73	49.13	48.79	64.18	125.85	107.74	135.66
	Oxa	0.07	0.29	0	0.07	0.01	0.06	0	0.03
	Sulf	0.42	0.27	0.30	0.29	0.20	0.28	0.18	0.14
	Cl ⁻	0.18	0.10	0.06	0.14	0.04	0.06	0	0.06
	FPZ	0	0	0	0	0	0	0	0
	EDA	0	0	0	0	0	0	2.00	0
	PZ	2522.4	2526.9	2427.1	2315.1	2380.2	2292.5	2224.5	2157.0
	1-MPZ	1144.1	1116.0	1219.4	1240.4	1229.7	1275.6	1234.5	1326.4
	1,4-DMPZ	736.22	737.75	621.61	589.96	429.04	483.09	543.50	348.70

Table D.30: Tabulated Experimental Data for TE30 (5 m PZ + 2.5 m 1-Methylpiperazine (1-MPZ)+ 0.5 m 1,4-Dimethylpiperazine (1,4-DMPZ), 0.3 mole CO₂ per mole alkalinity initially, 150 °C)

Time (wk)		0	4.2
Original Samples (mmol/kg)	Gly	0	0
	Ace	0	0.09
	Form	0.38	11.42
	Oxa	0	0.05
	Sulf	0.25	0.23
	Cl ⁻	0.10	0
	EDA	0	0
	PZ	2775.9	2530.9
	1-MPZ	1252.5	1376.9
	1,4-DMPZ	326.56	291.51
	CO ₂	2485.1	2399.5
	SD _{CO2}	11.82	19.22
	Alk	4084.5	4038.3
	SD _{Alk}	15.14	15.29
Hydrolyzed Samples (mmol/kg)	Gly	0	0
	Ace	0.22	0.25
	Form	1.70	42.72
	Oxa	0.06	0.06
	Sulf	0.30	0.27
	Cl ⁻	0.09	0
	EDA	0	0
	PZ	2759.8	2528.0
	1-MPZ	1330.3	1288.5
	1,4-DMPZ	436.88	356.84

Table D.31: Tabulated Experimental Data for TE31 (5 m PZ + 1.5 m 1-Methylpiperazine (1-MPZ) + 1.5 m 1,4-Dimethylpiperazine (1,4-DMPZ), 0.3 mole CO₂ per mole alkalinity initially, 150 °C)

Time (wk)		0	1.0	4.2
Original Samples (mmol/kg)	Gly	0	0	0
	Ace	0.13	0.54	0.48
	Form	0.68	4.12	15.39
	Oxa	0	0.07	0.04
	Sulf	0.25	0.24	0.30
	Cl ⁻	0.07	0.06	0.34
	EDA	0	0	0
	PZ	2570.0	2419.7	2128.4
	1-MPZ	840.48	888.19	1000.0
	1,4-DMPZ	912.95	811.22	446.24
	CO ₂	2337.6	2449.5	2261.7
	SD _{CO2}	15.86	15.26	9.49
	Alk	3932.1	3897.6	3861.6
	SD _{Alk}	15.16	27.05	23.87
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0
	Ace	0.05	0.22	0.69
	Form	3.80	14.82	57.01
	Oxa	0.12	0.13	0.07
	Sulf	0.21	0.28	0.33
	Cl ⁻	0.17	0	0
	EDA	0	0	0
	PZ	2470.0	2408.6	2276.3
	1-MPZ	749.86	798.15	1072.0 4
	1,4-DMPZ	678.61	730.74	551.52

Table D.32: Tabulated Experimental Data for TE32 (4 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 175 °C)

	Time (wk)	0	0.5	0.9	2.2	3.3	4.0	6.2	8.0	8.0	8.0	10.1	12.1	15.0
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0	0	0.62	1.97	4.23	4.27	7.83	9.14	12.43	12.32	15.07	18.67	23.66
	Form	0	14.08	30.67	76.51	106.00	111.12	147.69	157.21	151.91	149.82	164.73	179.33	191.42
	Oxa	0	0.24	0	0	0	0	0	0	0	0	0	0	0
	Sulf	0.09	0.09	0.09	0.12	0.11	0.09	0.08	0.07	0.10	0.09	0.09	0.11	0.08
	Cl ⁻	0	0	0	0	0	0	0	0	0	0	0	0	0
	EDA	0	0	11.69	30.23	37.88	33.61	33.39	36.15	32.09	39.97	36.08	34.38	28.12
	PZ	3031.3	2843.5	2850.6	2444.7	2396.7	2188.2	1815.6	1562.2	1664.2	1737.3	1567.9	1346.9	1018.7
	CO ₂	2667.3	2342.9	2289.5	2180.5	1959.4	1962.6	1765.1	1693.3	1683.8	1681.8	1774.3	1216.1	1133.8
	SD _{CO2}	16.73	2.54	18.89	152.20	15.18	8.93	7.38	17.18	13.36	11.83	33.50	8.41	35.36
	Alk	2715.3	2658.0	2611.2	2458.2	2364.7	2327.0	2168.7	2091.1	2117.9	2105.5	2036.6	1914.0	1759.0
	SD _{Alk}	0.44	5.88	1.48	1.88	19.56	3.51	4.41	8.01	1.49	1.57	10.88	7.07	4.34
	Fe ²⁺	0.76	8.04	15.22	25.64	28.99	28.25	30.29	30.40	26.26	28.24	32.86	31.37	30.93
	Ni ²⁺	0.25	9.21	17.44	44.74	62.93	66.92	97.84	104.90	111.22	103.37	119.49	141.98	169.60
	Cr ³⁺	1.22	9.69	9.18	11.86	12.12	11.35	8.82	7.70	7.48	7.58	10.47	7.43	5.69
Hydrolyzed Samples (mmol/kg)	Gly	0	1.09	0.79	1.42	1.71	1.40	2.16	1.52	2.96	1.32	2.54	2.50	2.83
	Ace	0	0.13	0.71	3.29	5.41	6.37	15.12	18.18	16.93	17.09	20.70	26.43	34.31
	Form	0.20	26.10	53.89	137.56	175.49	182.94	290.93	322.46	306.22	304.74	352.14	412.35	490.51
	Oxa	0	0.06	0.07	0.09	0.09	0.10	0.12	0.16	0.12	0.21	0.10	0.15	0.13
	Sulf	0.12	0.16	0.12	0.12	0.17	0.20	0.14	0.11	0.13	0.13	0.15	0.16	0.13
	Cl ⁻	0	0.07	0.13	0.07	0.20	0.32	0.08	0.06	0.13	0.05	0.18	0.07	0.10
	EDA	0	8.44	10.85	26.69	38.00	34.71	45.19	35.17	36.38	42.82	38.55	37.54	33.06
	PZ	2915.4	2752.9	2777.4	2540.4	2275.7	2201.2	1921.0	1764.3	1785.5	1848.5	1668.1	1455.5	1210.0

Table D.33: Tabulated Experimental Data for TE33 (12 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 175 °C)

Time (wk)		0	0.5	0.9	2.2	3.3	4.0	6.2	8.0	8.0	8.0	10.1	12.1	15.0
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0	0.08	0.39	2.08	4.63	6.23	10.85	13.10	13.52	13.19	16.25	18.50	22.57
	Form	0.08	14.11	26.66	60.96	89.60	110.91	165.40	191.31	192.22	188.43	215.34	229.57	255.31
	Oxa	0	0.02	0.02	0.03	0.03	0.04	0.05	0.04	0.05	0	0.05	0.05	0
	Sulf	0.20	0.15	0.13	0.19	0.16	0.17	0.18	0.15	0.19	0.15	0.19	0.17	0.23
	Cl ⁻	0	0.03	0.03	0.04	0.12	0.03	0.06	0.04	0.02	0.02	0.03	0.02	0.03
	FPZ	0	57.87	106.33	209.36	278.81	327.67	412.56	429.47	440.39	438.03	457.88	471.24	472.87
	EDA	0	17.75	26.64	50.58	63.68	69.84	83.79	85.38	83.62	83.75	78.99	74.46	61.80
	PZ	5226.6	4953.2	4763.1	4267.2	3784.1	3471.8	2784.0	2406.2	2375.6	2409.4	2003.1	1746.3	1247.7
	CO ₂	3005.1	2853.3	2909.2	2508.8	2281.8	2149.0	1798.7	1655.9	1649.9	1948.9	1468.7	1692.4	1408.9
	SD _{CO2}	5.06	13.80	4.56	14.94	5.77	17.34	5.59	9.04	11.89	8.33	12.79	4.00	3.69
	Alk	5106.4	4986.6	4899.9	4629.1	4368.1	4118.0	3807.4	3640.0	3634.8	3611.0	3385.3	3247.1	2906.2
	SD _{Alk}	4.64	11.08	48.36	15.93	6.50	19.67	25.58	59.91	12.41	16.61	39.18	142.42	125.17
	Fe ²⁺	0.22	120.09	159.35	320.23	486.65	561.14	494.03	454.06	437.68	454.93	396.09	416.61	293.47
	Ni ²⁺	0.16	21.14	26.77	58.11	110.09	174.82	291.87	374.15	374.47	372.57	451.00	507.92	552.33
	Cr ³⁺	0.29	31.46	40.87	79.80	114.90	124.68	87.84	70.55	68.22	68.00	52.83	41.99	24.60
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0.44
	Ace	0	0.20	0.88	4.06	7.23	10.76	18.31	22.50	22.83	22.60	28.17	31.78	40.06
	Form	0.21	58.92	108.29	231.90	336.06	420.69	603.39	694.11	693.44	685.40	782.54	853.46	971.95
	Oxa	0.02	0.05	0.08	0.10	0.13	0.21	0.17	0.21	0.19	0.18	0.23	0.24	0.28
	Sulf	0.11	0.20	0.13	0.17	0.20	0.16	0.25	0.18	0.21	0.20	0.23	0.21	0.26
	Cl ⁻	0.06	0.07	0.05	0.05	0.18	0.09	0.12	0.09	0.05	0.07	0.07	0.09	0.16
	FPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	EDA	0	16.51	26.22	51.18	65.78	71.45	87.85	90.17	89.63	89.65	89.46	84.20	71.91
	PZ	5054.7	4809.2	4659.0	4239.5	3868.8	3648.4	3036.7	2713.8	2722.1	2788.6	2468.0	2192.0	1694.5

Table D.34: Tabulated Experimental Data for TE34 (8 m PZ, 0.1 mole CO₂ per mole alkalinity initially, 175 °C)

Time (wk)	0	0.5	0.9	2.2	3.3	4.0	6.2	8.0	8.0	8.0	10.1	12.1	15.0
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0	0	0	0.37	1.34	1.66	2.54	3.39	3.20	9.17	10.43	12.65
	Form	0.10	9.95	18.34	32.19	48.86	60.16	76.96	86.78	87.26	100.45	109.12	102.18
	Oxa	0	0	0	0	0	0	0	0	0	0.05	0.03	0
	Sulf	0.13	0.10	0.12	0.11	0.12	0.11	0.11	0.16	0.11	0.16	0.18	0.17
	Cl ⁻	0	0.06	0.01	0.04	0.05	0.04	0.04	0.06	0.08	0.02	0.02	0.09
	FPZ	0	0	0	0	20.89	16.60	16.74	51.41	50.20	35.06	0	0
	EDA	0	0	9.30	24.21	33.50	39.76	50.92	71.86	74.67	71.86	75.98	71.07
	PZ	4497.3	4413.7	4291.1	4177.3	3827.0	3735.6	3453.0	3196.5	3252.1	3100.6	3183.0	2731.2
	CO ₂	1221.8	3202.0	1145.4	1023.1	2649.5	942.2	864.5	758.3	785.2	783.9	1272.5	812.8
	SD _{CO2}	1.96	13.87	3.34	1.65	3.45	2.77	6.96	2.97	3.41	2.12	5.49	0.30
	Alk	4446.7	4415.7	4350.6	4219.4	4114.0	4025.0	3906.9	3836.7	3810.8	3761.6	3673.4	3638.2
	SD _{Alk}	6.30	29.63	13.58	10.45	4.63	7.92	20.77	15.42	3.16	15.66	7.50	5.44
	Fe ²⁺	0.23	31.39	35.42	49.51	45.35	37.88	51.87	49.67	48.62	48.21	36.13	53.87
	Ni ²⁺	0.23	12.09	19.09	36.93	60.66	67.62	98.35	123.93	133.05	133.19	159.39	154.26
	Cr ³⁺	0.37	0.97	1.19	1.90	0.85	0.54	0.83	0.37	1.00	0.42	0.53	0.41
Hydrolyzed Samples (mmol/kg)	Gly	0	0.28	0.42	1.04	1.53	1.98	1.61	2.22	1.68	1.56	1.47	0
	Ace	0	0	0.45	1.66	2.50	3.28	5.16	6.23	6.08	6.67	8.61	14.58
	Form	0.67	20.93	37.00	71.05	100.53	122.60	171.20	183.11	175.43	189.51	221.95	216.44
	Oxa	0.04	0.06	0.07	0.05	0.14	0.12	0.13	0.11	0.10	0.10	0.24	0.10
	Sulf	0.33	0.14	0.25	0.32	0.16	0.24	0.14	0.18	0.16	0.16	0.24	0.22
	Cl ⁻	0.46	0.14	0.12	0.55	0.06	0.11	0.09	0.09	0.10	0.04	0.08	0.12
	FPZ	0	0	0	0	0	0	0	0	0	0	0	0
	EDA	0	0	11.36	28.76	42.31	43.84	42.76	56.21	56.29	76.61	80.62	66.27
	PZ	4386.4	4298.4	4169.1	4073.9	3905.5	3702.8	2839.0	3253.3	3259.5	2754.6	2923.7	2854.6

Table D.35: Tabulated Experimental Data for TE35 (8 m Morpholine (Mor), 0.3 mole CO₂ per mole alkalinity initially, 175 °C)

Time (wk)		0	1.0	2.0	4.0	6.0	6.0	8.0	10.0	15.0
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0
	Ace	0	0.94	1.78	2.55	2.87	4.86	4.93	3.70	2.79
	Form	0.38	11.34	18.93	27.79	18.03	49.05	49.47	24.71	35.62
	Oxa	0	0.09	0.08	0.06	0.11	0.03	0.01	0.02	0.04
	Sulf	0.33	0.25	0.16	0.28	0.19	0.38	0.22	0.15	0.36
	Cl ⁻	0.45	0.14	0.02	0.41	0.02	0.49	0.04	0.03	0.61
	Mor	3594.1	4260.6	4207.4	4001.8	3724.7	3471.5	3121.9	3414.3	2957.9
	CO ₂	1178.3	1185.9	1374.2	1354.8	1568.8	1173.6	981.6	1679.3	1540.1
	SD _{CO2}	2.54	4.80	5.67	7.81	7.36	1.84	2.82	8.85	14.42
	Alk	4330.5	4238.2	4165.7	4051.0	4061.9	3879.8	3811.3	3968.1	3823.1
	SD _{Alk}	1.30	13.25	9.16	3.34	NA	10.85	1.03	5.34	1.76
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0
	Ace	0	1.54	4.81	6.24	6.77	9.28	10.08	7.53	5.99
	Form	0.87	65.30	106.64	155.61	128.21	242.93	264.71	161.28	212.19
	Oxa	0.01	0.47	0.45	0.36	0.87	0.36	0.11	0.21	0.20
	Sulf	0.21	0.19	0.30	0.08	0.15	0.21	0.12	0.13	0.23
	Cl ⁻	0.27	0.05	0.69	0.12	0.05	0.24	0.24	0.13	0.27
	Mor	4166.3	4181.6	4165.3	3750.9	3571.5	2781.6	3315.5	3200.8	2997.5

Table D.36: Tabulated Experimental Data for TE36 (8 m Hexamethylenediamine (HMDA), 0.3 mole CO₂ per mole alkalinity initially, 175 °C)

Time (wk)		0	0.7	1.0	2.0	3.0	4.0	6.0	6.0	6.0	8.0	10.0	12.0	15.0
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0	0	0	0	0	0	0	0	0	0	0	0	0
	Form	0.26	9.44	12.51	18.10	31.02	28.97	36.92	39.53	42.52	41.94	50.69	58.90	71.43
	Oxa	0.01	0.01	0.02	0.01	0.03	0.03	0.02	0.02	0.03	0.03	0.03	0.04	0.03
	Sulf	0.43	0.31	0.23	0.28	0.22	0.22	0.20	0.23	0.24	0.20	0.24	0.19	0.19
	Cl ⁻	0.09	0.08	0.08	0.20	0.24	0.15	0.12	0.08	0.14	0.12	0.11	0.11	0.08
	HMDA	2500*	1930.6	1749.5	1407.5	1540.5	975.39	701.36	708.66	648.86	641.01	575.60	494.82	492.53
	CO ₂	752.89	2019.3	2030.7	2033.8	2001.7	2191.5	2093.6	2026.3	1975.1	2007.8	2025.1	2007.5	2060.8
	SD _{CO2}	3.04	16.71	24.75	16.72	8.24	24.86	13.72	11.62	11.96	8.96	8.24	3.34	5.06
	Alk	3404.4	3033.5	2998.4	3043.2	2953.1	3087.0	3114.3	3108.1	3093.4	3133.9	3168.4	3100.4	3183.5
	SD _{Alk}	22.64	7.39	4.96	9.30	5.09	12.98	10.09	8.10	0.96	0.39	11.44	22.82	7.98
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0	0	0	0	0	0	0	0	0	0	0	0	0
	Form	0.89	19.96	27.91	43.00	70.45	72.33	93.44	99.75	108.37	108.27	119.44	147.12	1.90
	Oxa	0.02	0.04	0.03	0.04	0.11	0.05	0.04	0.04	0.04	0.05	0.04	0.05	0.03
	Sulf	0.45	0.35	0.22	0.20	0.19	0.18	0.20	0.18	0.21	0.18	0.21	0.17	0.22
	Cl ⁻	0.14	0.10	0.15	0.08	0.18	0.04	0.08	0.07	0.07	0.07	0.04	0.04	0.17
	HMDA	2500*	1883.7	1715.8	1405.9	1541.1	983.1	733.6	738.1	677.5	660.2	594.6	517.5	520.3

* Concentration inferred due to broken sample vial

Table D.37: Tabulated Experimental Data for TE37 (8 m PZ, 0.3 mole H⁺ per mole alkalinity initially, 150 °C)

	Time (wk)	0	1.0	2.0	4.0	6.0	10.0	14.0	14.0	14.0	18.0	22.0	26.0	30.0
Original Samples (mmol/kg)	Gly	0	0	0.03	0.02	0.02	0.03	0.04	0.02	0.04	0.01	0.01	0.02	0
	Ace	0	0	0.19	0.09	0.12	0.21	0.44	0.19	0.18	1.08	0.27	0.24	0.21
	Form	0.37	1.26	0.65	0.46	0.93	0.78	1.82	0.64	0.62	0.77	0.79	0.78	0.49
	Oxa	0	0	0	0	0	0	0	0	0	0	0	0	0
	Sulf	0	0	0	0	0	0	0	0	0	0	0	0	0
	Cl ⁻	0.02	0.05	0.02	0.04	0.04	0.04	0.06	0.04	0.04	0.09	0.06	0.03	0.04
	NH ₄ ⁺	0	0.10	0	1.69	1.26	1.40	11.27	5.07	5.44	10.51	9.74	14.00	16.84
	FPZ	0	1.17	0.75	0.62	0.35	0.99	1.70	2.99	0.52	1.56	0.66	1.25	1.35
	EDA	0	0	0	1.00	1.98	3.10	4.72	4.81	4.80	6.42	10.06	13.38	15.30
	PZ	3803.8	3813.1	3814.3	3781.1	3781.8	3731.1	3687.0	3706.0	3716.0	3707.3	3687.8	3594.9	3675.9
	HEP	0	0	0	0	0	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	1-EPZ	0	0	0	0	0.39	0.78	1.50	1.17	1.27	1.76	2.37	3.16	3.86
	1,4-DMPZ	0	0	0	0.62	1.09	2.40	4.57	2.29	2.72	5.22	4.96	7.71	9.50
	AEP	0	0	0	0	0	0	0	0	0	0	0	0	0
	CO ₂	0	0	0	0	0	0	0	0	0	0	0	0	0
	SD _{CO2}	0	0	0	0	0	0	0	0	0	0	0	0	0
	Alk	2693.5	2668.2	2746.0	2674.2	2669.7	2678.7	2608.5	2694.0	2705.0	2693.3	2676.0	2678.4	2620.7
	SD _{Alk}	14.94	11.72	86.50	12.70	27.25	6.27	101.06	73.00	31.37	25.84	28.88	2.21	2.28
Hydrolyzed Samples (mmol/kg)	Gly	0.04	0.36	0.27	0.18	0.20	0.26	0.32	0.37	0.14	0.17	0.21	0.24	0.51
	Ace	0.23	0.59	0.38	0.35	0.29	0.45	0.85	0.34	0.44	0.57	0.68	0.77	0.39
	Form	0.36	2.14	1.26	1.31	0.72	1.53	3.13	1.22	1.33	1.81	1.75	2.06	1.51
	Oxa	0	0	0	0	0	0	0	0	0	0	0	0	0
	Sulf	0	0	0	0	0	0	0	0	0	0	0	0	0
	Cl ⁻	0.09	0.07	0.14	0.18	0.13	0.09	0.08	0.08	0.26	0.11	0.15	0.08	0.08
	NH ₄ ⁺	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	50.1
	FPZ	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	0
	EDA	0	0.90	0.46	1.30	1.17	4.54	7.79	7.68	7.12	7.54	13.39	16.87	17.42
	PZ	4384.2	4207.7	3802.9	4337.4	2959.2	4185.3	4296.9	4216.9	3790.2	2584.4	3306.3	5230.0	3517.1
	HEP	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	0
	1-MPZ	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	0
	1-EPZ	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	3.75
	1,4-DMPZ	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	0
	AEP	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	13.02

Table D.38: Tabulated Experimental Data for TE38 (2 m *trans*-2,5-Dimethylpiperazine (t2,5-DMPZ), 0.3 mole CO₂ per mole alkalinity initially, 150 °C)

	Time (wk)	0	1.9	4.1	6.0	10.0	14.0	14.0	18.0	22.0	26.0	30.0	0	1.9
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0.82	7.68	10.87	15.27	19.14	27.15	24.49	27.39	33.09	35.29	36.54	0.82	7.68
	Form	0.34	36.11	51.30	79.84	91.73	101.84	99.51	122.80	117.59	138.95	139.77	0.34	36.11
	Oxa	0.02	0.09	0.06	0.04	0.03	0.03	0.03	0.03	0.02	0.01	0.01	0.02	0.09
	Sulf	0.11	0.10	0.09	0.09	0.09	0.09	0.11	0.08	0.12	0.09	0.06	0.11	0.10
	Cl ⁻	0.03	0.05	0.05	0.02	0.06	0.06	0.07	0.04	0.05	0.07	0.03	0.03	0.05
	NH ₄ ⁺	0	15.42	30.37	35.45	62.83	76.35	72.06	97.92	101.74	133.74	136.81	0	15.42
	FPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	EDA	0.54	9.93	10.27	10.05	9.88	12.42	11.38	10.89	13.70	12.89	12.76	0.54	9.93
	t2,5-DMPZ	1438.0	1392.5	1358.1	1334.4	1311.2	1249.4	1285.7	1266.2	1231.4	1206.9	1200.7	1438.0	1392.5
	HEP	0	0	0	0	0	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	1.58	2.71	10.16	8.81	9.58	13.60	13.94	12.60	0	0
	1-EPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	1,4-DMPZ	0	0	0	1.38	2.38	8.91	7.73	8.40	11.93	12.23	11.06	0	0
	AEP	0	0	0	0	0	0	0	0	0	0	0	0	0
	CO ₂	923.44	778.50	925.94	774.09	746.57	730.11	742.54	751.04	689.50	727.69	701.96	923.44	778.50
	SD _{CO2}	2.27	3.69	34.65	2.56	4.51	3.80	3.53	4.77	0.80	33.35	2.69	2.27	3.69
	Alk	1610.6	1586.8	1572.8	1583.1	1499.0	1421.8	1453.5	1396.2	1396.2	1365.0	1369.3	1610.6	1586.8
	SD _{Alk}	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	1.47	10.32	13.84	18.32	17.44	30.41	28.23	30.77	36.53	38.46	40.03	1.47	10.32
	Form	0.72	41.14	57.48	90.33	82.19	115.19	115.03	141.51	136.29	160.14	166.53	0.72	41.14
	Oxa	0.02	0.15	0.07	0.05	0.04	0.05	0.05	0.05	0.03	0.03	0.03	0.02	0.15
	Sulf	0.16	0.15	0.13	0.21	0.08	0.18	0.14	0.14	0.19	0.17	0.13	0.16	0.15
	Cl ⁻	0.12	0.08	0.13	0.14	0.08	0.12	0.13	0.12	0.10	0.16	0.08	0.12	0.08
	NH ₄ ⁺	0	0	0	77.12	65.76	99.52	95.36	120.15	114.63	159.15	151.96	0	0
	FPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	EDA	1.28	11.76	11.70	11.71	8.78	14.27	13.33	12.17	15.10	13.71	14.09	1.28	11.76
	t2,5-DMPZ	1445.1	1402.2	1364.0	1336.9	1049.5	1272.2	1306.4	1270.9	1240.7	1224.6	1213.5	1445.1	1402.2
	HEP	0	0	0	0	0	0	0	0	0	0	0	0	0
	1-MPZ	0	0	1.38	5.13	4.56	10.51	8.52	9.74	14.61	14.81	14.62	0	0
	1-EPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	1,4-DMPZ	0	0	1.21	4.50	4.00	9.22	7.48	8.54	12.82	12.99	12.82	0	0
	AEP	0	0	0	0	0	0	0	0	0	0	0	0	0

Table D.39: Tabulated Experimental Data for TE39 (4 m PZ + 4 m *trans*-2,5-Dimethylpiperazine (t2,5-DMPZ), 0.3 mole CO₂ per mole alkalinity initially, 150 °C)

Time (wk)		0	1.0	1.9	4.1	6.0	10.0	14.0	14.0	18.0	22.0	26.0	30.0	0
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0	1.28	1.00	2.81	3.75	5.53	7.21	7.42	9.20	10.66	12.24	13.16	0
	Form	0	26.34	40.27	83.39	102.74	108.96	127.17	137.77	155.79	157.67	185.62	155.30	0
	Oxa	0	0.26	0.03	0.03	0.02	0.04	0.03	0.02	0.01	0.01	0.05	0.03	0
	Sulf	0.07	0.17	0.09	0.19	0.13	0.12	0.11	0.12	0.09	0.12	0.12	0.09	0.07
	Cl ⁻	0.02	0.10	0.06	0.07	0.07	0.05	0.03	0.06	0.06	0.07	0.08	0.04	0.02
	NH ₄ ⁺	0	12.45	56.01	120.87	165.55	227.22	282.77	285.18	334.08	374.43	451.49	457.76	0
	FPZ	0	42.74	69.74	144.58	184.45	214.78	256.93	265.15	307.55	329.76	337.24	392.06	0
	EDA	0	1.84	4.06	6.40	9.75	12.38	14.73	15.57	19.86	22.01	25.81	24.60	0
	PZ + t2,5-DMPZ	3698.4	3663.3	3484.1	3372.8	3305.7	3173.3	3052.6	3008.9	2934.9	2785.5	2711.6	2670.7	3698.4
	HEP	0	0	0	0	0	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0.70	1.25	1.80	2.54	2.42	3.45	3.84	4.29	4.83	0
	1-EPZ	0	0.37	0.86	3.32	5.32	8.98	13.61	14.08	19.47	23.72	31.57	31.63	0
	1,4-DMPZ	0	0	0	0.61	1.10	1.58	2.23	2.12	3.03	3.37	3.76	4.24	0
	AEP	0	0.19	0.26	0.35	0.47	0.64	0.93	0.85	1.13	1.34	4.42	4.41	0
	CO ₂	2495.7	2429.8	2348.4	2262.9	2227.6	2236.8	2168.1	2030.5	2009.3	2069.3	1898.1	1914.1	2495.7
	SD _{CO2}	32.87	14.18	8.35	2.79	9.99	12.85	17.09	20.23	17.21	86.17	28.65	13.18	32.87
	Alk	4098.0	4064.8	3830.4	3844.9	3754.9	3675.3	3630.4	3523.6	3543.3	3396.5	3420.6	3310.3	4098.0
	SD _{Alk}	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0	0	0	0	0
	Ace	0.14	2.23	1.92	4.67	6.94	8.76	11.41	12.28	11.31	14.57	19.87	21.06	0.14
	Form	0	56.84	85.33	173.80	221.26	254.79	310.65	339.19	384.32	393.30	487.07	498.40	0
	Oxa	0	0.48	0.05	0.05	0.04	0.06	0.07	0.05	0.05	0.06	0.09	0.08	0
	Sulf	0.13	0.13	0.12	0.13	0.11	0.11	0.10	0.14	0.11	0.09	0.14	0.11	0.13
	Cl ⁻	0.08	0.12	0.09	0.12	0.08	0.13	0.07	0.10	0.10	0.11	0.21	0.32	0.08
	NH ₄ ⁺	0	0	76.36	138.63	174.38	217.62	275.54	284.15	296.85	322.20	410.71	402.30	0
	FPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	EDA	0	3.60	5.15	9.12	11.60	14.48	16.65	17.74	17.42	21.03	27.68	26.99	0
	PZ + t2,5-DMPZ	3682.4	3646.9	3574.9	3429.9	3370.6	3282.6	3182.7	3159.0	2552.3	3053.5	2861.9	2849.0	3682.4
	HEP	0	0	0	0	0	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0	1.12	1.81	2.35	2.18	2.54	3.14	4.05	4.10	0
	1-EPZ	0	0.45	1.17	3.87	6.27	9.95	15.09	15.86	17.57	21.47	34.80	35.75	0
	1,4-DMPZ	0	0	0	0	0.99	1.59	2.06	1.92	2.23	2.75	3.56	3.59	0
	AEP	0	0.25	0.28	0.32	0.49	0.65	0.97	0.96	0.94	1.16	5.05	5.08	0

Table D.40: Tabulated Experimental Data for TE40 (3.9 m PZ + 3.9 m 1-Methylpiperazine (1-MPZ) + 0.2 m 1,4-Dimethylpiperazine (1,4-DMPZ), 0.3 mole CO₂ per mole alkalinity initially, 150 °C)

	Time (wk)	0	1.0	1.9	4.1	6.0	10.0	14.0	14.0	18.0	22.0	26.0	30.0
Original Samples (mmol/kg)	Gly	0.34	0.21	0.21	0.22	0.16	0.14	0.15	0.16	0.12	0.09	0.07	0.07
	Ace	0	0	0	0	0	0	0	0	0	0	0	0
	Form	0.30	4.48	7.68	10.78	25.40	18.20	29.86	17.72	38.93	47.77	50.54	54.44
	Oxa	0.02	0.05	0.05	0.06	0.03	0.13	0.06	0.05	0.05	0.03	0.03	0.03
	Sulf	0.13	0.13	0.14	0.15	0.13	0.19	0.15	0.15	0.13	0.15	0.13	0.12
	Cl ⁻	0.05	0.06	0.06	0.06	0.07	0.06	0.05	0.07	0.07	0.07	0.08	0.05
	NH ₄ ⁺	0	0	0	0	18.03	27.31	36.14	22.47	48.93	53.55	66.79	77.96
	FPZ	0	13.57	22.46	33.05	71.86	76.31	109.62	44.26	139.55	164.84	185.62	217.30
	EDA	0	0	0	0.24	0.61	0.72	1.55	1.12	2.61	2.82	4.09	3.61
	PZ	1985.3	1991.8	2006.1	1994.8	1998.4	1954.4	1937.9	2061.2	1918.0	1892.0	1863.8	1822.7
	HEP	0	0	0	0	0	0	0	0	0	0	0	0
	1-MPZ	1972.9	1910.4	1877.8	1803.2	1716.1	1631.7	1531.6	1783.9	1476.5	1421.0	1397.4	1360.0
	1-EPZ	0	0	0	0	0	0	14.19	0	12.58	12.47	19.30	20.39
	1,4-DMPZ	125.95	143.82	161.77	189.65	221.32	263.16	268.48	247.71	283.46	285.23	287.66	278.15
	AEP	0	0	0	0	0	1.09	3.33	0	4.14	8.17	16.44	14.48
	CO ₂	2386.9	2331.1	2421.2	2540.6	2362.9	2869.8	2556.5	1683.9	2401.7	2207.3	2167.6	2097.8
	SD _{CO2}	37.81	35.13	6.65	12.24	14.37	17.83	3.69	15.69	39.41	35.84	18.61	3.64
	Alk	4011.2	3991.3	3997.0	3937.8	3892.6	NT	NT	4049.3	3695.3	3675.0	3692.3	3619.1
	SD _{Alk}	8.58	27.27	19.12	0.36	4.03	NT	NT	13.67	43.10	1.44	26.94	34.06
Hydrolyzed Samples (mmol/kg)	Gly	0	0.54	2.51	0.81	2.25	0.32	3.90	11.48	3.97	3.96	5.59	5.93
	Ace	0	0	0	0.19	0.38	1.47	1.25	1.87	1.53	2.20	2.71	3.36
	Form	0.53	12.92	25.44	37.13	85.39	75.30	117.38	54.19	145.78	181.14	208.87	242.38
	Oxa	0.08	0.23	0.17	0.24	0.12	0.28	0.33	0.32	0.29	0.15	0.23	0.18
	Sulf	0.17	0.21	0.19	0.16	0.16	0.18	0.24	0.37	0.44	0.30	0.18	0.16
	Cl ⁻	0.13	0.11	0.13	0.10	0.16	0.17	0.28	0.91	1.27	0.71	0.18	0.16
	NH ₄ ⁺	0	0	0	0	0	0	0	0	0	0	0	0
	FPZ	0	0	0	0	0	0	0	0	0	0	0	0
	EDA	0	0	0.80	0.71	1.67	2.02	3.09	6.10	4.47	5.65	7.78	7.47
	PZ	1752.1	1060.0	1708.5	1771.2	2000.8	1950.9	1968.7	2068.5	1777.2	1960.0	1905.9	1911.1
	HEP	0	0	0	0	0	0	0	0	0	0	0	0
	1-MPZ	1705.5	937.6	1562.1	1549.5	1690.1	1586.2	1519.6	1750.8	1319.4	1450.3	1395.1	1377.4
	1-EPZ	0	0	0	0	0	0	14.95	11.41	17.50	17.29	21.04	22.64
	1,4-DMPZ	111.48	70.67	137.23	164.42	214.07	243.85	265.92	241.55	250.84	281.06	280.43	278.90
	AEP	0	0	0	0	1.28	1.75	1.85	0.93	3.22	10.10	14.22	15.84

Table D.41: Tabulated Experimental Data for TE41 (3.75 m PZ + 3.75 m 1-Methylpiperazine (1-MPZ) + 0.5 m 1,4-Dimethylpiperazine (1,4-DMPZ), 0.3 mole CO₂ per mole alkalinity initially, 150 °C)

	Time (wk)	0	1.0	1.9	6.0	10.0	14.0	14.0	14.0	18.0	22.0	26.0	30.0
Original Samples (mmol/kg)	Gly	0.30	0.19	0.23	0.13	0.10	0.09	0.09	0.11	0.08	0.05	0.04	0.04
	Ace	0	0	0	0.54	0.82	1.22	1.31	1.10	1.43	1.81	2.55	3.16
	Form	0.31	5.98	11.23	23.77	38.70	48.64	50.78	41.39	52.59	57.82	68.17	72.18
	Oxa	0.02	0.07	0.06	0.04	0.03	0.02	0.04	0.07	0.04	0.03	0.03	0.05
	Sulf	0.12	0.12	0.13	0.13	0.13	0.92	0.19	0.15	0.11	0.20	0.14	0.13
	Cl ⁻	0.03	0.03	0.10	0.06	0.05	0.08	0.05	0.10	0.07	0.06	0.06	0.06
	NH ₄ ⁺	0	0	0	16.28	23.47	42.98	49.41	39.06	71.29	88.00	91.12	98.99
	FPZ	0	19.91	32.58	73.15	122.13	155.93	159.29	128.78	173.22	197.13	242.74	269.59
	EDA	0	0	0	0	0.49	0.79	0.84	0.88	1.46	1.50	2.23	2.65
	PZ	1937.8	1933.3	1910.4	1906.6	1856.1	1821.4	1809.2	1861.8	1774.8	1740.3	1661.6	1594.2
	HEP	0	0	0	0	0	0	0	0	0	0	0	0
	1-MPZ	1853.1	1801.3	1761.2	1685.5	1577.3	1527.4	1508.9	1559.8	1470.9	1444.2	1374.4	1323.5
	1-EPZ	0	0	0	0	14.13	16.74	18.88	17.16	21.77	22.46	23.85	29.92
	1,4-DMPZ	296.20	302.96	308.28	333.48	339.91	341.70	339.76	351.79	340.58	345.17	324.08	317.45
	AEP	0	0	0	0	3.18	5.37	4.62	3.92	10.16	13.92	16.86	18.13
	CO ₂	2472.6	2495.6	2404.7	2386.4	2314.2	2236.2	2231.8	2149.1	2208.4	2078.9	2057.4	1981.2
	SD _{CO2}	25.09	34.59	12.10	10.12	9.37	15.11	19.41	18.79	14.69	13.93	11.37	17.98
	Alk	4008.4	3995.3	3926.9	3880.4	3810.7	3744.1	3736.4	3817.4	3699.1	3638.1	3577.9	3488.3
	SD _{Alk}	23.75	11.45	3.20	2.76	4.89	15.82	26.49	17.39	15.41	24.68	5.53	4.27
Hydrolyzed Samples (mmol/kg)	Gly	0	0.43	1.88	2.13	2.55	2.81	2.89	4.58	3.77	4.29	4.21	4.94
	Ace	0	0.37	0	0.99	1.43	2.04	2.12	1.11	1.26	2.97	4.76	5.43
	Form	3.07	22.05	31.90	85.09	139.16	180.39	183.81	133.27	184.62	228.53	299.50	346.97
	Oxa	0.08	0.19	0.29	0.17	0.17	0.17	0.24	0.49	0.35	0.55	0.22	0.25
	Sulf	0.17	0.16	0.24	0.20	0.16	0.98	0.19	0.15	0.25	0.42	0.16	0.09
	Cl ⁻	0.18	0.15	0.16	0.24	0.11	0.16	0.18	0.18	0.92	0.15	0.14	0.15
	NH ₄ ⁺	0	0	0	0	0	0	0	0	0	0	0	0
	FPZ	0	0	0	0	0	0	0	0	0	0	0	0
	EDA	0	0	0	1.11	2.35	3.09	2.90	2.06	2.27	5.45	6.10	7.79
	PZ	2090.1	1873.2	1027.9	1916.2	1878.1	1857.1	1794.2	1171.0	1070.8	1807.1	1775.0	1720.9
	HEP	0	0	0	0	0	0	0	0	0	0	0	0
	1-MPZ	2069.3	1753.1	889.5	1700.7	1613.3	1544.4	1484.9	926.1	833.6	1478.9	1431.4	1387.9
	1-EPZ	0	0	0	0	0	18.71	18.20	9.54	10.25	23.71	27.67	31.59
	1,4-DMPZ	318.7	294.7	161.9	333.2	336.1	340.2	329.8	212.3	196.7	341.2	328.4	321.4
	AEP	0	0	0	0	2.83	4.58	3.59	0.81	1.54	12.53	16.10	21.08

Table D.42A: Tabulated Experimental Data for TE42A (8 m PZ, 0.3 mole $^{13}\text{CO}_2$ per mole alkalinity initially, 175 °C)

	Time (wk)	0	2.0	5.9
Original Samples (mmol/kg)	Gly	0	0	0
	Ace	0	0	10.22
	Form	0.27	127.24	153.87
	Oxa	0.01	0.21	0.03
	Sulf	0.18	0.20	0.28
	Cl^-	0.02	0	0
	FPZ	0	200.07	307.10
	EDA	0	54.22	64.90
	PZ	2891.5	2285.5	1680.8
	CO_2	NT	NT	NT
	SD_{CO_2}	NT	NT	NT
	Alk	NT	NT	NT
	SD_{Alk}	NT	NT	NT
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0
	Ace	0	6.87	16.20
	Form	0.42	255.25	458.15
	Oxa	0.02	0.27	0.15
	Sulf	0.26	0.26	0.24
	Cl^-	0.09	0.26	0
	FPZ	0	0	0
	EDA	0.91	53.56	71.83
	PZ	2894.5	2406.2	1844.9

Table D.42B: Tabulated Experimental Data for TE42B (8 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 175 °C)

Time (wk)		0	2.0	5.9
Original Samples (mmol/kg)	Gly	0	0	0
	Ace	0	5.38	8.22
	Form	0.21	112.44	135.60
	Oxa	0	0.19	0.03
	Sulf	0.24	0.20	0.19
	Cl ⁻	0	0	0
	FPZ	0	210.57	280.61
	EDA	0	52.80	66.51
	PZ	2979.1	2412.9	1878.5
	CO ₂	NT	NT	NT
	SD _{CO2}	NT	NT	NT
	Alk	NT	NT	NT
	SD _{Alk}	NT	NT	NT
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0
	Ace	0	6.81	12.21
	Form	0.22	294.80	402.94
	Oxa	0	0.27	0.16
	Sulf	0.02	0.32	0.25
	Cl ⁻	0	0.25	0
	FPZ	0	0	0
	EDA	0	55.42	73.16
	PZ	3019.8	2555.4	2054.2

Table D.43: Tabulated Experimental Data for TE43 (8 m PZ, unloaded, 150 °C)

	Time (wk)	0	1.0	2.0	6.3	8.0	10.0	14.0	14.0	14.0	17.9	22.1	25.9	30.0
Original Samples (mmol/kg)	Gly	0	0.19	0.42	0.21	0.15	0.21	0.17	0.14	0.15	0.14	0.12	0.23	0.17
	Ace	0	0	0	0	0.20	0.28	0.32	0.36	0.30	0.55	0.37	0.33	0.12
	Form	0	0.41	0.59	1.24	1.25	1.51	1.51	1.86	1.51	1.84	2.06	1.28	0.57
	Oxa	0.03	0.02	0.04	0.07	0.08	0.12	0.09	0.06	0.06	0.05	0.04	0.03	0.01
	Sulf	0.12	0.09	0.14	0.15	0.15	0.19	0.14	0.14	0.12	0.12	0.17	0.10	0.18
	Cl ⁻	0	0.02	0.03	0	0	0	0	0	0	0	0	0	0
	NH ₄ ⁺	0	1.00	12.23	1.66	1.74	2.50	3.54	3.82	4.84	5.27	5.74	4.39	0
	FPZ	0	0	0	0	0.26	0.17	0.35	0.72	0.33	0.65	0.22	0.60	0
	EDA	0	0	0.07	0.21	0.62	1.05	0.66	0.64	0.75	1.18	0.94	1.03	1.34
	PZ	4355.7	4342.8	4396.5	4384.8	4350.6	4383.5	4378.5	4367.7	4368.2	4332.9	4385.0	4350.7	4359.9
	HEP	0	0	0	0	0	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	1-EPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	1,4-DMPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	AEP	0	0	0	0	0	0	0.19	0.44	0.24	0.53	0.18	0.27	0
	Alk	4826.0	4799.5	4806.4	5145.1	4826.8	4853.1	4798.6	4818.3	4755.0	4866.9	4904.4	4805.6	4816.1
	SD _{Alk}	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	0.05	0.37	0.67	1.06	0.99	1.19	1.57	1.03	1.20	1.95	2.02	2.20	1.76
	Ace	0.08	0.10	0.09	0.13	0.32	0.23	0.28	0.39	0.31	0.29	0.39	0.26	0.14
	Form	0.28	0.74	1.01	1.77	1.95	2.14	2.13	2.38	2.12	2.20	3.19	2.17	0.97
	Oxa	0.01	0.05	0.11	0.23	0.22	0.23	0.22	0.20	0.20	0.17	0.16	0.13	0.03
	Sulf	0.24	0.19	0.23	0.20	0.28	0.38	0.29	0.26	0.20	0.32	0.31	0.24	0.20
	Cl ⁻	0	0	0	0	0	0	0	0	0	0	0	0	0
	NH ₄ ⁺	0	0	0	0	0	0	0	0	0	0	0	0	0
	FPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	EDA	0	0.26	0.19	0.43	1.53	1.76	1.46	1.11	1.25	2.27	2.34	1.87	1.97
	PZ	4339.5	4375.8	4398.4	4365.0	4362.1	4401.8	4305.0	4308.6	4271.9	4286.3	4246.5	4261.8	4277.4
	HEP	0	0	0	0	0	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	1-EPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	1,4-DMPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	AEP	0	0	0	0	0	0.08	0.19	0.47	0.27	0.50	0.33	0.26	0

Table D.44: Tabulated Experimental Data for TE44 (8 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 165 °C)

	Time (wk)	0	1.0	2.0	3.0	4.0	5.0	6.0	6.0	6.0	9.3	12.0	14.9	20.0
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0.32	0.32	0.30	0.24	0.24	0.24	0.18	0.19	0.21	0.18	0.12	1.03	0
	Ace	0	0	0	0	1.21	0.63	1.13	1.14	0.76	1.97	7.57	15.59	21.12
	Form	0.07	11.96	14.74	25.81	26.69	39.92	47.17	49.09	42.93	58.39	88.10	107.31	107.47
	Oxa	0.05	0.03	0.02	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0
	Sulf	0.14	0.16	0.14	0.16	0.14	0.15	0.15	0.12	0.15	0.15	0.13	0.12	0.39
	Cl ⁻	0.05	0.06	0.05	0.07	0.07	0.05	0.06	0.04	0.06	0.06	0.06	0.05	0.05
	NH ₄ ⁺	3.43	17.99	1.49	27.19	40.42	62.89	92.52	85.55	89.85	140.04	237.07	392.88	495.57
	FPZ	0	40.99	55.77	69.49	100.25	137.02	165.65	173.15	159.32	221.14	311.10	394.61	557.36
	EDA	0	8.23	11.47	12.44	17.95	25.97	30.80	31.61	29.32	42.97	55.60	65.61	52.84
	PZ	3883.5	3987.3	4229.6	3600.4	3982.3	3821.6	3791.8	3797.1	3883.2	3561.9	3305.6	2819.2	2501.4
	HEP	0	0	0	0	0	0	0	0	0	11.45	14.55	15.57	61.16
	1-MPZ	0	0	0	0	1.43	1.79	2.24	2.24	1.82	3.29	4.62	4.77	20.53
	1-EPZ	0	0.83	0.75	1.81	3.47	3.25	6.35	6.87	6.33	12.58	22.62	34.56	54.44
	1,4-DMPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	AEP	0	2.74	3.72	13.36	10.45	17.35	26.20	25.23	21.49	43.93	72.32	102.48	118.27
	2-Imid	0	7.88	11.59	21.38	22.70	32.82	40.97	42.15	38.21	54.33	81.20	94.44	109.04
	CO ₂	2745.1	2699.2	2583.7	2517.4	2441.4	2372.7	2437.3	2292.4	2387.2	2179.2	2213.5	1948.1	1857.4
	SD _{CO2}	10.69	25.11	18.61	9.89	26.17	10.59	4.11	76.71	290.70	150.88	129.13	70.09	64.44
	Alk	4134.3	4055.3	4032.3	3977.7	3970.7	3899.9	3839.5	3839.8	3868.8	3725.3	3537.1	3326.3	3165.5
	SD _{Alk}	12.56	9.55	22.54	2.88	10.36	3.26	1.68	13.93	1.65	3.59	5.50	8.12	10.22
Hydrolyzed Samples (mmol/kg)	Fe ²⁺	0	48.97	21.61	40.15	36.05	36.13	40.92	43.36	46.14	NT	69.23	107.57	106.66
	Ni ²⁺	0	33.91	24.75	47.28	57.71	72.67	72.74	74.69	74.96	NT	156.98	267.18	240.23
	Cl ³⁺	0	34.51	26.68	50.99	28.96	41.37	23.28	57.10	34.00	NT	46.83	32.72	56.20
	Gly	0.63	0.83	0.85	0.94	1.23	1.27	1.17	0.60	0.52	0.85	1.08	1.40	0.52
	Ace	0	0.85	1.36	2.22	6.01	4.07	5.95	6.63	6.02	10.77	17.23	26.97	35.54
	Form	0.21	35.53	42.95	76.01	79.86	117.56	138.98	145.26	151.62	184.23	297.59	393.99	548.86
	Oxa	0	0.05	0.05	0.08	0.07	0.07	0.07	0.10	0.08	0.13	0.13	0.11	0
	Sulf	0.60	0.21	0.22	0.19	0.18	0.14	0.16	0.15	1.34	0.19	0.20	0.17	0.31
	Cl ⁻	0.03	0.06	0.07	0.06	0.06	0	0.09	0.08	1.21	0.16	0.19	0.12	0.05
	NH ₄ ⁺	0	36.72	43.28	29.41	32.47	32.02	107.82	104.53	60.88	166.26	254.93	379.83	501.52
	FPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	EDA	0	9.74	12.09	20.43	21.95	30.08	31.14	35.90	34.65	46.01	61.43	77.16	60.30
	PZ	4230.5	4166.0	4118.5	4075.4	4058.4	3967.5	3830.7	3844.7	2596.8	3626.3	3374.4	3022.7	2797.4
	HEP	0	0	0	0	9.90	7.60	10.68	10.66	11.02	13.82	13.78	15.56	58.88
	1-MPZ	0	0	0	0.96	1.24	1.80	2.43	2.66	1.96	2.34	4.67	4.56	20.28
	1-EPZ	0	0	1.43	2.18	3.52	4.86	6.35	6.92	6.67	8.00	27.80	41.64	58.01
	1,4-DMPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	AEP	0	2.75	4.39	8.84	11.16	21.32	26.66	25.68	26.45	44.93	74.37	108.99	130.51

Table D.45: Tabulated Experimental Data for TE45 (8 m PZ, 0.4 mole CO₂ per mole alkalinity initially, 165 °C)

	Time (wk)	0	1.0	2.0	3.0	4.0	5.0	6.0	6.0	6.0	9.3	12.0	14.9	20.0
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0.33	0.33	0.28	0.23	0.21	0.20	0.15	0.17	0.16	0.13	0.10	0.11	0
	Ace	0	0	0.15	0.61	1.33	1.77	2.85	2.32	2.80	11.54	14.41	18.58	26.55
	Form	0.09	12.74	26.28	36.76	52.71	51.48	73.33	61.98	67.04	93.13	97.00	105.09	107.56
	Oxa	0	0.01	0.02	0.02	0.02	0.01	0.03	0.02	0.02	0.03	0.02	0.01	0
	Sulf	0.13	0.13	0.10	0.13	0.13	0.14	0.06	0.11	0.11	0.13	0.12	0.12	0.16
	Cl ⁻	0.09	0.05	0.05	0.03	0.27	0.05	0.01	0.04	0.01	0.05	0.04	0.03	0.02
	NH ₄ ⁺	1.70	20.24	32.63	61.62	101.88	110.25	158.41	122.62	139.76	258.96	312.14	402.35	601.28
	FPZ	0	64.68	124.22	171.81	225.15	227.70	317.13	271.53	279.33	386.03	421.17	436.11	539.02
	EDA	0	10.30	18.18	26.69	37.92	38.24	49.63	43.17	47.48	59.50	63.57	65.30	60.38
	PZ	4225.4	4063.9	3925.5	3800.8	3607.0	3558.7	3295.0	3444.5	3456.0	3067.0	2893.9	2658.5	2173.1
	HEP	0	0	0	0	0	7.51	9.47	9.97	11.06	13.95	7.18	15.70	62.11
	1-MPZ	0	0	1.53	2.71	3.67	3.43	4.80	5.56	4.76	5.68	5.04	5.45	20.93
	1-EPZ	0	1.92	1.36	5.08	8.07	9.01	15.73	11.80	14.14	23.52	27.51	34.97	63.86
	1,4-DMPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	AEP	0	3.28	7.40	14.25	25.73	29.14	47.19	36.78	42.24	70.42	81.41	97.47	113.71
	2-Imid	0	12.56	25.67	40.72	57.01	59.92	83.54	71.83	77.08	102.75	107.65	129.94	131.81
	CO ₂	2877.1	3000.2	2716.7	2837.3	2721.5	2681.5	2564.2	2736.2	2682.1	2546.7	2268.2	2426.8	2141.4
	SD _{CO2}	223.93	26.80	27.69	18.41	79.23	23.48	52.83	60.40	22.71	31.37	48.34	21.01	28.37
	Alk	3988.8	3918.2	3881.9	3762.1	3715.1	3615.9	3596.1	3646.0	3613.4	3419.3	3289.6	3229.7	2785.1
	SD _{Alk}	2.79	7.47	3.16	35.73	44.84	16.53	19.56	14.01	2.47	10.96	19.04	52.03	16.79
	Fe ²⁺	0	41.47	45.53	48.52	85.56	54.55	105.21	57.85	111.10	148.83	119.24	NT	223.42
	Ni ²⁺	0	50.33	102.70	92.90	118.36	71.84	117.82	90.66	99.86	138.76	160.35	NT	283.52
	Cl ³⁺	0	51.94	141.77	64.80	135.42	96.43	154.98	114.09	128.50	158.29	125.85	NT	184.80
Hydrolyzed Samples (mmol/kg)	Gly	0.77	0.39	0.33	0.31	0.27	0.14	0.21	0.23	0.21	0.17	0.02	0.08	0
	Ace	0	1.11	4.39	3.88	7.18	7.37	12.46	9.61	10.45	22.53	24.17	29.99	36.14
	Form	0.49	46.86	93.73	131.43	189.89	186.93	276.18	225.98	245.27	369.49	425.03	480.63	584.56
	Oxa	0.01	0.04	0.03	0.04	0.05	0.03	0.08	0.04	0.05	0.06	0.05	0.04	0
	Sulf	0.17	0.20	0.17	0.18	0.19	0.17	0.17	0.18	0.18	0.16	0.58	0.20	0.17
	Cl ⁻	0.04	0.08	0.05	0.05	0.06	0.05	0.05	0.04	0.05	0.04	0.06	0.03	0.04
	NH ₄ ⁺	0	40.76	62.63	92.19	129.40	134.25	210.28	162.95	191.51	280.99	328.60	413.94	608.52
	FPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	EDA	0	12.26	17.18	27.45	37.60	39.53	54.85	44.30	53.96	63.90	67.93	71.35	72.03
	PZ	4123.5	4051.9	3964.9	3852.7	3738.7	3687.0	3505.9	3596.7	3543.6	3271.6	3148.4	2916.8	2666.7
	HEP	0	0	0	0	0	0	2.90	3.14	3.19	9.80	5.50	9.62	59.11
	1-MPZ	0	0	0	4.14	3.48	3.01	3.26	5.27	2.84	6.39	6.62	8.13	25.61
	1-EPZ	0	0	3.61	7.31	10.01	10.53	15.10	14.41	16.11	25.42	29.39	40.39	67.85
	1,4-DMPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	AEP	0	0	6.73	14.85	25.99	29.77	51.16	40.05	44.03	78.73	91.41	106.29	137.26

Table D.46: Tabulated Experimental Data for TE46 (8 m PZ, unloaded, 165 °C)

	Time (wk)	0	1.0	2.0	4.0	6.0	6.0	14.9	20.0
Original Samples (mmol/kg)	Gly	0	0.25	0.20	0.14	0.17	0.13	0.17	0.23
	Ace	0	0	0.10	0.10	0.14	0.14	1.00	0.96
	Form	0	0.34	0.41	1.11	1.77	0.90	5.62	8.75
	Oxa	0.05	0.04	0.04	0.04	0.04	0.04	0.05	0.05
	Sulf	0.23	0.15	0.15	0.12	0.11	0.14	0.16	0.12
	Cl ⁻	0.81	0.07	0.04	0.04	0.07	0.05	0.03	0.03
	NH ₄ ⁺	0	0	0	0	0	0	51.61	31.91
	FPZ	0	0	0	0	0	0	2.11	4.05
	EDA	0	0	0	0	0	0	38.35	26.26
	PZ	4676.4	4696.4	4641.4	4656.6	4617.4	4641.6	4452.8	4748.5
		48	05	52	84	98	84	38	91
	HEP	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0	0	0
	1-EPZ	0	0	0	0	0	0	4.92	4.13
	1,4-DMPZ	0	0	0	0	0	0	0	0
	AEP	0	0	0	0	0	0	1.15	1.87
	Alk	4720.8	4598.7	4747.6	4698.9	4718.5	4610.4	4641.4	4972.5
	SD _{Alk}	3.47							
Hydrolyzed Samples (mmol/kg)	Gly	0.09	0.63	0.52	0.65	0.99	0.57	1.34	3.13
	Ace	0	0	0.13	0.12	0.35	0.31	1.40	1.73
	Form	0	0.26	0.35	1.01	1.86	0.90	7.13	13.02
	Oxa	0.04	0.05	0.05	0.07	0.10	0.08	0.35	0.58
	Sulf	0.13	0.17	0.15	0.14	0.18	0.15	0.14	0.16
	Cl ⁻	0.05	0.12	0.06	0.10	0.10	0.10	2.79	0.09
	NH ₄ ⁺	0	0	0	0	0	0	91.96	83.82
	FPZ	0	0	0	0	0	0	0	0
	EDA	0	0	0	0	3.89	1.68	47.66	31.37
	PZ	4712.3	4705.4	4714.4	4738.1	4764.2	4769.5	4558.1	4851.4
	HEP	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0	0	0
	1-EPZ	0	0	0	0	0	0	4.24	3.93
	1,4-DMPZ	0	0	0	0	0	0	0	0
	AEP	0	0	0	0	0	0	2.98	2.60

Table D.47: Tabulated Experimental Data for TE47 (8 m PZ, 0.1 mole CO₂ per mole alkalinity initially, 165 °C)

	Time (wk)	0	1.0	2.0	4.0	6.0	6.0	15.0	19.9
Original Samples (mmol/kg)	Gly	0.40	0.43	0.39	0.36	0.29	0.32	0.17	0.22
	Ace	0	0	0.06	0.14	0.37	0.22	2.81	2.10
	Form	0	1.56	4.27	11.87	21.30	15.07	37.44	46.35
	Oxa	0.01	0.01	0.02	0.02	0.03	0.02	0.03	0.01
	Sulf	0.09	0.11	0.11	0.09	0.28	0.10	0.04	0.07
	Cl ⁻	0.02	0.09	0.03	0.03	0.07	0.02	0.02	0.04
	NH ₄ ⁺	0	0	0	0	17.06	0	102.14	98.59
	FPZ	0	4.26	9.53	20.12	40.07	29.54	71.28	54.45
	EDA	0	0	3.95	10.78	18.35	13.97	57.11	51.03
	PZ	4540.3	4452.2	4409.8	4331.6	4194.9	4229.4	3804.2	3629.5
	HEP	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0	3.46	0	3.26	1.46
	1-EPZ	0	0	0	0.97	2.41	1.96	24.69	16.46
	1,4-DMPZ	0	0	0	0	0	0	0	0
	AEP	0	1.61	0.59	3.51	7.65	5.81	44.34	55.68
	CO ₂	939.6	927.3	917.1	891.6	876.6	824.0	875.7	709.6
	SD _{CO2}	12.93	4.96	16.49	7.98	10.76	12.36	20.60	10.82
	Alk	4476.1	4489.0	4441.2	4376.5	4440.8	4362.0	NT	4150.7
	SD _{Alk}	NA	NA	NA	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	0.07	0.93	1.25	1.17	2.08	1.92	1.76	2.59
	Ace	0	0	0.08	0.31	0.68	0.25	5.66	3.45
	Form	0	3.58	9.60	23.25	45.59	32.24	87.87	102.15
	Oxa	0.03	0.07	0.07	0.10	0.13	0.10	1.10	0.30
	Sulf	0.16	0.13	0.14	0.17	0.34	0.14	0.26	0.18
	Cl ⁻	0.08	0.07	0.10	0.10	0.19	0.12	0.28	0.21
	NH ₄ ⁺	0	0	0	0	78.82	69.00	107.90	94.82
	FPZ	0	0	0	0	0	0	0	0
	EDA	0	3.36	6.68	13.28	23.13	18.56	68.91	58.31
	PZ	4505.7	4545.7	4508.7	4438.4	4272.3	4341.9	4279.6	3824.5
	HEP	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0	2.84	0	2.48	0
	1-EPZ	0	0	0	0.89	2.82	1.91	23.04	16.58
	1,4-DMPZ	0	0	0	0	0	0	0	0
	AEP	0	0	1.32	4.88	9.83	8.92	51.05	61.03

Table D.48: Tabulated Experimental Data for TE48 (8 m PZ, 0.3 mole H⁺ per mole alkalinity initially, 165 °C)

	Time (wk)	0.0	1.0	2.0	3.0	4.0	5.0	6.0	6.0	6.0	9.3	12.0	14.9	19.9
Original Samples (mmol/kg)	Gly	0.00	0.03	0.03	0.03	0.02	0.01	0.01	0.02	0.04	0.01	0.02	0.02	0.00
	Ace	0.11	0.13	0.11	0.10	0.19	0.20	0.30	0.22	0.12	0.36	0.52	0.76	1.40
	Form	0.19	0.53	0.52	0.46	0.72	0.83	1.35	1.08	0.45	1.57	1.56	1.99	2.07
	Oxa	0	0	0	0	0	0	0	0	0	0	0	0	0
	Sulf	0	0	0	0	0	0	0	0	0	0	0	0	0
	Cl ⁻	0.02	0.01	0.04	0.02	0.03	0.07	0.07	0.04	0.04	0.05	0.07	0.04	0.06
	NH ₄ ⁺	0	0	9.44	0	0	8.68	24.16	20.62	17.29	39.42	27.50	75.26	141.69
	FPZ	0	0	0	0	0	0	0	0	0	0	5.37	5.63	0
	EDA	0	1.14	1.92	3.49	3.91	9.59	13.67	10.67	6.46	16.31	31.03	39.79	59.20
	PZ	4357.3	4278.0	4236.9	4216.4	4259.5	4163.4	4070.2	4127.6	4064.8	4018.4	4069.4	3978.1	3623.0
	HEP	0	0	0	0	0	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	1-EPZ	0.00	0.00	0.00	0.00	0.96	1.06	2.96	1.43	1.65	3.02	6.99	8.70	18.09
	1,4-DMPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	AEP	0.00	0.51	0.32	1.36	1.51	2.26	4.17	2.64	2.31	5.64	14.41	20.73	46.51
	CO ₂	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
	SD _{CO2}	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
	Alk	2881.7	2916.5	2916.5	2834.6	2825.9	2888.0	2799.1	2804.3	2814.1	2814.4	2758.5	2741.9	2690.4
	SD _{Alk}	85.35	6.81	14.90	10.20	10.81	9.78	0.42	3.08	3.62	3.56	6.07	3.79	8.63
Hydrolyzed Samples (mmol/kg)	Gly	0.22	0.13	0.17	0.33	0.30	0.48	0.41	0.33	0.74	0.50	0.38	0.42	0.18
	Ace	0.32	0.39	0.39	0.36	0.49	0.45	0.71	0.64	0.28	1.35	1.23	1.76	2.64
	Form	0.37	0.76	0.68	0.95	1.40	1.94	3.11	2.95	0.88	4.76	3.92	5.69	6.85
	Oxa	0	0	0	0	0	0	0	0	0	0	0	0	0
	Sulf	0	0	0	0	0	0	0	0	0	0	0	0	0
	Cl ⁻	0.05	0.07	0.07	0.05	0.08	0.07	0.11	0.09	0.08	0.07	0.06	0.08	0.06
	NH ₄ ⁺	0	0	0	0	0	0	8.32	6.77	2.46	18.86	33.99	34.34	145.33
	FPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	EDA	0.00	1.62	2.43	4.11	4.54	10.32	14.73	11.10	6.34	18.11	34.78	39.46	59.03
	PZ	4465.83	4335.27	4405.46	4358.19	4269.55	4101.30	4184.36	4294.50	4318.63	4154.12	4085.68	3977.15	3620.53
	HEP	0	0	0	0	0	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	1-EPZ	0	0.35	0.25	0.84	0.92	1.29	2.68	1.47	1.93	3.00	7.40	8.68	17.80
	1,4-DMPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	AEP	0	0.68	0.58	1.79	2.27	2.56	4.30	3.08	2.49	6.99	15.56	21.25	46.18

Table D.49: Tabulated Experimental Data for TE49 (4 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 165 °C)

Time (wk)		0.0	0.9	5.8
Original Samples (mmol/kg)	Gly	0.39	0.21	0.12
	Ace	0	0	0.86
	Form	0.08	6.90	40.69
	Oxa	0	0.03	0.03
	Sulf	0.30	0.27	0.23
	Cl ⁻	0	0	0
	NH ₄ ⁺	0	0	0
	FPZ	0	10.92	69.59
	EDA	0	1.23	13.90
	PZ	2757.0	2714.6	2434.5
	HEP	0	0	0
	1-MPZ	0	0	0
	1-EPZ	0	0.25	5.89
	1,4-DMPZ	0	0	0
	AEP	0	0	8.87
	CO ₂	1613.7	1612.5	1465.8
	SD _{CO2}	8.91	11.07	26.68
	Alk	2757.6	2733.0	2584.7
	SD _{Alk}	4.52	18.29	6.31
Hydrolyzed Samples (mmol/kg)	Gly	0	0.27	0.24
	Ace	0.05	0.12	1.72
	Form	0.09	11.57	77.34
	Oxa	0	0.05	0.11
	Sulf	0	0	0
	Cl ⁻	0	0	0
	NH ₄ ⁺	0	34.47	109.17
	FPZ	0	0	0
	EDA	0	3.65	21.42
	PZ	3204.1	2496.7	2506.0
	HEP	0	0	30.32
	1-MPZ	0	0	0
	1-EPZ	0	0	8.27
	1,4-DMPZ	0	0	3.57
	AEP	0	0	24.90

Table D.50: Tabulated Experimental Data for TE50 (12 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 165 °C)

Time (wk)		0.0	0.9	1.8	3.8	5.8	5.8	9.9	14.8	19.8
Original Samples (mmol/kg)	Gly	0.40	0.42	0.33	0.25	0.21	0.24	0.14	0.12	0.09
	Ace	0	0	0	0.34	0.60	0.59	1.31	2.60	3.48
	Form	0.05	8.26	12.88	26.92	34.32	36.47	55.07	77.24	68.59
	Oxa	0	0.01	0	0.01	0.01	0	0.01	0	0
	Sulf	0.10	0.16	0.14	0.17	0.15	0.13	0.46	0.11	0.11
	Cl ⁻	0	0	0	0	0	0	0	0	0
	NH ₄ ⁺	0	19.00	45.91	55.98	87.29	132.52	214.17	328.33	464.01
	FPZ	0	85.77	117.24	185.72	252.85	257.55	373.62	451.96	603.17
	EDA	0	10.18	19.28	23.87	34.68	35.27	56.98	64.58	64.39
	PZ	5572.6	5172.6	4913.8	4157.6	3963.6	4417.2	3953.0	3466.0	2916.8
	HEP	0	0	0	4.27	7.48	26.18	46.26	50.69	53.05
	1-MPZ	0	0	8.22	2.24	3.79	27.49	19.25	27.43	25.40
	1-EPZ	0	0	2.11	4.52	7.90	8.70	20.34	34.87	52.81
	1,4-DMPZ	0	0	2.91	3.26	3.06	9.94	0	3.27	20.39
	AEP	0	2.27	8.63	33.09	47.37	34.48	61.77	90.23	111.08
	CO ₂	3358.9	3349.4	3192.2	2838.0	2756.0	2943.0	2644.8	2394.0	2008.7
	SD _{CO2}	65.87	20.31	15.37	58.42	37.25	46.61	36.78	36.78	32.04
	Alk	4991.5	4912.6	4860.0	4703.1	4562.7	4579.9	4332.8	4097.7	3778.7
	SD _{Alk}	6.56	8.71	2.16	7.81	14.59	2.35	17.37	4.35	15.86
Hydrolyzed Samples (mmol/kg)	Gly	0.45	0.32	0.25	0.26	0.22	0.29	0.16	0.07	0.04
	Ace	0	0.16	0.28	0.80	1.55	1.19	3.17	5.37	6.37
	Form	0.11	36.97	50.50	142.68	202.89	186.83	336.99	440.42	409.89
	Oxa	0	0.02	0	0.03	0.02	0.03	0.02	0.04	0.01
	Sulf	0.16	0.13	0.15	0.11	0.12	0.09	0.09	0.10	0.10
	Cl ⁻	0	0	0	0	0	0	0	0	0
	NH ₄ ⁺	0	22.90	46.06	97.22	134.60	134.82	52.76	325.26	484.80
	FPZ	0	0	0	0	0	0	0	0	0
	EDA	0	3.53	7.31	29.12	41.61	42.72	12.55	65.98	80.41
	PZ	3701.4	3888.9	3548.3	4672.3	4560.0	4613.3	1076.0	3637.9	3500.0
	HEP	0	0	0	0	0	0	34.49	46.05	64.10
	1-MPZ	0	0	8.60	18.43	16.79	23.99	6.84	30.06	23.75
	1-EPZ	0	2.76	1.32	10.52	10.93	9.25	3.89	36.49	62.38
	1,4-DMPZ	0	3.44	6.71	1.96	9.95	10.33	0	0	4.58
	AEP	0	1.60	8.45	21.82	34.64	31.82	16.04	94.10	135.07

Table D.51: Tabulated Experimental Data for TE51 (8 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 175 °C, N₂ headspace)

	Time (wk)	0.0	0.3	1.3	3.5	5.6	7.5	9.5	14.5
Original Samples (mmol/kg)	Gly	0.68	0.54	0.24	0.20	0.12	0.07	0.05	0.02
	Ace	0	0	0.35	2.23	5.50	8.83	12.13	18.38
	Form	0	9.86	21.01	92.72	126.69	166.37	214.10	198.77
	Oxa	0.02	0.03	0.04	0.02	0.03	1.59	0.04	0.05
	Sulf	0.14	0.13	0.10	0.30	0.10	0.10	0.12	0.13
	Cl ⁻	0.03	0.04	0.03	0.10	0.06	0.03	0.04	0.03
	NH ₄ ⁺	0	0	10.70	115.73	250.27	382.76	450.19	745.28
	FPZ	0	28.30	63.59	256.60	302.59	354.14	415.66	434.70
	EDA	0	4.18	23.83	41.55	53.30	59.35	69.99	59.53
	PZ	4096.1	4064.7	4686.8	3283.0	2715.8	2358.0	2139.1	1554.4
	HEP	0	0	0	6.99	10.69	0	13.80	31.34
	1-MPZ	0	0	0	2.39	8.65	5.19	5.51	18.18
	1-EPZ	0	0	2.68	18.26	33.57	48.84	56.07	90.27
	1,4-DMPZ	0	0	0	0	0	0	0	0
	AEP	0	0	6.82	44.12	91.88	120.74	132.87	143.71
	CO ₂	2350.8	2308.7	NT	1889.0	1902.9	1632.8	1368.2	1209.0
	SD _{CO2}	7.47	46.48	NT	7.94	5.95	28.97	6.18	3.29
Hydrolyzed Samples (mmol/kg)	Alk	4219.5	4162.8	NT	3673.2	3409.0	3207.9	3116.8	2804.8
	SD _{Alk}	46.67	33.37	NT	3.14	10.49	51.88	100.25	5.55
	Gly	0	0.45	1.66	0.52	0.42	0.87	1.73	1.63
	Ace	0	0.16	0.86	3.58	8.74	15.40	20.07	31.88
	Form	0	25.56	57.95	263.14	368.83	476.10	610.32	654.40
	Oxa	0.02	0.07	0.39	0.22	0.35	0.35	0.24	0.28
	Sulf	0.18	0.16	0.21	0.44	0.16	0.18	0.24	0.18
	Cl ⁻	0.21	0.09	0.20	0.80	0.14	0.11	0.12	0.15
	NH ₄ ⁺	0	0	0	74.13	180.25	293.20	346.66	596.57
	FPZ	0	0	0	0	0	0	0	0
	EDA	0	5.78	27.13	46.60	59.08	66.29	78.86	69.58
	PZ	4126.7	4090.3	4794.5	3413.3	2903.0	2544.6	2380.5	1816.5
	HEP	0	0	0	11.14	11.32	14.45	12.52	18.97
	1-MPZ	0	0	0	3.16	9.68	5.76	5.09	4.93
	1-EPZ	0	0	2.64	19.47	39.13	59.52	72.95	101.36
	1,4-DMPZ	0	0	0	0	0	0	0	0
	AEP	0	1.27	19.58	57.49	101.76	133.61	151.33	168.13

Table D.52: Tabulated Experimental Data for TE52 (8 m PZ, unloaded, 175 °C, N₂ headspace)

	Time (wk)	0	0.3	1.3	3.5	5.6	5.6	7.5	9.5	14.5
Original Samples (mmol/kg)	Gly	0	0.17	0.03	0.23	0.16	0.33	0.03	0.24	0.02
	Ace	0	0	0.06	0.21	0.35	0.29	0.31	0.26	0.66
	Form	0.05	0.25	0.39	3.39	5.69	1.72	3.52	3.17	7.19
	Oxa	0.03	0.01	0.02	0.02	0.02	0.02	0.01	0.02	0.02
	Sulf	0.13	0.11	0.13	0.14	0.14	0.10	0.16	0.37	1.03
	Cl ⁻	0.02	0.04	0.05	0.03	0.08	0.04	0.05	0.04	0.34
	NH ₄ ⁺	0	0	0	0	0	0	0	0	19.97
	FPZ	0	0	0	1.06	1.95	1.01	0.94	1.10	2.66
	EDA	0	0.16	0.86	3.94	8.64	2.36	9.13	5.80	28.49
	PZ	4678.7	4661.2	4661.1	4677.8	4579.6	4664.5	4643.5	4793.3	4564.3
	HEP	0	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0	0	0	0
	1-EPZ	0	0	0	0	0	0	0	0	2.34
	1,4-DMPZ	0	0	0	0	0	0	0	0	0
	AEP	0	0	0	0	0.74	0	0.63	0.69	2.56
	Alk	4751.1	4858.4	4806.0	4794.1	4808.9	4856.0	4783.3	5034.3	4738.6
	SD _{Alk}	47.02	NA	NA	NA	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0.35	0.98	1.48	0.91	0.80	1.04	1.35
	Ace	0	0	0.12	0.52	0.68	0.25	0.48	0.45	0.75
	Form	0	0	0.42	4.06	6.99	1.85	3.79	3.68	8.09
	Oxa	0.02	0.03	0.05	0.17	0.17	0.07	0.08	0.07	0.07
	Sulf	0.11	0.24	0.18	0.17	0.19	0.18	0.20	0.42	1.00
	Cl ⁻	0.06	0.16	0.13	0.10	0.15	0.12	0.23	0.13	0.45
	NH ₄ ⁺	0	0	0	0	0	0	0	0	0
	FPZ	0	0	0	0	0	0	0	0	0
	EDA	0	0	2.08	5.97	13.06	3.59	10.75	7.87	29.19
	PZ	4682.1	4634.3	4827.9	4873.9	4700.7	4774.3	4699.9	5018.6	4416.4
	HEP	0	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0	0	0	0
	1-EPZ	0	0	0	0	0	0	0	1.09	2.05
	1,4-DMPZ	0	0	0	0	0	0	0	0	0
	AEP	0	0	0	1.19	1.64	0	0.98	1.23	3.00

Table D.53: Tabulated Experimental Data for TE53 (8 m PZ, 0.2 mole CO₂ per mole alkalinity initially, 175 °C)

	Time (wk)	0	1.7	3.4	4.0	4.9	6.0	6.0	6.0	8.0	10.0	12.1	15.0
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0	0.29	0.25	0.25	0.18	0.16	0.15	0.19	0.11	0.08	0.06	0.04
	Ace	0	1.12	1.30	1.24	2.44	2.39	3.34	3.96	4.51	7.10	11.02	11.70
	Form	0	28.15	64.55	65.62	99.44	80.55	105.69	87.61	137.15	155.34	203.97	174.03
	Oxa	0.00	0.15	0.01	0.01	0.00	0.01	0.00	0.05	0.00	0.00	0.00	0.00
	Sulf	0.08	24.83	0.26	0.15	0.23	0.84	0.19	2.63	0.13	0.07	0.08	0.07
	Cl ⁻	0.08	0.05	0.06	0.05	0.04	0.02	0.01	0.02	0.02	0.02	0.02	0.02
	NH ₄ ⁺	5.09	90.40	94.30	101.16	176.53	163.28	236.66	80.70	300.58	388.37	562.26	606.21
	FPZ	0	118.95	139.90	140.63	201.25	169.64	210.22	214.27	259.06	283.12	320.09	345.33
	EDA	0	42.78	33.96	37.94	53.57	48.44	57.58	55.82	63.67	71.04	73.11	80.04
	PZ	4535.1	3634.3	3731.9	3668.5	3425.3	3505.3	3213.7	3350.8	2903.1	2655.6	2320.0	2205.5
	HEP	0	0	0	0	10.87	9.32	8.78	5.50	6.46	9.68	14.38	27.72
	1-MPZ	0	0	0	0	0	0	0	0	0	3.51	10.60	13.83
	1-EPZ	0	11.07	10.06	10.47	20.93	18.93	25.00	31.52	36.90	45.28	81.78	62.32
	1,4-DMPZ	0	0	0	0	0	0	0	0	0	0	0	0
	AEP	0	24.52	39.05	43.38	75.55	66.78	88.08	82.49	115.94	146.81	168.30	174.16
	CO ₂	1708.4	2575.1	1309.0	1292.2	1137.5	1218.3	1116.3	1215.3	948.39	934.48	768.92	770.11
	SD _{CO2}	27.66	27.21	14.02	3.24	8.79	7.79	25.37	30.07	14.20	9.78	7.91	12.48
	Alk	4407.8	NT	4083.8	4084.9	3920.7	3881.2	3810.1	4054.4	3661.3	3571.4	3302.5	3297.4
	SD _{Alk}	30.32	NT	89.80	15.13	46.81	29.36	16.03	NA	28.90	NA	83.17	51.00
	Fe ²⁺	0	NT	12.61	14.51	17.52	NT	NT	NT	22.36	13.58	41.03	75.62
	Ni ²⁺	0	NT	74.03	75.38	117.79	NT	NT	NT	195.13	218.85	270.28	302.73
	Cr ³⁺	0	NT	0	0	0	NT	NT	NT	0.09	0	1.54	1.75
Hydrolyzed Samples (mmol/kg)	Gly	0.11	NT	0.63	1.00	1.10	0.75	0.69	1.91	1.38	0.94	2.17	2.00
	Ace	0	NT	2.19	1.94	3.83	3.67	5.09	8.44	7.58	11.31	17.06	17.76
	Form	0	NT	152.76	153.60	224.78	188.90	248.90	241.79	321.54	393.66	454.14	457.73
	Oxa	0.01	NT	0.15	0.05	0.05	0.15	0.16	1.43	0.08	0.08	0.09	0.08
	Sulf	1.72	NT	0.31	0.22	0.26	0.82	0.26	2.88	0.20	0.14	0.13	0.14
	Cl ⁻	0.09	NT	0.26	0.11	0.08	0.08	0.06	0.20	0.11	0.13	0.09	0.08
	NH ₄ ⁺	0	NT	95.05	109.75	164.36	157.71	205.43	67.42	283.18	384.95	483.05	538.29
	FPZ	0	NT	0	0	0	0	0	0	0	0	0	0
	EDA	0	NT	36.52	41.61	56.05	51.41	59.68	66.75	68.28	78.56	76.71	85.48
	PZ	4539.1	NT	3834.1	3800.5	3437.7	3510.5	3248.8	3489.6	3111.5	2954.9	2403.9	2404.7
	HEP	0	NT	0	0	0	0	0	2.33	6.85	10.60	14.62	28.46
	1-MPZ	0	NT	0	0	0	0	0	0	0	3.33	12.13	13.08
	1-EPZ	0	NT	10.78	11.47	21.26	19.68	27.55	33.31	39.90	52.57	71.11	76.36
	1,4-DMPZ	0	NT	0	0	0	0	0	0	0	0	0	0
	AEP	0	NT	42.05	46.57	77.25	70.68	91.05	90.42	123.65	164.10	174.53	186.25

Table D.54: Tabulated Experimental Data for TE54 (8 m PZ, 0.47 mole CO₂ per mole alkalinity initially, 175 °C)

	Time (wk)	0	0.7	1.7	3.4	4.0	4.9	6.0	6.0	6.0	8.0	10.0	12.1	15.0
Original Samples (mmol/kg) (Metals are in units of µg/g)	Gly	0.70	0.56	0.34	0.39	0.35	0.27	0.28	0.22	0.28	0.21	0.11	0.07	0.08
	Ace	0	0	0.49	0.55	0.71	1.16	1.00	1.81	1.06	1.97	6.02	10.05	15.34
	Form	0.96	5.29	24.28	31.96	37.53	44.53	42.13	65.63	34.58	67.32	108.76	147.13	190.47
	Oxa	0.01	0.03	0.03	0.01	0.01	0.02	0.01	0.00	0.02	0.01	0.01	0.01	0.01
	Sulf	0.17	0.09	0.05	0.05	0.09	0.09	0.08	0.07	0.09	0.11	0.09	0.08	0.10
	Cl ⁻	0.34	0.03	0.05	0.04	0.04	0.05	0.05	0.05	0.06	0.05	0.05	0.04	0.07
	NH ₄ ⁺	7.65	8.16	57.27	51.80	59.88	95.48	79.22	129.46	81.11	102.72	291.15	441.44	644.66
	FPZ	0	41.50	176.30	186.40	214.60	258.53	238.53	344.01	253.36	356.58	493.20	599.57	679.04
	EDA	0	5.40	22.72	24.11	28.75	35.91	32.75	46.48	36.52	45.60	60.70	61.99	65.95
	PZ	4125.2	4021.3	3632.1	3705.9	3666.1	3532.6	3500.5	3299.1	3309.0	3227.6	2647.0	2134.6	1685.7
	HEP	0	0	0	0	0	0	0	8.50	7.67	9.06	8.59	8.27	12.30
	1-MPZ	0	0	0	0	0	0	0	0	0	3.86	5.25	6.06	5.07
	1-EPZ	0	0	4.65	4.09	6.09	9.73	8.27	14.97	9.58	15.41	32.51	46.05	56.22
	1,4-DMPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	AEP	0	2.04	15.63	16.64	21.71	36.07	32.38	51.03	36.71	53.45	96.35	111.54	126.40
	CO ₂	3022.2	3223.3	3005.1	2781.7	2785.5	2714.3	2768.4	2666.0	3042.3	2664.4	2416.6	2138.2	1901.3
	SD _{CO2}	28.70	42.18	27.75	40.06	8.47	29.39	44.85	20.20	37.76	12.03	10.02	23.84	15.93
	Alk	4183.1	4034.9	3797.6	3821.4	3883.9	3822.9	3739.9	3589.9	3668.9	3572.9	3235.2	2938.2	2623.8
	SD _{Alk}	37.60	53.09	40.92	29.74	8.55	50.22	10.07	42.38	3.78	4.80	67.84	16.58	2.94
	Fe ²⁺	0	NT	NT	69.90	78.26	NT	93.10	89.67	NT	98.55	174.76	206.43	195.06
	Ni ²⁺	0	NT	NT	40.01	55.01	NT	79.14	95.97	NT	84.51	190.74	229.93	286.11
	Cr ³⁺	0	NT	NT	45.75	74.22	NT	85.41	127.39	NT	97.16	113.40	120.75	154.70
Hydrolyzed Samples (mmol/kg)	Gly	0.84	0.63	0.41	0.40	0.35	0.27	0.31	0.22	0.29	0.22	0.09	0.02	0.00
	Ace	0	0	0.53	0.63	0.86	1.65	1.17	2.47	1.34	2.35	9.62	16.37	25.53
	Form	0	26.48	124.69	136.74	162.90	206.12	188.29	302.33	193.80	309.85	501.48	701.82	886.01
	Oxa	0.00	0.03	0.05	0.02	0.02	0.07	0.02	0.02	0.05	0.02	0.04	0.08	0.10
	Sulf	0.12	0.15	0.13	0.14	0.14	0.14	0.10	0.12	0.12	0.14	0.14	0.12	0.15
	Cl ⁻	0.07	0.08	0.09	0.09	0.11	0.12	0.09	0.08	0.11	0.09	0.08	0.09	0.12
	NH ₄ ⁺	0	0	66.83	66.12	54.31	88.29	76.91	124.53	87.67	130.92	280.21	417.68	586.15
	FPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	EDA	0	5.85	22.55	24.61	29.31	36.94	34.34	47.48	36.80	47.68	63.89	68.01	74.73
	PZ	4142.0	4039.8	3701.0	3753.7	3685.4	3622.3	3600.3	3422.0	3506.9	3454.4	2922.7	2516.8	2115.0
	HEP	0	0	0	0	0	0	0	0	0	9.48	5.66	9.15	14.40
	1-MPZ	0	0	0	0	0	0	0	3.79	2.53	4.26	5.42	7.16	5.74
	1-EPZ	0	0	4.56	4.64	5.64	10.29	9.18	16.40	10.09	17.37	40.71	62.47	83.36
	1,4-DMPZ	0	0	0	0	0	0	0	0	0	0	0	0	0
	AEP	0	1.90	15.89	17.04	22.62	37.98	34.29	54.01	38.56	57.61	106.34	131.14	155.62

Table D.55: Tabulated Experimental Data for TE55 (8 m PZ, 0.2 mole H⁺ per mole alkalinity initially, 175 °C)

	Time (wk)	0	0.7	1.7	3.4	4.0	6.0	6.0	6.0	9.0	12.0	15.0
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0	0	0
	Ace	0	0	0	0.23	0.50	0.44	0.34	0.31	0.53	0.77	0.47
	Form	0	0.2	0.5	2.2	3.7	3.9	3.7	3.3	3.7	4.8	2.6
	Oxa	0	0	0	0	0	0	0	0	0	0	0
	Sulf	0	0	0	0	0	0	0	0	0	0	0
	Cl ⁻	0.03	0.03	0.04	0.03	0.04	0.04	0.02	0.05	0.06	0.03	0.01
	NH ₄ ⁺	1.00	3.37	6.36	22.60	47.16	81.70	64.91	45.51	78.70	98.60	116.69
	FPZ	0	0.77	0.36	2.53	4.91	4.04	3.56	7.33	4.97	4.43	3.70
	EDA	0	2.07	6.80	55.60	43.30	49.34	42.83	39.90	60.18	83.98	75.53
	PZ	4729.6	4629.1	4428.0	4378.4	4297.9	4116.0	4258.1	4165.7	3965.6	3842.5	3753.1
	HEP	0	0	0	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0	0	0	0	0	0
	1-EPZ	0	0	0	4.02	6.11	8.73	8.23	7.89	12.86	16.54	18.10
	1,4-DMPZ	0	0	0	0	0	0	0	0	0	0	0
	AEP	0	1.04	2.89	9.55	17.74	23.98	21.45	20.49	35.47	49.24	55.21
	Alk	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0.64	0.31	0.66	0.34	0.38	0.66	0.40	0.28	0.70
	Ace	0	0	0	0.44	1.00	0.83	0.73	0.61	0.89	1.49	0.85
	Form	0	0.01	0.15	0.85	1.21	1.06	1.27	1.06	1.04	1.43	0.68
	Oxa	0	0	0	0	0	0	0	0	0	0	0
	Sulf	0	0	0	0	0	0	0	0	0	0	0
	Cl ⁻	0.08	0.07	0.09	0.05	0.09	0.07	0.66	0.11	0.09	0.14	0.08
	NH ₄ ⁺	0	0	0	0	66.94	47.85	69.17	71.98	55.88	85.65	94.25
	FPZ	0	0	0	0	0	0	0	0	0	0	0
	EDA	0	2.47	7.98	26.63	45.25	51.78	43.99	41.82	62.39	85.64	78.66
	PZ	4702.3	4641.6	4569.3	4398.9	4283.9	4114.0	4160.3	4274.5	3932.1	3866.1	3730.0
	HEP	0	0	0	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0	0	0	0	0	0
	1-EPZ	0	0	0	3.93	6.41	9.29	8.23	8.31	12.90	16.77	18.07
	1,4-DMPZ	0	0	0	0	0	0	0	0	0	0	0
	AEP	0	0.97	3.07	10.10	18.93	25.52	22.17	22.33	37.30	51.80	56.84

Table D.56: Tabulated Experimental Data for TE56 (8 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 175 °C, 100 mM Inhibitor A)

	Time (wk)	0	0.7	1.7	3.4	4.0	6.0	6.0	6.0	9.0	12.0	15.0
Original Samples (mmol/kg)	Gly	0.62	0.55	0.43	0.45	0.40	0.41	0.42	0.43	0.10	0.06	0.04
	Ace	0	0	0.40	0.38	0.68	0.95	0.76	0.77	4.21	9.12	11.43
	Form	1.00	6.15	32.76	32.92	34.93	55.51	46.96	47.38	117.84	185.78	191.64
	Oxa	0.01	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01
	Sulf	0.11	0.13	0.16	0.10	0.11	0.15	0.11	0.15	0.13	0.20	0.13
	Cl ⁻	0.04	0.03	0.07	0.04	0.03	0.08	0.04	0.08	0.03	0.04	0.03
	NH ₄ ⁺	1.78	6.35	40.83	45.43	49.67	79.99	73.51	81.64	322.21	494.87	567.58
	FPZ	0	16.86	105.11	103.96	110.92	158.90	146.88	147.77	337.96	447.98	480.49
	EDA	0	4.26	17.70	23.95	24.58	34.46	31.15	29.63	58.79	60.43	63.62
	PZ	4425.1	4294.6	4075.0	4021.7	3956.7	3627.4	3814.9	3815.5	2828.5	2272.7	2041.8
	HEP	0	0	0	0	0	0	0	0	32.62	42.41	48.49
	1-MPZ	0	0	0	11.04	16.02	15.36	13.60	12.21	14.62	23.08	23.46
	1-EPZ	0	0	3.72	3.90	5.17	8.45	7.22	7.29	34.00	65.15	73.42
	1,4-DMPZ	0	0	0	0	0	0	0	0	0	0	0
	AEP	0	1.88	14.90	18.74	21.59	39.98	35.11	35.19	101.73	139.30	148.16
	CO ₂	2300.6	2247.1	2224.2	2193.4	2268.6	1972.6	2060.3	2058.6	1969.5	1414.0	1315.9
	SD _{CO2}	39.65	25.12	13.48	24.37	4.65	13.03	18.64	55.10	2.54	17.18	11.75
	Alk	4157.2	4143.5	4140.4	4067.0	4074.6	3802.1	3952.8	3945.4	3286.1	3094.5	3012.9
	SD _{Alk}	51.07	0.84	36.51	64.78	112.59	268.09	33.25	46.51	NA	13.00	0.68
Hydrolyzed Samples (mmol/kg)	Gly	0.33	0.56	0.85	0.81	0.95	1.07	0.97	0.98	0.44	1.12	1.61
	Ace	0	0	0.79	0.80	1.30	1.62	1.37	1.31	8.53	15.53	19.12
	Form	0	12.13	91.39	90.85	98.28	153.62	134.41	134.56	376.29	567.18	607.76
	Oxa	0.01	0.05	0.06	0.07	0.07	0.05	0.07	0.05	0.31	0.22	0.15
	Sulf	0.07	0.15	0.13	0.20	0.18	0.21	0.17	0.14	0.15	0.22	0.22
	Cl ⁻	0.06	0.10	0.10	0.37	0.11	0.43	0.13	0.10	0.09	0.13	0.33
	NH ₄ ⁺	0	0	73.67	76.64	83.18	118.14	107.84	104.37	352.09	527.31	590.72
	FPZ	0	0	0	0	0	0	0	0	0	0	0
	EDA	0	5.71	22.09	23.75	27.17	35.99	32.39	32.64	62.26	69.26	71.42
	PZ	4341.5	4251.2	4081.6	4035.8	3967.6	3739.3	3865.0	3862.2	3033.5	2534.4	2294.2
	HEP	0	0	0	0	0	0	0	0	31.54	42.36	45.89
	1-MPZ	0	0	0	0	7.40	9.82	8.69	8.80	17.73	23.29	21.65
	1-EPZ	0	0	3.68	4.40	5.39	8.94	8.02	7.96	39.15	67.68	75.49
	1,4-DMPZ	0	0	0	0	0	0	0	0	0	0	0
	AEP	0	2.34	15.51	19.28	22.23	41.85	35.79	35.94	111.04	156.52	165.38

Table D.57: Tabulated Experimental Data for TE57 (20 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 175 °C)

Time (wk)		0	0.7	1.7	4.0	6.0	6.0	8.0	10.0	15.0
Original Samples (mmol/kg)	Gly	0.79	0.36	0.29	0.09	0.05	0.06	0	0	0
	Ace	0	0.31	0.79	3.75	7.40	6.92	9.08	11.10	11.64
	Form	0	23.37	45.67	133.75	182.85	175.30	206.74	216.23	199.91
	Oxa	0.05	0.02	0.07	0	0	0	0	0	0
	Sulf	0.10	0.08	0.12	0.12	0.16	0.13	0.15	0.16	0.12
	Cl ⁻	0.06	0.06	0.03	0.20	0.04	0.03	0.04	0.38	0.13
	NH ₄ ⁺	0	45.74	96.74	354.79	511.80	533.09	647.85	754.75	809.11
	FPZ	0	293.89	491.51	920.07	967.37	986.01	1005.0	975.47	950.12
	EDA	0	25.13	43.26	84.90	87.14	88.50	91.29	102.49	90.16
	PZ	5663.9	4925.4	4396.4	2783.6	2124.2	2173.1	1764.2	1525.9	1385.3
	HEP	0	0	0	9.60	17.93	18.32	24.66	29.07	31.82
	1-MPZ	0	7.42	16.22	31.09	31.87	32.30	31.11	29.32	26.90
	1-EPZ	0	4.23	10.68	50.01	80.79	80.87	89.10	101.63	104.83
	1,4-DMPZ	0	10.23	9.19	0	0	0	0	0	0
	AEP	0	11.01	27.56	84.45	101.54	101.04	111.43	118.82	123.06
	CO ₂	4042.2	3581.3	3178.2	2042.6	1570.0	1643.4	1318.6	1208.6	1148.1
	SD _{CO2}	61.25	71.78	44.38	24.65	9.05	11.99	12.62	15.17	16.70
	Alk	6121.5	5863.9	5452.0	4439.1	3910.5	3891.8	3761.8	3712.0	3559.7
	SD _{Alk}	NA	NA	NA	NA	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	1.05	0.47	0.31	0.05	0	0	0	0	0
	Ace	0	0.54	1.59	12.92	20.65	21.36	27.07	30.49	33.25
	Form	0	202.37	377.33	942.12	1153.83	1130.80	1263.22	1316.40	1299.36
	Oxa	0	0.07	0.18	0	0	0	0	0	0
	Sulf	0.15	0.11	0.14	0.13	0.13	0.15	0.09	0.10	0.20
	Cl ⁻	0	0	0	0	0	0	0	0	0
	NH ₄ ⁺	0	61.39	90.15	320.08	457.20	464.33	570.34	696.79	750.44
	FPZ	0	0	0	0	0	0	0	0	0
	EDA	0.22	26.70	47.35	95.93	101.04	102.49	108.68	122.77	109.63
	PZ	5671.7	5041.1	4634.6	3280.8	2665.4	2721.5	2344.3	2098.5	1945.3
	HEP	0	0	0	9.54	21.10	18.52	29.43	35.91	39.13
	1-MPZ	0	9.53	17.17	33.98	35.00	38.32	36.54	35.29	35.06
	1-EPZ	0	4.27	12.50	63.59	92.30	94.03	113.13	125.60	133.57
	1,4-DMPZ	0	11.44	9.70	5.03	0	0	0	0	0
	AEP	0	12.07	29.81	97.89	125.76	125.75	143.08	155.52	163.95

Table D.58: Tabulated Experimental Data for TE58 (20 m PZ, 0.1 mole CO₂ per mole alkalinity initially, 175 °C)

Time (wk)		0	0.7	1.7	4.0	6.0	6.0	8.0	10.0	15.0
Original Samples (mmol/kg)	Gly	0.52	0.43	0.33	0.22	0.20	0.20	0.14	0.13	0.09
	Ace	0	0	0.22	0.50	0.56	0.56	0.99	1.07	1.69
	Form	0.02	8.77	29.23	50.86	51.54	52.55	73.33	67.84	81.14
	Oxa	0.01	0.03	0.06	0.04	0.06	0.06	0.06	0.05	0.06
	Sulf	0.08	0.10	0.09	0.10	0.09	0.12	0.11	0.14	0.09
	Cl ⁻	0.03	0.16	0.04	0.05	0.06	0.04	0.04	0.04	0.06
	NH ₄ ⁺	0	8.57	26.67	71.44	85.87	85.14	139.53	150.20	225.89
	FPZ	0	58.96	191.78	298.84	300.81	304.66	385.63	367.47	425.74
	EDA	0.01	14.16	30.59	61.95	66.29	67.78	91.73	97.47	119.63
	PZ	6368.0	6097.8	5660.2	5178.7	5053.3	5054.5	4643.8	4668.9	4184.0
	HEP	0	0	0	0	0	0	9.39	9.41	4.80
	1-MPZ	0	0	3.68	7.64	12.25	8.48	9.87	9.27	12.38
	1-EPZ	0	0.81	3.75	10.78	12.57	12.62	22.69	21.65	35.35
	1,4-DMPZ	0	3.40	6.87	5.38	4.40	4.51	3.15	2.65	0.66
	AEP	0	2.97	11.78	29.82	33.58	33.95	55.91	54.20	83.80
	CO ₂	1441.7	1345.8	1191.9	1075.0	1400.0	853.2	917.6	730.9	1228.6
	SD _{CO2}	12.73	4.60	4.42	1.64	13.43	7.61	8.32	8.75	9.34
	Alk	6977.6	6912.6	6645.7	6464.9	6367.7	6362.2	6102.7	6152.5	5903.8
	SD _{Alk}	NA	NA	NA	NA	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	6.46	2.41	4.26	5.11	0.90	0.79	3.35	0.79	0.73
	Ace	0	0.60	1.04	2.24	2.00	2.02	3.18	3.42	5.52
	Form	0.55	142.42	151.83	252.83	232.98	243.07	401.41	309.55	385.67
	Oxa	0.01	0.77	0.46	0.89	0.36	0.31	0.85	0.31	0.36
	Sulf	0.11	0.20	0.13	0.09	0.18	0.12	0.09	0.13	0.08
	Cl ⁻	0.12	0	0	0	0	0	0	0	0
	NH ₄ ⁺	0	0	33.58	60.91	88.16	83.63	71.79	151.05	206.48
	FPZ	0	0	0	0	0	0	0	0	0
	EDA	4.12	23.44	46.06	66.60	69.44	71.34	71.24	103.41	129.42
	PZ	7345.6	3758.5	6820.3	4979.5	5204.3	5216.4	2982.2	4875.1	4497.5
	HEP	0	0	0	0	0	0	6.46	10.85	12.20
	1-MPZ	0	2.82	4.75	7.66	13.43	8.71	5.45	9.50	10.48
	1-EPZ	0	1.93	4.42	9.15	13.00	13.09	12.45	22.93	38.46
	1,4-DMPZ	0.99	3.78	7.69	4.80	4.38	4.35	1.56	3.15	1.75
	AEP	0	7.59	14.17	28.65	34.92	35.04	34.65	56.45	88.28

Table D.59: Tabulated Experimental Data for TE59 (8 m PZ + 1 m Ethylenediamine, 0.3 mole CO₂ per mole alkalinity initially, 175 °C)

	Time (wk)	0	0.1	0.4	0.7	1.0	1.5	1.9
Original Samples (mmol/kg)	Gly	0.13	0.14	0.13	0.13	0.10	0.10	0.10
	Ace	0	0	1.46	3.81	6.10	5.65	8.51
	Form	0.13	7.55	15.03	28.05	39.53	32.40	49.00
	Oxa	0	0.01	0.01	0.01	0.01	0.01	0.01
	Sulf	0.10	0.10	0.14	0.12	0.09	0.10	0.09
	Cl ⁻	0.03	0.02	0.04	0.04	0.02	0.02	0.02
	NH ₄ ⁺	6.05	38.46	89.22	134.46	198.12	229.15	273.45
	FPZ	0	30.04	78.13	154.91	162.62	193.82	224.89
	EDA	502.16	222.32	186.27	173.01	171.09	187.12	179.25
	PZ	3987.6	3898.5	3722.3	3638.7	3499.8	3428.8	3310.3
	HEP	0	0	0	0	0	0	0
	1-MPZ	0	16.28	16.04	16.35	14.24	13.63	13.18
	1-EPZ	0	0	1.22	2.40	5.09	5.07	7.49
	1,4-DMPZ	0	0	5.63	7.59	2.85	1.94	1.82
	AEP	0	17.80	48.13	67.69	90.74	105.34	119.76
	2-Imid	0	244.41	274.86	280.38	255.96	247.51	238.58
	CO ₂	2849.9	2588.2	2459.9	2461.4	2411.1	2419.8	2319.7
	SD _{CO2}	28.51	14.61	27.75	18.45	23.24	19.37	18.08
	Alk	4517.2	4282.0	4140.9	4175.6	4024.1	4016.3	3934.9
	SD _{Alk}	10.33	90.93	0.82	126.45	44.79	56.87	5.09
Hydrolyzed Samples (mmol/kg)	Gly	0	0.21	0.27	0.39	0.41	0.62	0.58
	Ace	0	1.26	4.72	8.13	9.10	13.37	0
	Form	0.50	26.54	68.09	99.61	98.84	148.47	182.89
	Oxa	0.02	0.04	0.05	0.07	0.05	0.06	0.06
	Sulf	0.14	0.11	0.14	0.16	0.10	0.14	0.12
	Cl ⁻	0.03	0.05	0.08	0.09	0.02	0.10	0.04
	NH ₄ ⁺	0	14.40	53.55	85.48	137.80	160.41	192.29
	FPZ	0	0	0	0	0	0	0
	EDA	486.9	223.5	188.8	168.6	174.0	185.6	183.7
	PZ	3935.9	3851.8	3718.4	3622.2	3551.9	3506.5	3355.4
	HEP	0	0	0	0	0	0	0
	1-MPZ	0	13.83	17.20	15.66	14.10	13.46	12.52
	1-EPZ	0	0	1.54	2.89	5.39	5.73	11.53
	1,4-DMPZ	0	0	2.06	3.78	2.23	1.72	1.92
	AEP	0	21.18	50.66	63.80	98.62	105.05	124.59

Table D.60: Tabulated Experimental Data for TE60 (8 m PZ + 1 m Ethylenediamine, 0.3 mole CO₂ per mole alkalinity initially, 150 °C)

	Time (wk)	0	0.4	1.0	1.5	1.9	3.0	3.9
Original Samples (mmol/kg)	Gly	0.15	0.19	0.22	0.32	0.19	0.15	0.18
	Ace	0	0	0	0	0	0	0
	Form	0.07	2.28	5.02	7.25	8.86	8.62	14.82
	Oxa	0	0.00	0.01	0.00	0.01	0.01	0.00
	Sulf	0.11	0.14	0.13	0.15	0.18	0.13	0.13
	Cl ⁻	0	0	0	0	0	0	0
	NH ₄ ⁺	6.21	15.77	22.94	28.18	38.52	46.03	61.09
	FPZ	0	10.04	19.31	42.46	64.41	104.65	102.01
	EDA	492.62	381.42	296.09	277.19	263.03	261.63	235.42
	PZ	4212.1	4190.3	4168.8	4162.3	4125.1	4074.9	4044.7
	HEP	0	0	0	0	0	0	0
	1-MPZ	0	12.00	19.34	22.41	26.64	25.33	29.06
	1-EPZ	0	0	0	0	0	0	0
	1,4-DMPZ	0	0	0	0	0	0	0
	AEP	0	7.41	9.78	14.94	17.77	25.41	33.03
	2-Imid	0	95.68	172.00	192.16	206.89	198.73	222.89
	CO ₂	2884.6	2718.1	2699.2	2654.4	2564.5	2566.8	2511.5
	SD _{CO2}	15.87	57.01	5.72	32.54	22.93	38.01	71.39
	Alk	4551.1	4429.5	4345.6	4376.7	4267.9	4246.5	4208.6
	SD _{Alk}	33.21	3.95	21.87	131.54	37.21	1.42	19.54
Hydrolyzed Samples (mmol/kg)	Gly	0.14	0.17	0.16	0.15	0.16	0.15	0.17
	Ace	0	0.05	0.08	0.12	0.15	0.24	0.34
	Form	0.20	8.43	17.22	26.58	32.63	47.62	65.22
	Oxa	0.01	0.01	0.01	0.01	0.01	0.01	0.02
	Sulf	0.11	0.15	0.13	0.15	0.16	0.14	0.16
	Cl ⁻	0	0	0	0	0	0	0
	NH ₄ ⁺	0	2.86	33.18	42.86	71.10	62.83	68.52
	FPZ	0	0	0	0	0	0	0
	EDA	492.17	384.59	300.21	278.85	258.17	260.77	238.64
	PZ	4186.3	4188.9	4159.9	4132.9	4125.4	4106.2	4124.2
	HEP	0	0	0	0	0	0	0
	1-MPZ	0	19.64	20.08	26.16	23.09	21.05	27.62
	1-EPZ	0	0	0	0	0	0	0
	1,4-DMPZ	0	0	0	0	3.23	3.90	4.31
	AEP	0	3.63	10.01	16.01	16.24	28.65	37.05

Table D.61: Tabulated Experimental Data for TE61 (4 m PZ, 0.3 mole H⁺ per mole alkalinity initially, 175 °C)

Time (wk)		0	1.0	1.9	3.9	6.1	6.1	6.1	8.0	9.9
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0
	Ace	0	0	0.1	0.3	0.6	0.5	0.6	1.0	1.3
	Form	0	0.3	0.4	0.8	1.0	0.8	1.1	1.5	1.6
	Oxa	0	0	0	0	0	0	0	0	0
	Sulf	0	0	0	0	0	0	0	0	0
	Cl ⁻	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	NH ₄ ⁺	1.1	3.6	9.0	33.7	51.3	39.4	51.5	113.1	162.8
	FPZ	0	0	0.8	1.6	1.8	1.4	1.6	2.7	3.0
	EDA	0	3.3	9.5	25.2	30.5	26.5	30.7	43.4	52.2
	PZ	2515.8	2481.9	2441.3	2305.1	2280.6	2323.4	2286.4	2167.1	2077.6
	HEP	0	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0	0	0	0
	1-EPZ	0	0	3.1	8.7	11.6	9.5	11.4	20.2	26.8
	1,4-DMPZ	0	0	0	0	0	0	0	0	0
	AEP	0	1.1	3.8	15.1	22.1	17.1	22.0	38.1	49.0
	Alk	NT	NT	NT	NT	NT	NT	NT	NT	NT

Table D.62: Tabulated Experimental Data for TE62 (12 m PZ, 0.3 mole H⁺ per mole alkalinity initially, 175 °C)

Time (wk)		0	1.0	1.9	3.9	6.1	6.1	6.1	8.0	9.9
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0
	Ace	0	0	0	0.12	0.20	0.21	0.21	0.45	0.80
	Form	0.57	0.12	0.33	0.90	1.00	0.77	1.04	1.64	2.41
	Oxa	0	0	0	0	0	0	0	0	0
	Sulf	0	0	0	0	0	0	0	0	0
	Cl ⁻	0.03	0.03	0.04	0.03	0.04	0.05	0.03	0.04	0.03
	NH ₄ ⁺	0.77	3.02	9.10	39.42	69.64	70.09	71.80	122.52	315.37
	FPZ	0	1.12	1.61	2.62	4.06	3.57	3.89	19.41	9.56
	EDA	0	4.16	12.69	34.55	46.66	51.81	46.32	68.24	143.27
	PZ	4568.2	4459.3	4310.9	4076.9	3945.6	3893.8	3871.8	4056.9	3185.4
	HEP	0	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0	0	0	0
	1-EPZ	0	0.90	3.21	8.21	12.55	13.20	13.43	24.31	42.13
	1,4-DMPZ	0	0	0	0	0	0	0	0	0
	AEP	0	1.14	4.94	21.41	32.58	35.72	36.22	75.59	130.05
	Alk	NT	NT	NT	NT	NT	NT	NT	NT	NT

Table D.63: Tabulated Experimental Data for TE63 (8 m PZ, 0.6 mole H⁺ per mole alkalinity initially, 175 °C)

Time (wk)		0	1.0	1.9	3.9	6.1	6.1	6.1	8.0	9.9
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0
	Ace	0	0	0	0.21	0.26	0.23	0.23	0.46	0.58
	Form	0	0.25	0.07	0.14	0.14	0.10	0.21	0.16	0.66
	Oxa	0	0	0	0	0	0	0	0	0
	Sulf	0	0	0	0	0	0	0	0	0
	Cl ⁻	0.01	0.03	0.03	0.04	0.06	0.02	0.04	0.05	0.04
	NH ₄ ⁺	0.96	5.25	10.25	48.85	58.47	51.71	56.81	115.67	181.34
	FPZ	0	1.12	1.55	2.23	2.93	2.66	3.52	3.83	5.41
	EDA	0	8.66	16.29	45.81	49.05	44.08	48.82	71.36	89.28
	PZ	3398.7	3331.7	3284.4	3207.9	3097.2	3127.4	3090.3	2995.3	2850.3
	HEP	0	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0	0	0	0
	1-EPZ	0	2.16	3.81	11.05	12.19	10.40	12.17	18.50	25.80
	1,4-DMPZ	0	0	0	0	0	0	0	0	0
	AEP	0	2.89	6.90	26.72	32.26	26.89	31.52	55.79	79.59
	Alk	NT	NT	NT	NT	NT	NT	NT	NT	NT

Table D.64: Tabulated Experimental Data for TE64 (8 m PZ + 1 m 2-Imidazolidone, 0.3 mole CO₂ per mole alkalinity initially, 150 °C)

	Time (wk)	0	0.2	0.6	0.7	1.0
Original Samples (mmol/kg)	Gly	0.30	0.24	0.19	0.25	0.15
	Ace	0	0	0	0	0
	Form	0.16	0.29	1.31	1.43	1.49
	Oxa	0.00	0.01	0.01	0.01	0.01
	Sulf	0.14	0.13	0.09	0.31	0.17
	Cl ⁻	0.04	0.03	0.02	0.51	0.07
	NH ₄ ⁺	0	4.63	4.62	6.25	8.19
	FPZ	0.19	1.59	4.23	4.46	5.81
	EDA	0	42.61	119.82	139.12	162.33
	PZ	3688.2	3654.8	3679.3	3719.2	3695.5
	HEP	0	0	0	0	0
	1-MPZ	0	42.05	36.47	35.56	32.99
	1-EPZ	0	0	0	0	0
	1,4-DMPZ	0	0	0	0	0
	AEP	0	0	1.17	1.82	3.10
	2-Imid	538.89	434.94	356.42	329.90	297.73
	CO ₂	2488.3	2579.4	2579.0	2617.6	2601.5
	SD _{CO2}	48.53	18.23	7.39	31.84	5.95
Hydrolyzed Samples (mmol/kg)	Alk	3957.4	4032.2	4121.0	4121.6	4210.5
	SD _{Alk}	7.99	35.72	18.12	54.01	158.71
	Gly	0.29	0.24	0.25	0.26	0.25
	Ace	0	0	0	0	0
	Form	0.26	1.64	6.19	5.78	7.35
	Oxa	0.02	0.03	0.01	0.02	0.02
	Sulf	0.19	0.17	0.11	0.13	0.20
	Cl ⁻	0.05	0.12	0.03	0.06	0.11
	NH ₄ ⁺	0	0	0	0	0
	FPZ	0	0	0	0	0
	EDA	0	51.38	122.23	141.27	168.24
	PZ	3794.6	3713.2	3747.5	3790.0	3795.3
	HEP	0	0	0	0	0
	1-MPZ	0	25.76	20.60	19.97	17.97
	1-EPZ	0	0	0	0	0
	1,4-DMPZ	0	0	0	0	0
	AEP	0	0	1.75	1.60	3.33

Table D.65: Tabulated Experimental Data for TE65 (8 m PZ, 0.1 mole HCO_3^- per mole alkalinity initially, 175 °C)

Time (wk)		0	1.0	2.1	4.0	5.9	5.9	5.9	7.9	10.0
Original Samples (mmol/kg)	Gly	0.19	0.27	0.36	0.35	0.23	0.24	0.27	0.25	0.24
	Ace	0	0	0	0.08	0.11	0.12	0.12	0.31	0.22
	Form	0.01	0.79	0.35	3.79	5.84	5.98	6.38	12.66	11.13
	Oxa	0	0	0.02	0.02	0.01	0.02	0.02	0.02	0.01
	Sulf	0.61	0.49	0.43	0.39	0.31	0.27	0.30	0.21	0.28
	Cl^-	0.01	0.01	0.02	0.02	0.01	0.02	0.02	0.03	0.03
	NH_4^+	1.31	1.68	1.45	4.01	7.04	7.17	6.95	29.86	16.90
	FPZ	0	0	0	0.62	1.04	0.98	0.94	1.88	1.33
	EDA	0	1.40	0.89	5.68	8.98	8.90	9.50	17.64	15.19
	PZ	3962.2	3971.2	3988.1	3955.5	3933.3	3919.8	3914.8	3849.5	3900.6
	HEP	0	0	0	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0	0	0	0
	1-EPZ	0	0	0	0.14	0.21	0.18	0.20	1.96	0.51
	1,4-DMPZ	0	0	0	0	0	0	0	0	0
	AEP	0	0.12	0.09	0.67	1.20	1.20	1.11	4.55	2.73
	CO_2	NT	NT	NT	NT	NT	NT	NT	NT	NT
	Alk	NT	NT	NT	NT	NT	NT	NT	NT	NT

Table D.66: Tabulated Experimental Data for TE66 (8 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 175 °C, 200 mM formate)

	Time (wk)	0	0.2	0.3	0.4	0.6	0.7
Original Samples (mmol/kg)	Gly	0.09	0.11	0.13	0.13	0.10	0.12
	Ace	0.14	0.14	0.15	0.17	0.17	0.21
	Form	153.64	50.12	54.22	51.10	52.00	52.83
	Oxa	0.02	0.01	0.01	0.01	0.01	0.02
	Sulf	0.07	0.14	0.12	0.16	0.14	0.15
	Cl ⁻	0.05	0.03	0.04	0.08	0.06	0.07
	NH ₄ ⁺	0.40	1.21	1.97	2.88	4.21	5.89
	FPZ	1.73	203.74	205.94	214.79	220.29	230.77
	EDA	0	3.03	4.09	4.82	6.26	7.95
	PZ	3578.1	3429.2	3473.7	3402.6	3399.8	3345.7
	HEP	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0
	1-EPZ	0	0.11	0.28	0.41	0.54	0.88
	1,4-DMPZ	0	0	0	0	0	0
	AEP	0	0.31	0.66	1.03	1.50	2.42
	CO ₂	NT	NT	NT	NT	NT	NT
	Alk	NT	NT	NT	NT	NT	NT
Hydrolyzed Samples (mmol/kg)	Gly	0.35	0.61	0.70	0.73	1.05	0.98
	Ace	0.25	0.25	0.25	0.30	0.31	0.40
	Form	160.79	169.16	164.95	172.93	175.62	183.62
	Oxa	0.02	0.02	0.03	0.03	0.03	0.03
	Sulf	0.06	0.13	0.12	0.30	0.08	0.16
	Cl ⁻	0.04	0.04	0.04	0.64	0.04	0.08
	NH ₄ ⁺	0	0	0	0	0	0
	FPZ	0	0	0	0	0	0
	EDA	0	3.21	4.50	5.73	8.89	9.41
	PZ	3669.1	3603.6	3541.4	3556.4	3474.4	3485.9
	HEP	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0
	1-EPZ	0	0.13	0.31	0.47	0.58	0.98
	1,4-DMPZ	0	0	0	0	0	0
	AEP	0	0.38	0.72	1.13	1.60	2.76

Table D.67: Tabulated Experimental Data for TE67 (8 m PZ, 0.3 mole CO₂ per mole alkalinity initially, 175 °C, 200 mM FPZ)

Time (wk)		0	0.2	0.3	0.4	0.6	0.7
Original Samples (mmol/kg)	Gly	0.13	0.11	0.13	0.12	0.10	0.11
	Ace	0.04	0.06	0.11	0.09	0.11	0.11
	Form	8.71	49.90	50.07	44.36	49.73	50.60
	Oxa	0.00	0.02	0.02	0.02	0.02	0.01
	Sulf	0.12	0.08	0.12	0.11	0.18	1.26
	Cl ⁻	0.08	0.03	0.04	0.06	0.10	0.11
	NH ₄ ⁺	0.60	1.01	2.87	3.51	4.52	4.90
	FPZ	276.11	232.87	240.58	238.46	251.89	256.17
	EDA	0	3.32	4.55	4.59	5.74	6.74
	PZ	3738.7	3727.9	3716.7	3600.7	3688.3	3671.5
	HEP	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0
	1-EPZ	0	0.10	0.27	0.34	0.43	0.61
	1,4-DMPZ	0	0	0	0	0	0
	AEP	0	0.30	0.89	0.98	1.34	1.98
	CO ₂	NT	NT	NT	NT	NT	NT
	Alk	NT	NT	NT	NT	NT	NT
Hydrolyzed Samples (mmol/kg)	Gly	1.40	0.43	0.60	0.73	0.90	0.99
	Ace	0.05	0.12	0.15	0.15	0.20	0.23
	Form	182.86	189.43	191.19	194.03	197.17	199.02
	Oxa	0	0.04	0.04	0.03	0.04	0.03
	Sulf	0.13	0.11	0.12	0.12	0.17	1.32
	Cl ⁻	0.03	0.05	0.12	0.12	0.10	0.12
	NH ₄ ⁺	0	0	0	0	0	0
	FPZ	0	0	0	0	0	0
	EDA	0.44	4.23	5.29	5.94	7.24	8.28
	PZ	3902.6	3976.9	3944.3	3997.8	3909.7	3874.3
	HEP	0	0	0	0	0	0
	1-MPZ	0	0	0	0	0	0
	1-EPZ	0	0	0	0.31	0.55	0.75
	1,4-DMPZ	0	0	0	0	0	0
	AEP	0	0.50	0.99	1.21	1.61	2.13

Appendix E – Tabulated Data from Oxidation Experiments

All tabulated experimental data that follows maintains the same format. Original sample data are the raw values from the experimental samples. The base hydrolyzed data is the post-NaOH treatment data where the difference between the two would represent amide concentrations. Data shown are not sulfate-adjusted. Outlier data have not been removed. Abbreviations are as follows:

Fe^{2+} , iron added as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
 Cu^{2+} , copper added as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
 Cr^{3+} , chromium added as $\text{Cr}_2(\text{SO}_4)_3 \cdot 3.8\text{H}_2\text{O}$ or $\text{CrK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$
 Ni^{2+} , nickel added as $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$
 V^{4+} , vanadium added as NaVO_3
A, Inhibitor A
B, Inhibitor B
OOR, Original Oxidation Reactor
TOR, Teflon Oxidation Reactor
Gly, Glycolate (Anion IC)
Ace, Acetate (Anion IC)

Form, Formate (Anion IC)
NO₂⁻, Nitrite (Anion IC)
Oxa, Oxalate (Anion IC)
NO₃⁻, Nitrate (Anion IC)
Sulf, Sulfate (Anion IC)
Cl⁻, Chloride (Anion IC)
NH₄⁺, Ammonium (Cation IC)
FPZ, N-Formyl PZ (Cation IC)
EDA, Ethylenediamine (Cation IC)
PZ, Piperazine (Cation IC)
CO₂ (TIC), Carbon Dioxide
SD_{CO2}, standard deviation of three CO₂ measurements
Alk, total alkalinity (Acid Titration)
SD_{Alk}, standard deviation of two total alkalinity titrations
NT, value not tested
NA, not applicable; when only one measurement was made, calculation of standard deviation was not possible

Table E.1: Tabulated Experimental Data for OE1 (10 m PZ, 2 kPa CO₂, 98 kPa O₂, 55 °C, 0.27 mM Fe²⁺, 0.65 mM Cr³⁺, 0.26 mM Ni²⁺, OOR)

		10 m PZ + Fe + Cr + Ni									
Time (hr)		0	23.5	74.0	120.5	171.5	271.8	315.8	360.8	461.0	603.5
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0	0
	Ace	0	0	0	0	0	0	0	0	0	0
	Form	0.07	0.21	1.38	1.82	0.62	1.15	1.26	1.61	1.99	2.96
	NO ₂ ⁻	0	0	0	0	0	0	0	0	0	0
	Oxa	0.13	0.02	0	0.02	0.00	0.09	0.05	0.05	0.06	0.08
	NO ₃ ⁻	0	0	0	0	0	0	0	0.22	0.26	0.23
	EDA	0	0	0	0	0	0	0	0	0	0
	PZ	4915.2	4959.9	4846.4	4894.9	4779.8	4972.4	4515.0	4503.5	4316.4	4271.0
	CO ₂	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
	Alk	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
Hydrolyzed Samples (mmol/kg)	Gly	0	0.05	0	0.11	0.10	0.09	0.08	0.03	0.08	0.11
	Ace	0	0.09	0.11	0.11	0.13	0.16	0.13	0.12	0.17	0.20
	Form	0.42	0.92	2.24	3.26	3.76	4.09	4.32	4.63	6.40	7.28
	NO ₂ ⁻	0	0	0	0	0	0.10	0.04	0.06	0.06	0.11
	Oxa	0	0	0.08	0.06	0.09	0.08	0.06	0.11	0.15	0.22
	NO ₃ ⁻	0	0	0	0	0.12	0.08	0.07	0.10	0.18	0.10
	EDA	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
	PZ	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT

Table E.2: Tabulated Experimental Data for OE2 (10 m PZ, 2 kPa CO₂, 98 kPa O₂, 55 °C, 3.94 mM Cu²⁺, OOR)

		10 m PZ + Cu											
Time (hr)		0.0	22.0	68.0	118.0	166.5	210.0	257.8	309.0	352.5	400.5	451.5	495.0
Original Samples (mmol/kg)	Gly	0.26	0	0	0	0	0	0	0	0	0	0.04	0.05
	Ace	0	0.38	0.69	2.11	2.20	1.21	1.24	1.25	1.27	0.90	1.05	1.01
	Form	0.17	3.56	14.76	30.02	41.14	48.46	56.79	60.89	62.79	63.35	65.36	68.25
	NO ₂ ⁻	0	0.46	1.83	3.33	3.28	3.63	3.01	2.96	2.85	2.93	2.88	2.80
	Oxa	0	0.19	0.59	1.62	2.66	3.80	5.00	5.68	5.95	7.14	8.33	9.49
	NO ₃ ⁻	0	0.61	1.12	0	0	2.10	2.25	2.23	2.20	2.54	2.36	2.00
	EDA	19.71	98.10	144.18	167.64	191.81	200.29	222.90	223.04	220.76	221.16	233.92	232.77
	PZ	4480.5	4207.3	3883.4	3493.4	3314.7	3225.9	3146.4	3120.5	3076.4	3026.9	3023.9	2983.2
	CO ₂	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT	NT
	Alk	4496.1	4274.5	4058.3	3822.1	3684.8	3543.6	3548.7	3461.5	3367.3	3330.5	3315.7	3294.3
Hydrolyzed Samples (mmol/kg)	SD _{Alk}	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Gly	0.40	0.59	0.72	0.98	0.28	0.41	0.53	0.32	0.59	0.52	0.39	0.41
	Ace	0.14	0.41	1.08	1.65	0.96	1.32	1.28	1.36	2.32	2.53	2.40	2.44
	Form	5.17	43.17	93.97	126.65	143.78	157.24	174.20	174.26	164.84	171.42	178.89	184.68
	NO ₂ ⁻	0	0.19	1.28	2.00	2.90	2.83	2.94	2.65	2.89	2.91	1.73	1.67
	Oxa	0	4.66	15.86	26.31	34.39	41.15	49.57	46.93	45.22	50.10	24.29	25.77
	NO ₃ ⁻	0	0.47	0.52	1.71	2.00	2.32	1.67	1.95	2.19	2.22	1.24	1.35
	EDA	NT	NT	NT	NT	NT	NT	NT	NT	261.79	296.64	NT	309.45
	PZ	NT	NT	NT	NT	NT	NT	NT	NT	3199.7	3489.8	NT	3212.7

Table E.3: Tabulated Experimental Data for OE3 (8 m PZ, 2 kPa CO₂, 98 kPa O₂, 55 °C, 0.10 mM Fe²⁺, 0.10 mM V⁴⁺, OOR)

		8 m PZ + Fe + V								
Time (hr)		0	48.0	92.5	143.5	193.5	241.0	286.0	333.0	381.0
Original Samples (mmol/kg)	Gly	0	0	0.01	0.02	0.02	0.03	0.03	0.04	0.07
	Ace	0	0.01	0	0.01	0.03	0.03	0.01	0.01	0.13
	Form	0.05	0.26	0.40	0.64	1.01	1.46	1.79	2.12	5.05
	NO ₂ ⁻	0	0.04	0.09	0.12	0.21	0.30	0.36	0.44	0.65
	Oxa	0	0.02	0.01	0.02	0.04	0.03	0.04	0.05	0.07
	NO ₃ ⁻	0	0.17	0.28	0.41	0.45	0.49	0.58	0.64	0.99
	Sulf	0.34	0.36	0.28	0.41	0.40	0.48	0.49	0.34	8.57
	EDA	0	0	0	0	0	0	0	0	0
	PZ	4371.5	4481.6	4472.3	4403.3	4380.3	4294.4	4455.2	4106.9	4374.1
	CO ₂	2563.4	NT	2291.9	NT	2050.5	NT	1886.8	NT	1752.6
	SD _{CO2}	22.72	NT	48.32	NT	47.19	NT	30.44	NT	12.86
	Alk	4157.5	4338.3	4262.2	4182.6	4185.8	4126.1	4075.2	4019.7	3963.8
	SD _{Alk}	8.94	51.58	12.66	5.47	12.74	1.42	3.42	9.86	14.95
Hydrolyzed Samples (mmol/kg)	Gly	0.11	0.07	0.07	0.08	0.13	0.18	0.14	0.18	0.23
	Ace	0.10	0.08	0.13	0.09	0.12	0.57	0.16	0.18	0.62
	Form	0.33	1.02	1.87	2.44	3.50	6.33	4.99	6.32	10.54
	NO ₂ ⁻	0	0.03	0.09	0.13	0.14	0.40	0.36	0.44	0.70
	Oxa	0.02	0.04	0.05	0.07	0.04	0.14	0.15	0.18	0.25
	NO ₃ ⁻	0	0.11	0.30	0.39	0.27	0.60	0.59	0.66	0.95
	Sulf	0.39	0.37	0.30	0.39	0.24	0.54	0.43	0.41	0.55
	EDA	0	0	0	0	0	0	0	0	0
	PZ	4432.2	4613.6	4415.5	4370.7	4347.3	4241.5	4209.1	4039.8	4323.9

Table E.4: Tabulated Experimental Data for OE4 (8 m PZ, 2 kPa CO₂, 98 kPa O₂, 55 °C, 0.1 mM Fe²⁺, 5.02 mM Cu²⁺, 100.15 mM Inhibitor A, OOR)

		8 m PZ + Fe + Cu + A														
	Time (hr)	0	50.8	96.0	146.5	191.0	242.5	290.5	340.0	410.5	456.5	504.5	552.0	598.5	670.3	742.3
Original Samples (mmol/kg)	Gly	0.07	0.01	0.01	0.00	0.02	0.03	0.03	0.03	0.04	0.04	0.03	0.01	0.02	0.05	0.01
	Ace	0.02	0.09	0.08	0.09	0.04	0.03	0.11	0.10	0.07	0.10	0.06	0.10	0.06	0.14	0.11
	Form	0.11	1.17	1.79	2.35	2.86	3.23	3.88	4.30	4.89	5.23	5.61	6.49	7.05	7.71	7.91
	NO ₂ ⁻	0	0.26	0.32	0.30	0.39	0.42	0.36	0.37	0.39	0.35	0.37	0.48	0.52	0.51	0.43
	Oxa	0	0.01	0.02	0.03	0.05	0.07	0.10	0.12	0.15	0.15	0.19	0.26	0.30	0.34	0.34
	NO ₃ ⁻	0.04	0.10	0.16	0.25	0.24	0.19	0.33	0.35	0.36	0.32	0.36	0.54	0.67	0.58	0.41
	Sulf	8.13	8.05	8.09	7.79	8.07	7.93	8.16	8.08	8.41	7.74	7.75	11.05	11.14	10.39	7.35
	EDA	0	3.62	7.36	4.80	7.33	3.24	4.60	6.88	7.36	4.61	9.20	0	0	0	6.68
	PZ	4378.2	4347.8	4240.8	4109.1	4089.9	4070.2	4072.2	4050.1	3977.7	3926.8	3906.6	3869.0	3777.1	3660.9	3744.1
	CO ₂	2437.3	2213.5	2089.1	2049.9	1914.2	1828.9	1768.3	1711.3	1616.3	1627.1	1547.8	1462.6	1299.1	1352.3	1347.5
	SD _{CO2}	41.71	40.28	36.34	31.23	33.65	20.65	51.30	45.35	10.74	27.43	27.54	24.20	8.25	4.98	2.79
	Alk	4002.5	3999.9	3983.1	3937.2	3925.4	3896.6	3843.2	3833.7	3833.6	3809.3	3746.5	3713.0	3628.2	3532.1	3589.2
	SD _{Alk}	0.82	0.14	0.23	10.50	0.05	2.93	6.00	5.26	5.35	0.33	0.38	1.00	8.54	105.49	44.35
Hydrolyzed Samples (mmol/kg)	Gly	0.35	0.09	0.08	0.11	0.15	0.15	0.12	0.11	0	0.06	0.04	0.06	0.10	0.06	0.03
	Ace	0.52	0.30	0.30	0.46	0.43	1.15	0.47	0.45	0	0.68	0.44	0.50	0.42	0.53	0.63
	Form	0.71	5.07	6.18	7.67	8.26	9.98	9.53	11.38	14.56	15.17	13.50	15.00	15.90	16.13	20.48
	NO ₂ ⁻	0.05	0.40	0.46	0.41	0.42	0.43	0.52	0.51	0.49	0.43	0.38	0.49	0.55	0.43	0.51
	Oxa	0.01	0.15	0.25	0.61	0.44	0.40	0.63	0.70	0.77	0.85	0.70	0.84	1.01	0.93	1.27
	NO ₃ ⁻	0	0.19	0.19	0.24	0.27	0.55	0.23	0.25	0.39	0.38	0.36	0.55	0.40	0.39	0.50
	Sulf	8.15	8.20	8.32	8.15	8.08	8.19	8.66	9.27	9.40	9.04	7.64	10.13	12.07	7.46	9.05
	EDA	0	3.52	6.81	3.16	3.65	0	0	0	8.07	9.02	2.82	0	0	2.97	4.33
	PZ	4369.8	4155.5	4273.8	4151.7	4062.5	3987.1	3981.7	4026.0	2708.3	2590.2	3859.7	3840.0	3742.5	3442.0	2415.6

Table E.5: Tabulated Experimental Data for OE5/OE5B (8 m PZ, 2 kPa CO₂, 98 kPa O₂, 55 °C, 1.03 mM Fe²⁺, OOR)

		8 m PZ + Fe							
		Time (hr)	0	20.0	47.5	70.3	70.3	117.8	162.5
Original Samples (mmol/kg)	Gly		0.045	0.010	0.021	0.077	0.073	0.116	0.107
	Ace		0.145	0.274	0.174	0.052	0.073	0.147	0.054
	Form		0.353	0.480	0.288	0.496	0.369	0.555	0.658
	NO ₂ ⁻		0	0.044	0.024	0.027	0	0.010	0.012
	Oxa		0.077	0.068	0.051	0	0	0	0
	NO ₃ ⁻		0.062	0.026	0.023	0.062	0	0	0
	Sulf		2.924	3.009	3.006	2.988	0.966	0.969	0.940
	Cl ⁻		0.266	0.123	0.153	0.154	0.031	0.040	0.044
	EDA		0	0	0	4.759	0	0	0
	PZ		4243.0	4038.6	4061.9	4066.4	4159.4	3973.1	3924.8
	CO ₂		2520.0	2457.6	2512.9	2502.0	2477.0	2344.2	2296.9
	SD _{CO2}		23.857	12.908	24.298	14.499	8.673	9.545	6.324
	Alk		4083.6	3940.2	3888.4	3832.1	3812.4	3605.3	3575.9
	SD _{Alk}		28.186	8.822	7.624	13.337	19.238	11.016	14.935
Hydrolyzed Samples (mmol/kg)	Gly		0.104	0.243	0.612	0.564	0	0	0
	Ace		0	0	0	0.645	0.065	0.012	0
	Form		0.399	0.553	0.975	2.393	1.461	1.798	2.132
	NO ₂ ⁻		0.033	0.015	0.016	0.055	0	0.018	0.019
	Oxa		0.033	0.034	0.004	0.053	0.041	0.043	0.057
	NO ₃ ⁻		0.011	0.024	0.024	0.091	0.190	0.010	0.014
	Sulf		1.784	1.649	1.630	1.991	1.003	0.952	1.062
	Cl ⁻		0.198	0.067	0.042	0.598	0.044	0.055	0.076
	EDA		0	0	0	0	0	0	0
	PZ		4211.8	4583.0	4754.8	4030.2	4030.5	4342.1	3934.4

Reactor contents removed for foaming test, and then restarted.

Table E.6: Tabulated Experimental Data for OE6/OE6B (8 m PZ, 2 kPa CO₂, 98 kPa O₂, 55 °C, 1.03 mM Fe²⁺, 100.36 mM Inhibitor A, OOR)

		8 m PZ + Fe + A							
Time (hr)		0	20.0	47.5	70.3	70.3	117.8	162.5	
Original Samples (mmol/kg)	Gly	0.06	0.04	0.04	0.02	0.03	0	0	Reactor contents removed for foaming test, and then restarted.
	Ace	0.24	0.02	0.02	0.03	0.17	0.02	0	
	Form	0.25	0.37	0.34	0.53	0.38	0.53	0.76	
	NO ₂ ⁻	0.01	0.01	0.01	0.01	0.05	0.02	0.04	
	Oxa	0.01	0.01	0.03	0	0.02	0.01	0.04	
	NO ₃ ⁻	0.02	0.20	0.03	0	0	0	0.03	
	Sulf	1.59	1.74	1.65	1.76	1.64	1.41	1.67	
	Cl ⁻	0.17	0.43	0.12	0.04	0.29	0.08	0.17	
	EDA	0	0	0	0	0	0	0	
	PZ	4251.8	4288.3	4342.4	4333.9	4360.5	4232.2	4443.5	
	CO ₂	2481.5	2267.4	2258.5	2231.0	2227.3	2514.7	2687.4	
	SD _{CO2}	21.15	5.14	8.83	13.39	4.67	6.89	30.69	
	Alk	4049.3	4121.2	4153.1	4169.8	4178.1	4023.1	4307.7	
	SD _{Alk}	21.38	22.20	6.85	11.90	11.38	5.07	7.33	
Hydrolyzed Samples (mmol/kg)	Gly	0.21	0.08	0.07	0.20	0	0	0	
	Ace	0	0	0	0	0	0	0.01	
	Form	0.33	0.55	0.98	1.29	0.79	1.07	1.39	
	NO ₂ ⁻	0	0.01	0.01	0.02	0.03	0.03	0.03	
	Oxa	0	0	0.03	0.12	0.03	0.03	0.04	
	NO ₃ ⁻	0	0	0	0	0	0.14	0	
	Sulf	1.54	1.46	1.51	1.81	2.05	1.83	1.88	
	Cl ⁻	0.06	0	0	0.26	0.48	0.17	0.20	
	EDA	0	0	0	0	0	0	0	
	PZ	4542.0	4808.3	4912.7	4260.2	4406.9	4297.5	4496.4	

Table E.7: Tabulated Experimental Data for OE7 (8 m PZ, 2 kPa CO₂, 98 kPa O₂, 55 °C, 1.00 mM Fe²⁺, 20.82 mM Inhibitor B, OOR)

		8 m PZ + Fe + Inh B				
Time (hr)		0.0	19.5	71.3	119.0	163.8
Original Samples (mmol/kg)	Gly	0	0.01	0.02	0.01	0.02
	Ace	0.01	0.01	0.00	0.03	0.03
	Form	0.15	0.20	0.23	0.20	0.24
	NO ₂ ⁻	0	0	0	0	0
	Oxa	0	0	0	0	0
	NO ₃ ⁻	0	0	0.01	0.01	0.01
	Sulf	16.95	18.50	17.87	17.98	18.23
	Cl ⁻	0.04	0.10	0.07	0.14	0.05
	EDA	0	0	0	0	0
	PZ	4396.3	4212.2	4145.3	4152.1	4217.8
	CO ₂	2709.1	2710.6	2665.7	2686.2	2667.3
	SD _{CO2}	5.60	11.76	24.49	25.68	9.48
	Alk	4082.2	4042.3	3978.5	3998.5	4020.8
	SD _{Alk}	21.35	0.15	0.96	11.94	3.42
Hydrolyzed Samples (mmol/kg)	Gly	0.24	0	0	0.04	0.08
	Ace	0.01	0.02	0.01	0	0
	Form	0.47	0.65	0.50	0.55	0.61
	NO ₂ ⁻	0.02	0.06	0.00	0	0
	Oxa	0	0	0	0	0
	NO ₃ ⁻	0	0	0.01	0	0
	Sulf	16.53	18.94	17.92	17.95	18.25
	Cl ⁻	0.06	0.50	0.04	0.06	0.03
	EDA	0	0	0	0	0
	PZ	4516.2	4275.7	4159.6	4135.6	4177.8

Table E.8: Tabulated Experimental Data for OE8 (8 m PZ, 2 kPa CO₂, 98 kPa O₂, 55 °C, 1.0 mM Fe²⁺, 29.89 mM Inhibitor C, OOR)

		8 m PZ + Fe + Inh C				
Time (hr)		0	19.5	71.3	119.0	163.8
Original Samples (mmol/kg)	Gly	0.02	0	0	0	0
	Ace	0.06	0.10	0.04	0	0
	Form	0.25	1.83	3.95	6.37	8.10
	NO ₂ ⁻	0	0.05	0.04	0.09	0.09
	Oxa	0	0	0.08	0.29	0.32
	NO ₃ ⁻	0	0.04	0	0	0
	Sulf	1.37	1.26	1.04	1.15	1.16
	Cl ⁻	0.13	0.11	0.26	0.42	0.16
	EDA	0	11.17	30.67	50.90	51.76
	PZ	4231.7	4235.0	4065.2	4097.9	3974.9
	CO ₂	2680.9	2582.8	2497.5	2517.5	2547.9
	SD _{CO2}	34.76	33.03	36.82	3.06	28.56
	Alk	4027.4	4012.6	3944.3	3935.9	3927.3
SD _{Alk}	1.93	3.97	3.07	3.63	19.35	
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0
	Ace	0	0	0	0	0.07
	Form	0.68	3.46	10.28	15.77	18.44
	NO ₂ ⁻	0.06	0.05	0.07	0.11	0.10
	Oxa	0.02	0.12	1.35	2.70	4.36
	NO ₃ ⁻	0.12	0	0	0.08	0
	Sulf	1.43	1.18	1.20	1.11	1.18
	Cl ⁻	0.26	0.23	0.24	0.33	0.32
	EDA	0	15.64	33.08	50.30	70.50
	PZ	4269.9	4382.0	4058.6	4117.2	4041.0

Table E.9: Tabulated Experimental Data for OE9 (8 m PZ, 2 kPa CO₂, 98 kPa N₂, OOR)

		8 m PZ + N ₂							
Time (hr)		0	48.0	96.8	145.8	192.3	240.8	287.8	336.3
Original Samples (mmol/kg)	Gly	0.38	0.42	0.43	0.25	0.40	1.46	0.37	0.50
	Ace	0	0	0	0	0	0	1.92	0
	Form	0.51	1.28	0.60	0.78	1.26	0.83	1.73	1.07
	NO ₂ ⁻	0	0	0	0	0	0	0	0
	Oxa	0	0	0	0	0	0	0	0.02
	NO ₃ ⁻	0	0	0	0	0	0	0	0
	Sulf	0.44	0.41	0.41	0.42	0.41	0.41	0.43	0.40
	Cl ⁻	0.09	0.05	0.08	0.09	0.07	0.08	0.07	0.10
	EDA	0	0	0	0	0	0	0	0
	PZ	4368.7	4271.0	4199.9	4138.0	4237.2	4195.1	4081.3	4210.7
	CO ₂	2733.8	2671.3	2597.3	2605.5	2696.1	2599.1	2551.0	2665.3
	SD _{CO2}	5.04	9.94	20.02	1.49	5.22	11.40	4.70	11.79
	Alk	4108.7	3987.4	3916.6	3869.7	3989.5	3856.4	3753.2	3915.5
	SD _{Alk}	5.32	9.67	3.13	4.25	5.04	0.35	3.99	4.54
Hydrolyzed Samples (mmol/kg)	Gly	0.18	0.18	0.18	0	0	0.30	0	0
	Ace	0	1.37	0	0	0	0	0	0
	Form	1.82	2.18	1.86	1.82	2.65	2.32	2.78	2.54
	NO ₂ ⁻	0	0	0	0	0	0	0	0
	Oxa	0	0	0	0	0.01	0.01	0.01	0.03
	NO ₃ ⁻	0	0	0	0	0	0	0	0
	Sulf	0.28	0.27	0.20	0.19	0.26	0.29	0.55	0.36
	Cl ⁻	0.08	0.07	0.04	0.10	0.06	0.07	0.09	0.26
	EDA	0	0	0	0	0	0	0	0
	PZ	4402.0	4317.1	4176.2	4094.1	4234.8	4188.8	4069.9	4142.3

Table E.10: Tabulated Experimental Data for OE10 (8 m PZ, 2 kPa CO₂, 98 kPa N₂, 55 °C, 19.77 mM K₂SO₄, OOR)

		8 m PZ + N ₂							
Time (hr)		0	46.0	94.3	142.0	191.0	239.8	293.8	336.3
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0
	Ace	0	0	0	0	0	0	0	0
	Form	0.10	0.33	0.47	0.62	0.68	0.69	1.06	1.07
	NO ₂ ⁻	0	0	0	0	0	0	0	0
	Oxa	0	0	0	0	0	0	0	0
	NO ₃ ⁻	0	0	0	0	0	0.01	0.01	0.03
	Sulf	16.99	16.73	16.76	15.83	16.18	15.28	18.93	19.33
	Cl ⁻	0.03	0.06	0.04	0.03	0.06	0.03	0.04	0.03
	EDA	0	0	0	0	0.71	1.55	3.24	3.60
	PZ	4343.5	4336.1	4293.2	4319.6	4288.8	4252.4	4750.2	4862.7
	CO ₂	2639.8	2733.5	2681.5	2645.5	2638.6	2612.7	2628.0	2877.1
	SD _{CO2}	6.06	6.38	40.69	6.44	6.15	10.28	17.85	2.76
	Alk	4100.3	4056.1	4040.3	4038.3	4090.5	4013.3	4522.1	4611.1
	SD _{Alk}	40.31	11.31	6.36	0.00	476.59	0.71	2.83	45.25
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0
	Ace	0	0	0	0	0	0	0	0
	Form	0.38	1.43	1.80	2.35	2.72	3.23	4.55	4.67
	NO ₂ ⁻	0	0	0.01	0.02	0.03	0.07	0.09	0.10
	Oxa	0	0.04	0.06	0.08	0.09	0.08	0.13	0.14
	NO ₃ ⁻	0	0.02	0.05	0.02	0.03	0.04	0.09	0.07
	Sulf	16.69	16.66	17.67	17.48	17.52	17.53	20.14	20.47
	Cl ⁻	0.03	0.05	0.08	0.05	0.08	0.06	0.40	0.09
	EDA	0	0	0	0	0	0.93	2.59	3.06
	PZ	4371.4	4344.1	4270.0	4335.0	4277.2	4276.3	4767.5	4852.8

Table E.11: Tabulated Experimental Data for OE11 (8 m PZ, 2 kPa CO₂, 98 kPa O₂, 55 °C, 20.12 mM K₂SO₄, OOR)

		8 m PZ + O ₂							
Time (hr)		0	53.3	96.0	142.0	191.8	234.5	262.0	314.0
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0
	Ace	0	0.08	0	0	0	0	0	0
	Form	0.20	0.18	0.26	0.54	0.54	0.56	0.48	0.96
	NO ₂ ⁻	0.06	0.06	0.06	0.05	0.05	0.05	0.06	0.06
	Oxa	0.03	0	0	0	0	0.05	0	0
	NO ₃ ⁻	0.01	0.02	0.06	0.01	0	0.01	0.02	0.01
	Sulf	0.59	18.01	17.47	17.79	17.58	16.72	17.00	16.66
	Cl ⁻	0.09	0.02	0.02	0.03	0.02	0.02	0.02	0.03
	EDA	0	1.85	2.86	4.10	4.47	5.91	5.10	5.85
	PZ	4531.5	4442.4	4349.1	4323.8	4277.7	4261.6	4253.8	4238.7
	CO ₂	2582.9	2669.3	2658.6	2614.9	2576.7	2556.5	2567.6	2466.6
	SD _{CO2}	12.86	20.20	7.84	6.90	6.12	28.99	5.97	13.21
	Alk	4134.8	4114.4	4015.3	4035.8	4006.2	3957.4	3992.8	3883.0
	SD _{Alk}	19.80	9.19	28.28	44.55	10.61	19.09	8.49	14.85
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0
	Ace	0	0	0	0	0	0	0	0
	Form	0.31	0.88	1.21	1.44	3.23	2.20	1.62	2.40
	NO ₂ ⁻	0.04	0.05	0.05	0.05	0.21	0.07	0.06	0.06
	Oxa	0.03	0.01	0.02	0.03	0.05	0.05	0.03	0.09
	NO ₃ ⁻	0.03	0.01	0.01	0.02	0.06	0.02	0.02	0.02
	Sulf	0.41	16.85	16.97	15.87	18.16	17.54	17.25	16.97
	Cl ⁻	0.17	0.03	0.06	0.03	3.80	0.09	0.04	0.09
	EDA	3.26	2.27	10.57	5.49	294.65	4.78	3.50	14.17
	PZ	4464.2	4408.9	4340.8	4331.7	4303.4	4217.6	4232.4	4174.3

Table E.12: Tabulated Experimental Data for OE12 (8 m PZ, 2 kPa CO₂, 98 kPa O₂, 55 °C, 20.09 mM K₂SO₄, OOR)

		8 m PZ + O ₂						
Time (hr)		0	52.5	100.3	150.0	216.5	244.0	296.0
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0	0
	Ace	0	0	0	0	0	0	0
	Form	0.19	0.15	0.25	0.32	0.44	0.60	0.51
	NO ₂ ⁻	0	0	0	0	0	0	0
	Oxa	0	0	0	0	0.07	0.08	0.09
	NO ₃ ⁻	0	0	0	0	0	0	0
	Sulf	16.74	16.23	17.33	17.21	17.85	16.87	17.93
	Cl ⁻	0	0	0	0	0	0	0.22
	EDA	0	0	0	0	0	0	0
	PZ	4431.9	4404.6	4376.3	4312.8	4314.5	4169.6	4284.4
	CO ₂	2390.8	2564.8	2531.9	2563.8	2579.0	2434.0	2560.5
	SD _{CO2}	14.19	17.86	3.66	31.61	30.21	13.41	11.51
	Alk	4114.2	4097.8	4074.3	4055.8	4077.1	3863.9	4049.4
	SD _{Alk}	3.77	0.46	1.83	11.29	4.79	1.95	1.72
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0
	Ace	0	0	0	0	0	0	0
	Form	0.35	0.63	0.82	0.97	1.49	2.15	1.82
	NO ₂ ⁻	0	0	0	0	0	0	0
	Oxa	0	0.10	0.12	0.12	0.13	0.22	0.17
	NO ₃ ⁻	0	0	0	0	0	0	0
	Sulf	16.85	17.65	17.51	17.32	16.62	16.86	18.75
	Cl ⁻	0	0.55	0	0	0.07	0	4.55
	EDA	0	0	0	0	0	0	0
	PZ	4384.0	4368.8	4328.7	4324.4	4082.6	4159.4	4278.4

Table E.13: Tabulated Experimental Data for OE13 (8 m PZ, 2 kPa CO₂, 98 kPa O₂, 55 °C, 1.00 mM Fe²⁺, OOR)

		8 m PZ + Fe + Cu + A								
Time (hr)		0.3	40.3	99.0	164.8	238.0	310.0	380.5	454.0	523.0
Original Samples (mmol/kg)	Gly	0.66	0.63	0.59	0.58	0.56	0.56	0.72	0.52	0.52
	Ace	0.11	0.23	0.45	0.52	0.53	0.53	0.14	0.49	0.55
	Form	0.05	0.09	0.34	0.57	0.86	1.08	2.11	1.55	1.76
	NO ₂ ⁻	0	0	0.01	0.01	0.01	0.01	0.01	0.01	0.01
	Oxa	0.01	0.01	0.01	0.02	0.02	0.03	0.03	0.04	0.07
	NO ₃ ⁻	0	0.01	0.03	0.02	0.02	0.02	0.03	0.03	0.03
	Sulf	1.08	0.98	0.93	0.99	0.98	1.00	1.11	0.94	1.00
	Cl ⁻	0.02	0.06	0.08	0.08	0.10	0.15	0.04	0.11	0.04
	EDA	0	0	0	0	0	0	0	0	2.00
	PZ	3855.6	3749.4	3738.2	3617.1	3582.2	3602.7	3786.8	3548.6	3497.3
	CO ₂	2632.7	2558.7	2585.6	2536.3	2504.3	2513.7	2706.2	2409.5	2413.6
	SD _{CO2}	43.10	33.40	10.85	20.61	6.35	22.25	7.53	20.26	6.35
	Alk	4094.0	3979.5	3986.0	3838.7	3830.5	3784.4	4104.5	3710.0	3696.0
	SD _{Alk}	6.28	4.65	2.34	10.55	25.00	0.90	8.97	3.62	10.49
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0
	Ace	0.80	1.80	2.72	3.86	4.63	5.81	9.70	7.16	8.51
	Form	0	0	0	0	0	0	0	0	0
	NO ₂ ⁻	0.00	0	0	0.01	0.01	0.01	0.01	0.01	0.01
	Oxa	0.02	0.02	0.04	0.06	0.08	0.11	0.17	0.14	0.18
	NO ₃ ⁻	0.00	0.03	0.01	0.02	0.04	0.06	0.03	0.03	0.04
	Sulf	1.11	1.18	0.98	1.04	1.01	1.06	1.03	1.05	1.04
	Cl ⁻	0.27	0.26	0.15	0.20	0.17	0.20	0.11	0.13	0.34
	EDA	0	0	0	0	0	0	0	0	0
	PZ	3791.1	3635.6	3699.2	3580.6	3532.9	3570.9	3698.3	3438.7	3443.1

Table E.14: Tabulated Experimental Data for OE14 (8 m PZ, 2 kPa CO₂, 98 kPa O₂, 55 °C, 1.00 mM Fe²⁺, 100.11 mM Inhibitor A, OOR)

		8 m PZ + Fe + A						
Time (hr)		0.3	40.3	99.0	164.8	238.0	310.0	380.5
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0	0
	Ace	0	0.03	0.03	0.04	0.19	0.03	0.06
	Form	0.18	0.60	0.86	1.17	4.05	1.54	1.34
	NO ₂ ⁻	0	0	0	0	0.04	0	0
	Oxa	0	0	0	0.34	0.05	0.06	0.11
	NO ₃ ⁻	0	0	0	0	0.14	0	0
	Sulf	1.21	1.13	1.15	1.84	1.19	1.16	1.50
	Cl ⁻	0.03	0.44	0.04	0.03	0.04	0.02	0.02
	FPZ	0.52	1.67	2.56	3.75	5.28	4.38	3.42
	EDA	0	0	0	0	0	0	6.24
	PZ	3952.8	3894.2	4001.3	4055.5	4027.5	4014.0	3669.3
	CO ₂	2465.0	2531.8	2622.5	2674.1	2635.2	2662.3	2424.4
	SD _{CO2}	20.44	14.67	0.33	19.75	7.89	3.43	11.63
	Alk	4027.6	3982.6	4080.7	4121.2	4102.0	4099.3	3729.7
	SD _{Alk}	3.73	1.16	7.56	14.74	2.32	4.11	6.08
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0
	Ace	0	0.08	0.28	0.06	2.25	0.09	0.40
	Form	0.34	1.76	3.20	4.25	6.75	5.02	3.60
	NO ₂ ⁻	0	0	0	0	0.24	0	0
	Oxa	0.01	0.04	0.09	0.19	0	0.15	0.11
	NO ₃ ⁻	0	0	0	0	0	0	0
	Sulf	1.25	1.17	1.25	1.67	0.19	1.35	1.34
	Cl ⁻	0.14	0.50	0.11	0.07	0.06	0.05	0.07
	FPZ	0	0	0	0	0	0	0
	EDA	0	0	0	0	0	0	0
	PZ	3939.9	3902.4	4003.2	4079.9	4128.2	4135.9	3760.2

Table E.15: Tabulated Experimental Data for OE15 (8 m PZ, 2 kPa CO₂, 98 kPa O₂, 55 °C, 0.41 mM Fe²⁺, 0.10 mM Cr³⁺, 0.05 mM Ni²⁺, OOR)

		8 m PZ + Fe + Cr + Ni						
Time (hr)		0	70.0	142.3	213.8	284.0	358.0	426.5
Original Samples (mmol/kg)	Gly	0.52	0.48	0.54	0.54	0.55	0.55	0.56
	Ace	0	0	0.32	0.36	0.40	0.41	0.43
	Form	0	0	0.37	0.73	0.94	1.15	1.29
	NO ₂ ⁻	0.02	0.01	0.02	0.02	0.02	0.02	0.02
	Oxa	0.07	0.05	0.09	0.06	0.10	0.13	0.14
	NO ₃ ⁻	0	0.03	0.03	0.06	0.05	0.06	0.05
	Sulf	0.66	0.65	0.64	0.73	0.62	0.72	0.71
	Cl ⁻	0.16	0.12	0.04	0.24	0.13	0.07	0.06
	EDA	0	0.43	2.04	2.87	5.83	4.43	6.14
	PZ	4342.4	4330.6	4359.5	4322.4	4363.3	4408.8	4436.9
	CO ₂	2681.7	2766.5	2717.7	2714.2	2849.0	2838.4	2719.9
	SD _{CO2}	16.60	34.41	100.00	8.17	96.88	75.33	154.21
	Alk	4122.5	4069.4	4095.7	4085.7	4112.1	4172.6	4205.8
	SD _{Alk}	NA	NA	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	0.02	0.31	0.20	0.06	0.05	0.04	0.04
	Ace	0	0.03	0.07	0	0.11	0.12	0.14
	Form	0.14	0.71	1.92	2.93	3.67	4.24	4.81
	NO ₂ ⁻	0	0.01	0.02	0.02	0.02	0.02	0.02
	Oxa	0	0.04	0.08	0.14	0.18	0.27	0.30
	NO ₃ ⁻	0	0	0	0.04	0.05	0.06	0.06
	Sulf	0.64	0.70	0.63	0.74	0.77	0.79	0.75
	Cl ⁻	0.08	0.09	0.13	0.11	0.15	0.11	0.09
	EDA	0	1.12	2.65	3.19	3.82	4.61	5.55
	PZ	4328.8	4261.3	4373.5	4318.4	4315.5	4352.1	4411.8

Table E.16: Tabulated Experimental Data for OE16 (8 m PZ, 2 kPa CO₂, 98 kPa O₂, 55 °C, 0.40 mM Fe²⁺, 0.10 mM Cr³⁺, 0.05 mM Ni²⁺, 10.06 mM Inhibitor A, OOR)

		8 m PZ + Fe + Cr + Ni + A						
Time (hr)		0	70.0	142.3	213.8	284.0	358.0	426.5
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0	0
	Ace	0.06	0.34	0.09	0.08	0.10	0.11	0.10
	Form	0.06	0.36	0.23	0.35	0.47	0.49	0.50
	NO ₂ ⁻	0	0.01	0.01	0.01	0.02	0.02	0.02
	Oxa	0	0.02	0.02	0.03	0.03	0.04	0.04
	NO ₃ ⁻	0	0	0.02	0.02	0.02	0.03	0.02
	Sulf	0.56	0.39	0.62	0.62	0.62	0.63	0.62
	Cl ⁻	0.16	0.03	0.09	0.17	0.15	0.28	0.14
	EDA	0	0	0	0	0	0	0
	PZ	4398.8	4133.6	4200.2	4036.6	4176.5	4247.6	4299.9
	CO ₂	2603.3	2682.6	2632.8	2592.1	2598.0	2664.4	2573.8
	SD _{CO2}	57.60	120.35	14.52	14.65	18.89	61.48	199.56
	Alk	4137.1	3959.3	3928.0	3919.2	3919.5	3983.3	4036.4
	SD _{Alk}	2.46	2.56	3.94	4.42	4.26	13.84	1.58
Hydrolyzed Samples (mmol/kg)	Gly	0	0.01	0.01	0.02	0.02	0.03	0.03
	Ace	0.05	0.05	0.05	0.08	0.04	0.04	0.06
	Form	0.11	0.38	0.62	0.77	0.93	1.03	1.34
	NO ₂ ⁻	0	0.01	0.01	0.02	0.02	0.02	0.02
	Oxa	0	0.04	0.05	0.07	0.07	0.08	0.09
	NO ₃ ⁻	0	0.03	0.02	0.03	0.04	0.03	0.03
	Sulf	0.76	0.73	0.73	0.75	0.73	0.73	0.83
	Cl ⁻	0.11	0.18	0.17	0.26	0.17	0.16	0.16
	EDA	0	0	0	0	0	0	0
	PZ	4374.9	4220.5	4186.7	4196.4	4185.0	3772.1	3907.4

Table E.17: Tabulated Experimental Data for OE17 (8 m PZ, 2 kPa CO₂, 98 kPa O₂, 55 °C, 1.0 mM Fe²⁺, TOR)

		8 m PZ + Fe (1 st TOR)						
Time (hr)		0	65.3	144.3	220.5	281.3	358.0	424.3
Original Samples (mmol/kg)	Gly	0.11	0.09	0.16	0.12	0.12	0.11	0.12
	Ace	0.10	0.11	0.18	0.18	0.16	0.33	0.17
	Form	0.39	0.58	0.85	1.04	1.16	1.42	1.43
	NO ₂ ⁻	0	0	0	0	0	0.00	0.01
	Oxa	0.19	0.09	0.06	0.06	0.07	0.05	0.06
	NO ₃ ⁻	0	0	0.03	0.13	0.05	0.04	0.08
	Sulf	5.73	5.70	5.68	5.67	5.55	5.58	5.63
	Cl ⁻	0.28	0.26	0.24	0.16	0.09	0.30	0.10
	EDA	0	0	0	2.54	4.52	5.97	8.64
	PZ	4857.3	3174.3	4207.0	4135.5	4146.5	4116.7	4105.7
	CO ₂	2658.9	2614.9	2598.7	2612.0	2562.1	2581.8	2604.2
	SD _{CO2}	6.19	27.06	33.04	18.72	22.04	35.07	13.10
	Alk	4070.7	4021.9	3993.6	3934.6	3911.6	3962.4	4006.3
	SD _{Alk}	33.09	1.72	8.92	3.95	13.48	20.98	12.06
Hydrolyzed Samples (mmol/kg)	Gly	0.53	0.61	1.46	0.32	4.20	0.13	0.14
	Ace	0.09	0.15	0.86	0.12	0.34	0.16	0.14
	Form	0.62	1.79	8.90	2.77	4.36	3.30	3.44
	NO ₂ ⁻	0.00	0.08	0.08	0.06	0.03	0.02	0.07
	Oxa	0.06	0.07	0.12	0.16	0.14	0.15	0.16
	NO ₃ ⁻	0.03	0.02	0.09	0.08	0.09	0.06	0.21
	Sulf	5.66	5.71	5.82	5.55	5.56	5.58	5.64
	Cl ⁻	0.30	0.33	0.13	0.09	0.11	0.47	0.19
	EDA	0	0	4.18	5.63	7.25	6.66	7.88
	PZ	4256.6	4211.9	4044.2	4117.5	3965.7	4136.8	4217.3

Table E.18: Tabulated Experimental Data for OE18 (8 m PZ, 2 kPa CO₂, 98 kPa O₂, 55 °C, 0.40 mM Fe²⁺, 0.10 mM Cr³⁺, 0.05 mM Ni²⁺, TOR)

		8 m PZ + Fe + Cr + Ni								
Time (hr)		0	71.3	152.3	223.5	291.0	368.0	437.3	487.8	575.5
Original Samples (mmol/kg)	Gly	0	0.03	0.05	0.04	0.08	0.10	0.11	0.10	0.10
	Ace	0	0.17	0	0	0.06	0.09	0.49	0.38	0.10
	Form	0.53	0.39	1.04	1.24	1.77	1.89	2.42	2.82	2.07
	NO ₂ ⁻	0	0	0	0	0	0	0	0	0
	Oxa	0.05	0.04	0.03	0.04	0.04	0.04	0.04	0.05	0.04
	NO ₃ ⁻	0	0	0	0	0	0	0	0	0
	Sulf	4.35	3.42	4.83	4.80	4.73	4.79	4.58	4.15	4.64
	Cl ⁻	0.07	0.06	0.10	0.16	0.15	0.14	0.07	0.54	0.07
	EDA	0	0	0	0	0	0	0	0	0
	PZ	4255.1	4280.1	4263.5	4315.0	4243.9	4213.3	4390.4	4294.8	4189.3
	CO ₂	3140.6	3187.8	3186.5	3181.4	3140.5	3018.6	2955.6	2606.6	2844.3
	SD _{CO2}	976.81	143.15	765.20	750.81	170.68	137.53	126.69	741.42	165.79
	Alk	4131.6	4180.6	4172.8	4202.3	4201.0	4158.4	4296.8	4179.0	4037.1
	SD _{Alk}	12.75	26.93	25.92	18.49	0.56	7.99	49.96	68.98	19.39
Hydrolyzed Samples (mmol/kg)	Gly	0.05	0.25	0.09	0.06	0.06	0.06	0.06	0.08	0.04
	Ace	0.12	0.14	0.08	0.43	0.14	0.19	0.13	0.16	0.11
	Form	0.47	1.36	2.46	3.56	3.55	3.66	3.63	4.02	4.28
	NO ₂ ⁻	0	0	0	0	0	0	0	0	0
	Oxa	0	0	0	0	0	0	0	0	0
	NO ₃ ⁻	0	0.05	0.05	0.07	0.14	0.05	0.04	0.07	0.05
	Sulf	6.79	6.98	6.87	7.38	6.89	6.86	6.44	6.88	6.98
	Cl ⁻	0.26	0.33	0.16	0.37	0.28	0.21	0.23	0.25	0.24
	EDA	0	0	0	0	0	0	0	0	0
	PZ	3890.3	3893.8	3926.3	3939.5	3870.1	3912.6	3830.9	3896.2	3794.7

Table E.19: Tabulated Experimental Data for OE19 (8 m PZ, 2 kPa CO₂, 98 kPa O₂, 70 °C, 0.40 mM Fe²⁺, 0.10 mM Cr³⁺, 0.05 mM Ni²⁺, TOR)

		8 m PZ + Fe + Cr + Ni (70 °C)								
Time (hr)		0	69.0	141.5	215.8	282.3	357.8	427.0	473.8	572.0
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0
	Ace	0	0	0	0	0	0	0.29	0.27	0.24
	Form	0.29	1.54	2.81	4.78	4.66	6.04	6.82	7.54	8.21
	NO ₂ ⁻	0	0	0.08	0	0	0	0	0	0
	Oxa	0	0	0.07	0	0	0	0	0	0
	NO ₃ ⁻	0	0	0	0.33	1.78	0.16	0.17	0.21	0.24
	Sulf	4.66	5.90	5.00	5.77	5.70	5.73	5.49	5.45	5.39
	Cl ⁻	0	0	0.07	0.02	0.12	0.01	0	0	0
	EDA	0	0	11.97	0	9.36	13.66	14.80	26.68	18.48
	PZ	3943.0	4147.2	4132.2	3850.8	3897.3	3838.6	3927.7	3930.4	3830.9
	CO ₂	2677.1	2302.4	2143.1	2078.5	2655.8	1977.4	2717.9	2266.1	2202.7
	SD _{CO2}	13.83	23.60	6.83	5.69	2.59	6.83	14.85	9.38	8.64
	Alk	4103.9	4213.9	4142.1	4121.5	4046.4	4035.6	4014.0	3967.1	3920.6
	SD _{Alk}	4.08	34.88	14.18	35.18	4.76	18.93	62.62	3.78	6.37
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0
	Ace	0.09	0	0.12	0.25	0.36	0.38	0.38	0.37	0.52
	Form	0.32	4.31	7.81	10.78	12.86	13.78	15.49	17.38	18.85
	NO ₂ ⁻	0	0	0.08	0.09	0.08	0	0	0	0
	Oxa	0	0.09	0.09	0.17	0.20	0	0	0	0
	NO ₃ ⁻	0	0	0	0	0	0.21	0.20	0.23	0.22
	Sulf	4.71	5.06	4.96	5.12	4.88	5.39	5.35	5.31	5.35
	Cl ⁻	0.40	0.12	0.05	0.24	0.14	0.03	0.08	0.14	0.04
	EDA	0	0	0	0	40.92	11.45	11.67	14.54	16.59
	PZ	4244.0	4329.0	4246.9	4348.7	4076.1	3906.9	3868.1	3884.0	3814.1

Table E.20: Tabulated Experimental Data for OE20 (8 m PZ, 2 kPa CO₂, 98 kPa O₂, 70 °C, 0.40 mM Fe²⁺, 0.10 mM Cr³⁺, 0.05 mM Ni²⁺, 500 mM Formate, TOR)

8 m PZ + Fe + Cr + Ni + Formate (70 °C)							
Time (hr)		0	66.5	141.3	211.3	285.0	358.3
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0
	Ace	0.85	1.10	0.98	1.04	0.86	0.97
	Form	322.14	184.95	176.24	170.14	173.44	173.99
	NO ₂ ⁻	0.00	0.01	0.03	0.04	0.05	0.04
	Oxa	0	0	0	0.04	0.05	0.04
	NO ₃ ⁻	0.08	0.08	0.09	0.10	0.09	0.10
	Sulf	0.89	0.93	0.87	0.90	0.86	0.89
	Cl ⁻	0.05	0.07	0.05	0.10	0.07	0.07
	EDA	0	0	0	0	0	0
	PZ	4095.6	4060.1	4248.4	4001.6	4108.5	3869.7
	CO ₂	2501.2	2403.9	2110.0	2309.6	2321.2	2292.7
	SD _{CO2}	12.07	14.04	8.92	1.84	6.84	9.53
	Alk	4051.9	4100.1	4239.7	4193.0	4090.7	4099.0
	SD _{Alk}	17.59	5.61	2.03	73.86	9.29	0.90
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0
	Ace	1.07	1.42	2.42	0.93	0.92	1.03
	Form	470.39	490.12	506.12	494.88	491.92	496.09
	NO ₂ ⁻	0.01	0.03	0.05	0.05	0.05	0.06
	Oxa	0.03	0.05	0.06	0.08	0.10	0.12
	NO ₃ ⁻	0.09	0.09	0.09	0.09	0.11	0.11
	Sulf	0.92	1.01	1.06	0.97	0.92	1.01
	Cl ⁻	0.14	0.15	0.19	0.09	0.12	0.23
	EDA	0	0	0	0	0	0
	PZ	3663.5	4133.4	4003.5	3998.7	3988.5	4071.3

Table E.21: Tabulated Experimental Data for OE21 (8 m PZ, 2 kPa CO₂, 98 kPa O₂, 70 °C, 0.40 mM Fe²⁺, 0.10 mM Cr³⁺, 0.05 mM Ni²⁺, 500 mM Formaldehyde, TOR)

		8 m PZ + Fe + Cr + Ni + Formaldehyde (70 °C)						
Time (hr)		0	0	22.8	46.3	71.3	94.5	115.3
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0	0
	Ace	0	0	0	0	0	0	0
	Form	0.12	0.24	0.60	0.83	0.95	1.12	1.34
	NO ₂ ⁻	0	0	0	0	0	0.00	0.00
	Oxa	0	0	0	0	0	0	0.03
	NO ₃ ⁻	0	0	0	0	0	0	0
	Sulf	5.39	5.24	5.48	5.52	5.50	5.37	5.36
	Cl ⁻	0.04	0.02	0.03	0.03	0.03	0.03	0.02
	FPZ	0.43	0.64	1.56	1.75	2.57	2.94	3.09
	EDA	1.30	0	0.98	2.13	2.70	4.33	5.27
	PZ	4093.4	3853.3	NT	3819.2	3780.6	3741.8	3763.7
	CO ₂	2582.3	2458.8	2064.9	1961.6	1904.4	1876.7	1850.8
	SD _{CO2}	13.94	4.80	5.22	9.57	2.46	6.48	12.50
	Alk	4132.4	3950.6	4061.3	3925.1	3848.4	3845.1	3794.9
	SD _{Alk}	33.74	0.23	13.72	17.77	5.14	24.00	2.24
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0
	Ace	0	0	0	0.18	0.10	0.05	0.10
	Form	0.24	0.50	1.70	2.26	2.58	2.98	3.69
	NO ₂ ⁻	0.01	0.01	0.01	0.01	0.01	0.01	0.00
	Oxa	0	0	0	0.04	0.05	0.07	0.07
	NO ₃ ⁻	0	0	0	0	0	0	0
	Sulf	5.41	5.44	5.63	5.52	5.33	5.32	5.36
	Cl ⁻	0.05	0.03	0.04	0.06	0.07	0.04	0.08
	FPZ	0	0	0	0	0	0	0
	EDA	0	0	1.19	1.98	3.05	4.38	4.65
	PZ	4021.3	3882.9	3900.7	3796.2	3729.0	3714.4	3647.8

Table E.22: Tabulated Experimental Data for OE22 (8 m PZ, 60 kPa CO₂, 40 kPa O₂, 70 °C, 0.40 mM Fe²⁺, 0.10 mM Cr³⁺, 0.05 mM Ni²⁺, TOR)

		8 m PZ + Fe + Cr + Ni (70 °C)								
Time (hr)		0	70.0	143.5	213.0	287.8	359.5	430.0	501.0	575.0
Original Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0
	Ace	0	0	0	0	0	0	0	0	0
	Form	0	0.26	0.52	0.59	0.80	0.90	0.90	1.03	1.11
	NO ₂ ⁻	0	0.01	0.01	0	0.00	0.00	0.00	0.00	0.00
	Oxa	0	0	0	0	0	0	0	0	0
	NO ₃ ⁻	0	0.04	0.07	0.10	0.07	0.06	0.06	0.16	0.10
	Sulf	5.23	5.11	4.93	4.95	4.97	5.03	4.84	4.96	4.80
	Cl ⁻	0.01	0.01	0.02	0.02	0.03	0.34	0.02	0.13	0.02
	EDA	0	1.95	3.27	4.99	6.30	6.72	7.67	7.86	9.16
	PZ	2902.3	2845.0	2730.4	2710.3	2699.3	2664.7	2632.9	2635.3	2607.0
	CO ₂	3073.7	2812.6	2717.3	2624.8	2702.7	2643.8	2642.1	2782.5	2804.3
	SD _{CO2}	11.15	12.44	8.74	5.26	0.90	2.43	14.82	8.23	11.44
	Alk	3947.6	3841.3	3689.8	3662.2	3643.4	3580.2	3561.6	3573.1	3531.2
	SD _{Alk}	18.51	3.15	4.22	2.51	6.75	4.93	0.08	7.01	5.48
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0	0
	Ace	0	0	0	0	0	0	0	0	0
	Form	0.29	1.04	1.56	1.98	2.37	2.63	2.96	2.66	2.95
	NO ₂ ⁻	0	0.00	0.00	0.00	0.00	0	0.01	0.00	0.00
	Oxa	0	0	0	0	0	0	0	0	0
	NO ₃ ⁻	0	0.03	0	0	0.08	0.08	0.07	0.06	0.10
	Sulf	5.31	5.17	5.02	5.06	5.04	5.00	5.00	4.84	4.85
	Cl ⁻	0.07	0.05	0.05	0.04	0.05	0.05	0.05	0.11	0.03
	EDA	0	2.07	3.48	4.80	6.44	0	6.43	8.75	9.39
	PZ	2866.7	2796.8	2686.0	2666.0	2611.1	1791.1	NT	2574.6	2604.3

Table E.23: Tabulated Experimental Data for OE23 (8 m PZ, 6 kPa CO₂, 40 kPa O₂, 70 °C, 4.0 mM Cu²⁺, TOR)

		8 m PZ + Cu (70 °C)						
Time (hr)		0	48.5	93.5	144.3	192.8	284.5	332.5
Original Samples (mmol/kg)	Gly	0.29	0.15	0.28	0.14	0.16	0.19	0.14
	Ace	0	0	0	0	0	0	0
	Form	0.39	11.17	27.82	20.61	24.85	29.67	32.24
	NO ₂ ⁻	0	0.05	0.28	0.03	0.02	0.02	0.02
	Oxa	0	0.54	1.32	1.53	2.31	3.91	4.41
	NO ₃ ⁻	0	0.08	0.19	0.11	0.13	0.21	0.17
	Sulf	3.68	2.89	3.94	2.26	2.41	2.77	2.64
	Cl ⁻	0.02	0.04	0.06	0.01	0.00	0.02	0.02
	NH ₄ ⁺	0.16	4.96	9.54	4.07	2.91	3.05	3.29
	FPZ	0	43.52	55.83	61.45	69.68	76.57	76.24
	EDA	0	67.19	92.95	105.32	108.88	120.65	124.04
	PZ	4389.1	3178.3	3070.3	3069.4	2965.7	2919.6	2874.5
	CO ₂	2596.9	1947.1	1899.6	1833.3	1788.4	1755.8	1718.5
	SD _{CO2}	13.99	6.54	5.93	20.31	20.63	11.85	7.96
	Alk	4147.8	3096.6	3039.0	3045.2	2962.6	2954.6	2930.3
	SD _{Alk}	NA	NA	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	0.64	0.81	0.40	0.45	0.39	0.22	0.36
	Ace	0.30	1.07	2.31	3.23	3.59	2.46	4.23
	Form	3.58	30.64	39.67	58.68	58.98	37.80	65.06
	NO ₂ ⁻	0.02	0.06	0.06	0.05	0.02	0.01	0.02
	Oxa	0.15	6.66	8.75	13.31	13.26	8.08	14.78
	NO ₃ ⁻	0	0.07	0.11	0.18	0.16	0.15	0.19
	Sulf	2.77	2.40	2.11	2.98	2.77	1.44	2.54
	Cl ⁻	0.07	0.04	0.02	0.06	0.02	0.06	0.03
	NH ₄ ⁺	0	0	0	0	0	0	0
	FPZ	0	0	0	0	0	0	0
	EDA	9.37	81.61	105.30	122.16	127.17	130.06	135.02
	PZ	4349.5	3166.2	3009.6	2737.3	3045.2	2855.8	2951.6

Table E.24: Tabulated Experimental Data for OE24 (8 m PZ, 6 kPa CO₂, 40 kPa O₂, 70 °C, 4.0 mM Cu²⁺, 100 mM Inhibitor A, TOR)

		8 m PZ + Cu + A (70 °C)						
Time (hr)		0	48.5	93.5	144.3	192.8	284.5	332.5
Original Samples (mmol/kg)	Gly	0.26	0.34	0.31	0.36	0.30	0.34	0.28
	Ace	0	0	0	0	0	0	0
	Form	0.14	2.67	2.41	3.69	3.95	4.07	4.24
	NO ₂ ⁻	0.02	0.10	0.04	0.03	0.01	0.01	0.01
	Oxa	0	0.11	0.14	0.29	0.37	0.53	0.51
	NO ₃ ⁻	0	0.26	0.23	0.30	0.31	0.37	0.31
	Sulf	2.68	3.86	2.65	3.57	3.40	3.35	2.73
	Cl ⁻	0.03	0.04	0.03	0.03	0.04	0.26	0.16
	NH ₄ ⁺	1.31	2.62	1.10	1.43	1.75	1.12	0.84
	FPZ	0	0	0	0	0	0	0
	EDA	0	12.55	14.53	9.91	10.83	8.06	12.49
	PZ	4341.3	4633.4	4156.6	4309.5	4113.3	3994.7	4063.4
	CO ₂	2464.0	2786.1	2466.1	2413.9	2414.5	2405.4	2347.7
	SD _{CO2}	12.59	26.08	26.51	13.55	32.19	44.55	10.96
	Alk	4080.6	4044.3	3958.9	3938.8	3875.0	3786.7	3809.3
	SD _{Alk}	NA	NA	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	0.26	0.49	0.39	0.40	0.35	0.27	0.28
	Ace	0	0	0	0	0.19	0.42	0.42
	Form	1.06	8.90	9.13	9.64	10.82	11.72	12.44
	NO ₂ ⁻	0.03	0.09	0.04	0.03	0.02	0.01	0.01
	Oxa	0	1.01	1.24	1.49	1.88	2.19	2.58
	NO ₃ ⁻	0	0.25	0.26	0.28	0.32	0.32	0.34
	Sulf	3.47	3.78	3.32	3.04	3.38	3.15	3.29
	Cl ⁻	0	0.10	0.14	0.05	0.08	0.04	0.05
	NH ₄ ⁺	0	0	0	0	0	0	0
	FPZ	0	0	0	0	0	0	0
	EDA	5.05	10.60	12.08	11.52	10.28	11.89	13.64
	PZ	4261.5	4219.0	4153.2	4128.0	4049.7	4015.2	3935.0

Table E.25: Tabulated Experimental Data for OE25 (8 m PZ, 6 kPa CO₂, 94 kPa O₂, 70 °C, 4.0 mM Cu²⁺, TOR)

		8 m PZ + Cu (70 °C)							
Time (hr)		0	50.3	93.5	138.5	193.0	239.3	284.3	331.0
Original Samples (mmol/kg)	Gly	0.64	0	0	0	0	0	0	0
	Ace	0	0	0	0	0	0	0	0
	Form	1.13	24.84	46.06	63.96	93.84	120.99	143.91	168.74
	NO ₂ ⁻	0	0.26	0.45	0.66	0.97	1.18	1.71	1.90
	Oxa	0	2.04	5.46	10.34	18.42	26.19	34.54	42.10
	NO ₃ ⁻	0	0.31	0.62	0.94	1.80	2.31	2.80	2.81
	Sulf	3.67	3.76	4.29	5.12	6.23	7.33	8.08	9.08
	Cl ⁻	0.07	10.44	0	0	0	0	0	0
	NH ₄ ⁺	0	0	0	0	0	3.77	3.56	3.13
	FPZ	0	103.33	150.60	201.22	240.57	265.50	280.16	300.32
	EDA	1.15	184.21	269.73	331.27	335.37	310.54	267.05	224.24
	PZ	4389.0	3325.2	2679.8	2326.3	1828.7	1543.9	1342.3	1222.4
	1-MPZ	0	0	0	0	0	0.68	0.64	0.56
	1-EPZ	0	0	0	0	0	0	0	0
	1,4-DMPZ	0	0	0	0	0	0	0	0
	AEP	0	0	0	0	0	0	0	0
	CO ₂	2479.1	1986.8	1630.5	1420.5	993.6	760.2	580.7	442.4
	SD _{CO2}	16.38	26.68	10.46	17.13	9.77	6.50	5.53	0.78
	Alk	4117.7	3643.3	3217.9	2888.8	2416.2	2105.2	1736.7	1618.4
	SD _{Alk}	NA	NA	NA	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	0	1.21	0	0	0	0	0	0
	Ace	0	0.66	1.92	2.17	2.86	2.98	3.29	3.62
	Form	2.47	93.74	189.35	232.30	310.27	400.78	459.50	554.88
	NO ₂ ⁻	0	0.36	0.60	0.78	1.06	1.57	1.76	1.94
	Oxa	0.23	30.59	47.55	44.75	95.52	51.08	55.53	104.56
	NO ₃ ⁻	0	0.32	0.79	1.02	1.47	1.98	2.42	2.98
	Sulf	3.74	3.63	4.48	4.53	4.60	6.01	6.54	6.83
	Cl ⁻	0.10	0	0	0	0	0	0	0
	NH ₄ ⁺	0	60.50	77.16	67.76	72.64	85.79	107.50	130.90
	FPZ	0	0	0	0	0	0	0	0
	EDA	3.34	221.93	421.42	452.06	514.02	518.96	501.01	486.98
	PZ	4370.5	3548.7	2178.2	2430.0	2009.0	1747.5	1565.3	1453.1
	1-MPZ	0	0	0	0	1.99	2.34	2.90	3.27
	1-EPZ	0	0	0	0	0	0	0	0
	1,4-DMPZ	0	0	0	0	0	0	0	0
	AEP	0	0	0	0	0	0	0	0

Table E.26: Tabulated Experimental Data for OE26 (8 m PZ, 6 kPa CO₂, 94 kPa O₂, 70 °C, 0.40 mM Fe²⁺, 0.10 mM Cr³⁺, 0.05 mM Ni²⁺, TOR)

		8 m PZ + Fe + Cr + Ni (70 °C)							
Time (hr)		0	50.3	93.5	138.5	193.0	239.3	284.3	331.0
Original Samples (mmol/kg)	Gly	0.52	0.55	0.56	0.56	0.56	0.54	0.52	0.50
	Ace	0	0	0	0	0	0.06	0.08	0.14
	Form	0	0.21	0.41	0.70	1.06	1.37	1.59	1.85
	NO ₂ ⁻	0	0.03	0.03	0.02	0.02	0.02	0.02	0.02
	Oxa	0	0	0	0.00	0.00	0.01	0.01	0.01
	NO ₃ ⁻	0	0.03	0.05	0.05	0.07	0.07	0.06	0.08
	Sulf	5.16	5.19	5.09	4.95	4.99	4.90	4.77	4.80
	Cl ⁻	0.03	0.03	0.06	0.03	0.18	0.04	0.05	0.04
	NH ₄ ⁺	1.78	0	0.43	1.46	0	0	0	2.19
	FPZ	0	2.94	3.44	4.32	4.61	5.16	5.98	6.96
	EDA	0	3.35	5.10	6.54	8.72	10.50	11.47	12.60
	PZ	4406.7	4388.5	4321.8	4189.1	4193.1	4091.0	4050.1	4012.5
	1-MPZ	0	0	0	0	0	0	0	0
	1-EPZ	0	0	0	0	0	0	0	0
	1,4-DMPZ	0	0	0	0	0	0	0	0
	AEP	0	0	0	0	0	0	0	0
	CO ₂	2439.1	2500.4	2465.6	2472.3	2415.4	2409.5	2361.9	2336.5
	SD _{CO2}	7.66	46.29	5.83	15.88	11.82	29.25	22.34	20.55
	Alk	4238.4	4220.1	4187.0	4045.5	4047.3	3987.8	3957.2	3858.4
	SD _{Alk}	NA	NA	NA	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	0.37	0.36	0.43	0.39	0.38	0.22	0.24	0.22
	Ace	0	0	0	0	0	0	0	0
	Form	0	1.21	2.07	2.92	3.85	4.57	5.09	5.82
	NO ₂ ⁻	0	0.02	0.03	0.02	0.02	0.02	0.02	0.02
	Oxa	0	0.02	0.03	0.10	0.11	0.17	0.19	0.21
	NO ₃ ⁻	0	0.03	0.04	0.05	0.06	0.07	0.10	0.08
	Sulf	5.20	5.19	5.12	4.94	5.00	4.91	4.89	4.72
	Cl ⁻	0.09	0.06	0.07	0.09	0.08	0.10	0.38	0.08
	NH ₄ ⁺	0	0	0	0	0	0	0	0
	FPZ	0	0	0	0	0	0	0	0
	EDA	0	3.57	5.14	6.90	8.45	10.14	11.76	12.99
	PZ	4431.9	4320.9	4325.8	4175.5	4211.4	4122.5	4099.1	4008.3
	1-MPZ	0	0	0	0	0	0	0	0
	1-EPZ	0	0	0	0	0	0	0	0
	1,4-DMPZ	0	0	0	0	0	0	0	0
	AEP	0	0	0	0	0	0	0	0

Table E.27: Tabulated Experimental Data for OE27 (8 m PZ, 2 kPa CO₂, 40 kPa O₂, 55 °C, 4.0 mM Cu²⁺, TOR)

		8 m PZ + Cu							
Time (hr)		0	75.5	147.0	217.0	290.0	367.3	439.3	506.5
Original Samples (mmol/kg)	Gly	0.51	0.40	0.21	0.29	0.25	0.15	0.13	0.12
	Ace	0	0	0	0	0	0	0	0
	Form	0.11	6.43	10.29	13.44	15.27	16.72	17.83	18.43
	NO ₂ ⁻	0	0.14	0.18	0.17	0.18	0.17	0.14	0.13
	Oxa	0	0.21	0.48	0.68	1.00	1.23	1.52	1.79
	NO ₃ ⁻	0	0	0.12	0.13	0.14	0.16	0.16	0.16
	Sulf	3.74	3.84	3.67	3.69	3.64	3.67	3.62	3.52
	Cl ⁻	0	0	0	0	0	0	0	0
	NH ₄ ⁺	0	2.42	1.61	1.33	0.77	1.17	0.96	2.58
	FPZ	2.06	27.14	34.80	39.63	41.93	43.77	44.93	45.75
	EDA	1.55	62.09	84.74	101.34	113.35	120.96	126.82	131.88
	PZ	3740.8	3446.9	3308.7	3302.6	3284.0	3229.9	3209.4	3169.6
	1-MPZ	0	0	0	0	0	0	0	0
	1-EPZ	0	0	0	0	0	0	0	0
	1,4-DMPZ	0	0	0	0	0	0	0	0
	AEP	0	0.84	1.12	1.03	0.98	0.84	0.74	0.79
	CO ₂	2479.8	2228.6	2194.8	2106.6	2048.8	2001.9	1947.2	1916.6
	SD _{CO2}	29.70	8.15	11.01	18.49	17.74	6.00	4.26	2.16
	Alk	4080.7	4002.7	3953.5	3935.3	3984.3	3977.2	3803.3	3655.9
	SD _{Alk}	NA	NA	NA	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	1.03	1.49	1.03	0.62	0.85	0.40	0.31	0.32
	Ace	0	0	0	0.27	0.71	0.47	0.47	0.46
	Form	1.81	30.11	38.96	43.31	47.37	50.19	51.96	53.06
	NO ₂ ⁻	0	0.20	0.23	0.22	0.21	0.20	0.18	0.17
	Oxa	0.20	6.12	9.40	9.27	10.15	11.26	11.22	11.29
	NO ₃ ⁻	0	0.11	0.13	0.15	0.23	0.18	0.17	0.18
	Sulf	3.78	3.83	3.73	3.68	3.81	3.97	3.63	3.65
	Cl ⁻	0	0	0	0	0	0	0	0
	NH ₄ ⁺	0	0	0	0	0	0	0	0
	FPZ	0	0	0	0	0	0	0	0
	EDA	3.37	73.11	100.99	115.29	128.79	137.11	143.14	145.98
	PZ	3793.9	3517.5	4821.9	3759.5	3402.4	3329.4	3278.7	3208.9
	1-MPZ	0	0	0	0	0	0	0	0
	1-EPZ	0	0	0	0	0	0	0	0
	1,4-DMPZ	0	0	0	0	0	0	0	0
	AEP	0	0.40	0.33	0.35	0.37	0.33	0.31	0.28

Table E.28: Tabulated Experimental Data for OE28 (8 m PZ, 2 kPa CO₂, 98 kPa O₂, 55 °C, 0.40 mM Fe²⁺, 0.10 mM Cr³⁺, 0.05 mM Ni²⁺, TOR)

		8 m PZ + Fe + Cr + Ni							
Time (hr)		0	75.5	147.0	217.0	290.0	367.3	439.3	506.5
Original Samples (mmol/kg)	Gly	0.49	0.41	0.48	0.50	0.48	0.50	0.48	0.42
	Ace	0	0	0	0	0	0	0	0
	Form	0	0	0.08	0.12	0.12	0.21	0.35	0.35
	NO ₂ ⁻	0	0	0	0	0	0	0	0
	Oxa	0	0	0	0	0	0	0	0
	NO ₃ ⁻	0	0	0	0	0	0	0	0
	Sulf	5.03	5.03	5.07	5.12	5.01	4.99	4.96	4.95
	Cl ⁻	0.04	0.03	0.02	0.03	0	0	0	0
	NH ₄ ⁺	0	0	0.20	0	0.36	0.10	0.30	1.69
	FPZ	0	0	0	0.91	0.82	1.21	1.28	1.35
	EDA	0	0.14	0.24	0.59	0.51	0.64	0.84	0.95
	PZ	3780.4	3640.3	3708.1	3739.8	3743.4	3711.4	3648.9	3665.7
	1-MPZ	0	0	0	0	0	0	0	0
	1-EPZ	0	0	0	0	0	0	0	0
	1,4-DMPZ	0	0	0	0	0	0	0	0
	AEP	0	0	0	0	0	0	0	0
	CO ₂	2362.2	2267.2	2179.6	2229.9	2165.0	2148.1	2108.1	2111.6
	SD _{CO2}	26.77	12.67	238.88	13.95	10.31	23.17	23.49	35.11
	Alk	4225.2	4114.6	4136.7	4247.9	4198.6	4154.1	4046.6	4082.1
	SD _{Alk}	NA	NA	NA	NA	NA	NA	NA	NA
Hydrolyzed Samples (mmol/kg)	Gly	0	0	0	0	0	0	0	0
	Ace	0	0	0	0	0	0	0	0
	Form	0	0	0.27	0.56	0.78	1.01	1.21	1.24
	NO ₂ ⁻	0	0	0	0	0	0	0	0
	Oxa	0	0	0	0	0	0	0	0
	NO ₃ ⁻	0	0	0	0	0	0	0	0
	Sulf	5.01	5.70	5.14	5.17	5.02	5.10	6.07	5.04
	Cl ⁻	0	0	0	0	0	0	0	0
	NH ₄ ⁺	0	0	0	0	0	0	0	0
	FPZ	0	0	0	0	0	0	0	0
	EDA	0	0	0.13	0.31	0.50	0.70	0.90	1.02
	PZ	3816.8	4179.1	3779.3	3808.3	3775.6	3747.0	3697.3	3775.3
	1-MPZ	0	0	0	0	0	0	0	0
	1-EPZ	0	0	0	0	0	0	0	0
	1,4-DMPZ	0	0	0	0	0	0	0	0
	AEP	0	0	0	0	0	0	0	0

Appendix F – Measurements of Heat of Absorption of CO₂ into Concentrated PZ

The heat of absorption of 8 m PZ was measured at Norges Teknisk-Naturvitenskapelige Universitet (The Norwegian University of Science and Technology – NTNU) under the guidance of Dr. Inna Kim and Prof. Hallvard Svendsen. NTNU has a well-developed method for determining the heat of absorption of CO₂ into amine solutions using a reaction calorimeter. Numerous amines have been tested by their group with success (Kim and Svendsen, 2007).

F.1 REACTION CALORIMETER

F.1.1 Apparatus description

The reaction calorimeter (ChemiSens AB, Lund, Sweden) is a 2 L stainless steel jacketed vessel as shown in Figure F.1. There is a top mounted stainless steel stirrer operated by a separate stirrer motor. The heating/cooling system, or recirculator, uses cooling water (process water from the fume hood) and electrical power to heat and cool the silicon oil that circulates in the jacket around the reactor. There is a small electrical heater sticking into the vessel for calibration (not shown on figure). The CO₂ and solvent inlets are on the top of the vessel, as is the outlet for the vacuum pump system. The CO₂ flow is controlled by a mass flow controller attached to two small CO₂ tanks whose temperature is controlled in a water bath. The control box links the stirrer, recirculator, mass flow controller, temperature gauges, and pressure gauges to the computer. The InTouch program (ChemiSens AB) is used to control all the aspects of the system.

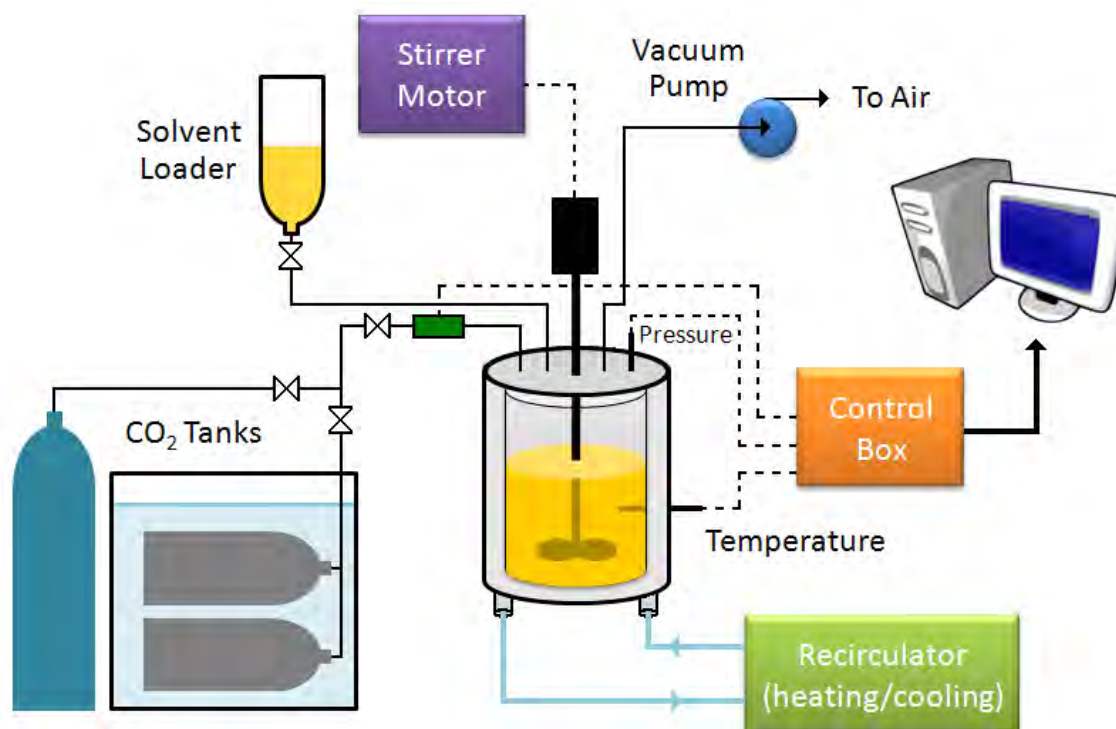


Figure F.1: Simplified Schematic of Reaction Calorimeter (ChemiSens AB)

F.1.2 Measurement procedure

To perform a heat of absorption measurement, the reactor is first evacuated to a gauge pressure of -0.9 to -0.95 bar. Then, CO₂ is then added to the reactor to a gauge pressure of approximately 2 bar to ensure that no air is in the reactor. The CO₂ is again evacuated to a reactor pressure of -0.9 to -0.95 bar. The solvent loader is flushed with N₂ and filled with solvent. The solvent loader is attached to the solvent inlet on the top of the reactor and the vacuum in the reactor is used as suction to draw the solvent into the calorimeter. The desired temperature and stirring speed are then set for the experiment. Once an initial equilibrium has been achieved, a small amount of CO₂ is added to the reactor, usually between 0.2 and 0.3 moles CO₂. The system is allowed time to reach an equilibrium before another pulse of CO₂. This process is repeated until the pressure in the reactor builds up as to not allow further addition of CO₂. The maximum total pressure of the calorimeter can be varied from 3 to 10 bars. All experiments were performed with a maximum pressure of 10 bars.

F.1.3 Data recording

The InTouch software allows the user to control nearly every aspect of the calorimeter operation. During an experiment, data is logged continuously every 10 seconds. For the calculation of heat of absorption, nine variables are of particular importance while other parameters are useful for seeing the stability of the experiment. The following variables are needed for the calculations:

Reactor_temp – temperature of the reactor

Reference_temp – temperature of the thermostating fluid (silicon oil)

HB_dT_reactor – temperature difference in the thermostating fluid entrance and exit

HLoss_dT_reactor – temperature difference across the insulation

dT_dt_reactor – instantaneous time derivative of the reactor temperature (°C/s)

Total_power – online measurement of power provided by recirculator (W)

Pressure_A – pressure of the reactor

Pressure_B – pressure of one of the two CO₂ cylinder

Convert_B2 – temperature of one of the CO₂ cylinders

During the experiment, the following variables are also of use to observe the stability of the system and to estimate the progress.

Lin_in_A1 – CO₂ mass flow controller reading

Calibration_power – power imparted by calibration electric heater, up to 30 W

Convert_A2 – temperature of the second CO₂ cylinder

F.1.4 Theory of heat of absorption measurements

The heat of absorption of CO₂ into amine systems is measured by directly measuring the heat released from the reaction. This is accomplished by measuring the heat need to be added to the system in order to maintain a constant temperature during reaction. The online power (recorded as Total_power in the InTouch software) is calculated using calibration parameters as discussed in detail in the next section. The calculation is based on the heat balance principle. The heat produced during the reaction creates an increase in temperature in the reactor contents. In order to maintain the experimental temperature, the thermostating media (silicon oil), must change in temperature to accommodate the energy balance. The basic heat balance equation applied to this calorimeter in is shown in the following equation (ChemiSens).

$$\text{Total Energy} = m_{\text{oil}} C_{P,\text{oil}} (T_{\text{oil, out}} - T_{\text{oil, in}})$$

In order to relate to the calorimeter system, this equation can be rewritten in terms of time and power instead of energy.

$$\text{Total Power} = \dot{m}_{\text{oil}} C_{P,\text{oil}} (T_{\text{oil, out}} - T_{\text{oil, in}})$$

This expression is described by the manufacturer, ChemiSens AB, as describing the system at a steady state operation in the absence of heat losses (ChemiSens). The product ($\dot{m}_{\text{oil}} C_{P,\text{oil}}$) are not measured separately, but the product is fitted during calibration as a parameter named FlowCp.

The heat loss from the calorimeter to the surroundings is estimated as the heat flow through the insulation out of the reactor. This is captured by a term multiplying a heat conductivity coefficient (HlossC, a calibrated parameter) and the difference in temperature across the insulation. Including this heat loss term results in the following equation which fully characterizes the steady state heat balance on the calorimeter.

$$\text{Total Power} = \dot{m}_{\text{oil}} C_{P,\text{oil}} \times (T_{\text{oil, out}} - T_{\text{oil, in}}) + \text{HlossC}(T_{\text{HL(inner)}} - T_{\text{HL(outer)}})$$

The difference in temperature across the insulation is a measured variable (Hloss_DT_reactor) which represents ($T_{\text{HL(inner)}} - T_{\text{HL(outer)}}$) in the total power equation.

When the calorimeter is actively controlling temperature, heat ‘accumulates’ in the reactor contents and various metallic parts on the inside of the reactor before it can be compensated for with the thermostating fluid. This dynamic heat is accounted for in a separate term in the total power equation. This dynamic term includes a heat capacity term (C_R , a calibrated parameter) that is a total heat capacity for the solvent in the reactor, stirrer, and interior reactor walls that interact with the solvent multiplied by the time derivative of the reactor temperature. This time derivative of the reactor temperature is a

measured parameter ($dT_{dt\_reactor}$) and it is assumed that the internal metallic parts of the calorimeter follow the same dT/dt behavior as the solution.

$$\text{Total Power} = \dot{m}_{oil} C_{P,oil} \times (T_{oil, out} - T_{oil, in}) + H_{loss} C (T_{HL(inner)} - T_{HL(outer)}) + C_R \frac{dT}{dt}$$

The final term in the power equation is a term representing the dynamic changes in the reactor jacket. This term is represented as the heat flow from the thermostating media to the outer reactor jacket including a coefficient the average total heat transfer (BKA, a calibrated parameter). This term is important because the external metallic parts of the jacket have a significantly higher heat capacity than the solution itself, so its contribution could be significant during CO₂ pulses.

$$\begin{aligned} \text{Total Power} = \dot{m}_{oil} C_{P,oil} \times (T_{oil, out} - T_{oil, in}) + H_{loss} C (T_{HL(inner)} - T_{HL(outer)}) \\ + C_R \frac{dT}{dt} + BKA \times (T_{ref} - T_j) \end{aligned}$$

The final part of the Total Power equation is an adjustment made to capture any final heat leakages from the system. In addition, the small pressure drop across the jacket produces a small amount of heat that will cause an offset in the experimental heat measured. These phenomena are fixed through the addition of a baseline correction through a calibrated parameter (Baseline) (ChemiSens).

The complete equation for the total power with descriptions of each term is included below (ChemiSens).

$$\text{Total Power} = \underbrace{\overbrace{\dot{m}_{oil} C_{P,oil}}^{\text{Calibration constant}} \times \left(T_{oil, out} - T_{oil, in} - \underbrace{\text{Baseline}}_{\text{Calibration Constant}} \right)}_{\text{heat exchange with thermostating media}} + \underbrace{\overbrace{H_{loss} C}^{\text{Calibration Constant}} \times (T_{HL(inner)} - T_{HL(outer)})}_{\text{heat loss through the jacket}}$$

$$+ \underbrace{\overbrace{\widehat{C}_R}^{\text{Calibration constant}} \frac{dT}{dt}}_{\text{dynamic heat of reactor}} + \underbrace{\overbrace{\widehat{BKA}}^{\text{Calibration constant}} \times (T_{\text{ref}} - T_j)}_{\text{dynamic heat of jacket}}$$

F.1.5 Data analysis

For each experiment, it is advisable to begin with a calibration procedure. There are 5 calibrated parameters and one constant as described in Table F.1. All of the calibrated parameters are strong functions of temperature and functions of the solvent system in use to a lesser extent. After the reactor is loaded with the solvent and brought up to the experimental temperature, the electrical calibration heater inside the reactor is set to generate 30W of power for 15 to 20 minutes. After the system has regained equilibrium (approximately 1 hour later), the parameters are fitted by matching a calculated power curve to the curve showing the calibration power (Calibration_power). The calculated power curve, or Calc_power, is produced with the equation described in the preceding section for the Total_power. In the Graph window of the InTouch program, the calibrated parameters can be adjusted to visually fit the two curves. An additional check is to verify that the area under both the Calc_power and Calibration_power curves are the same. When the curves are as similar as possible, the new values of the calibrated parameters are found.

Once the calibration is complete, the experiment can proceed. After each differential addition of CO₂, the system is allowed to reach equilibrium where the reactor temperature (T_r), reactor pressure (P_r), CO₂ tank temperature (T_{CO2}), CO₂ tank pressure (P_{CO2}), and the recirculator system power (Total_power) have all reached a steady value. The heat given or taken away from the reactor by the silicon oil during the pulse of CO₂ and subsequent time for equilibrium is continually measured and recorded. The Total_power measurement is directly in Watts of power. Integration of the time vs.

Total_power curve produces Joules of energy exchanged over a specified time range, known as the dH_{online} , or online energy measurement.

Table F.1: Description of calibration parameters for calorimeter

Parameter	Description
FlowCp	Product of the volumetric flow rate, density, and heat capacity of the silicon oil, usually 600 – 900 W/°C
Baseline	Establishes a baseline power
HlossC	Heat conductivity coefficient to characterize heat losses through the thermal shield, usually 1 – 1.4 W/°C
BKA	Average total heat transfer coefficient, represents heat transfer between the thermostating media (silicon oil) and the outer reactor jacket, calibrated parameter based on dynamic system response during calibration
CB	Heat capacity of the reactor jacket, constant for this calorimeter at 1500 J/°C
CR	Heat capacity of the reactor contents, including the solution, contributions from the stirrer, reactor base, and interior walls; calibrated parameter based on solvent and temperature in use, usually 5500 – 7800 J/°C.

Once the dH_{online} is calculated, it can be directly associated with the amount of CO₂ or amine to calculate the heat of absorption per mol CO₂ or per mol amine. The amount of amine charged is known from when the solvent was loaded into the system at the beginning of the experiment. The amount of CO₂ added to the calorimeter during each differential addition is calculated using the Peng-Robinson equation of state. The pressure explicit version of the Peng-Robinson equation is used, whose terms are shown below (Smith et al., 1995; Tester and Modell, 1997).

$$P = \frac{nRT}{V - nb} - \frac{n^2 a \alpha}{V^2 + 2bnV - (nb)^2}$$

$$a = \frac{0.45724 R^2 T_C^2}{P_C}$$

$$b = \frac{0.07780 RT_C}{P_C}$$

$$\alpha = [1 + (0.37464 + 1.54226\omega - 0.26952\omega^2)(1 - \sqrt{T_R})]^2$$

The critical constants for CO₂ used in the Peng-Robinson calculations are listed in Table F.2.

Table F.2: Critical constants for CO₂ (Perry and Green, 1997)

Constant	Value
T _C	304.21 K
P _C	73.9 bar
ω	0.224

The moles of CO₂ present in the CO₂ storage tanks are calculated before and after each CO₂ injection and the difference is the amount injected into the reactor. In the instances where the reactor pressure increased after a CO₂ pulse, the change in vapor pressure of CO₂ is calculated based on this pressure increase. The increase in reactor pressure is due to a portion of the CO₂ not being absorbed into the liquid because an equilibrium limit had been reached. The amount of CO₂ remaining in the vapor phase is subtracted from the total amount added to the reactor to calculate the moles of CO₂ that have been absorbed into the solvent during each CO₂ pulse. Once the moles absorbed into the solvent are known, the loading at each point can be calculated based on the known amount of amine charged initially.

During the experiment, the progress can be estimated by using the mass flow controller reading to estimate the amount of CO₂ inputted into the reactor during each impulse. A calibration equation is used to produce a curve of the CO₂ flow in liters per second. Integration of this curve over time produces a rough estimate of the liters of CO₂ entering the reactor.

To perform these calculations, a MATLAB program written by Inna Kim is used (Kim, 2008). An input file for each experiment contains the P_{CO2}, T_{CO2}, and P_r before

and after each impulse as well as the integrated values for dH_{online} and the estimate for liters of CO_2 . The amount of CO_2 added to the reactor during each impulse is more accurately calculated as described above and the final values for the heat of absorption as a function of CO_2 loading are produced.

F.2 RESULTS OF HEAT OF ABSORPTION MEASUREMENTS

My efforts for the latter half of the second quarter of 2008 were focused on measuring the heat of absorption of CO_2 in aqueous concentrated PZ solutions. These experiments were performed in collaboration with Inna Kim and Hallvard Svendsen of the Norwegian Technical University (NTNU) in Trondheim, Norway.

The first series of experiments were calibration and verification tests performed on 30wt% (7 m MEA) and 2.4 m (2.0 M) PZ. The heats of absorption for these solutions were compared to the previous work of Inna Kim and Marcus Hilliard to verify my experimental procedure.

The first measurements conducted were with 7m MEA at 40°C and 80°C. The results of both are shown in Figure F.2 and Figure F.3 below. Only a few points were taken since the data seemed to match well with the previous work of Kim and Svendsen.(Kim and Svendsen, 2007) After the completion of testing with 8 m PZ, a short test with 7 m MEA was conducted at 120C since this temperature was not testing with 40 and 80 in the beginning. This test was also important to validate the data obtained for PZ at 100 and 120C where more data scatter was observed. The results for 7 m MEA at 120 compared to the data of Kim are shown in Figure F.4.(Kim and Svendsen, 2007)

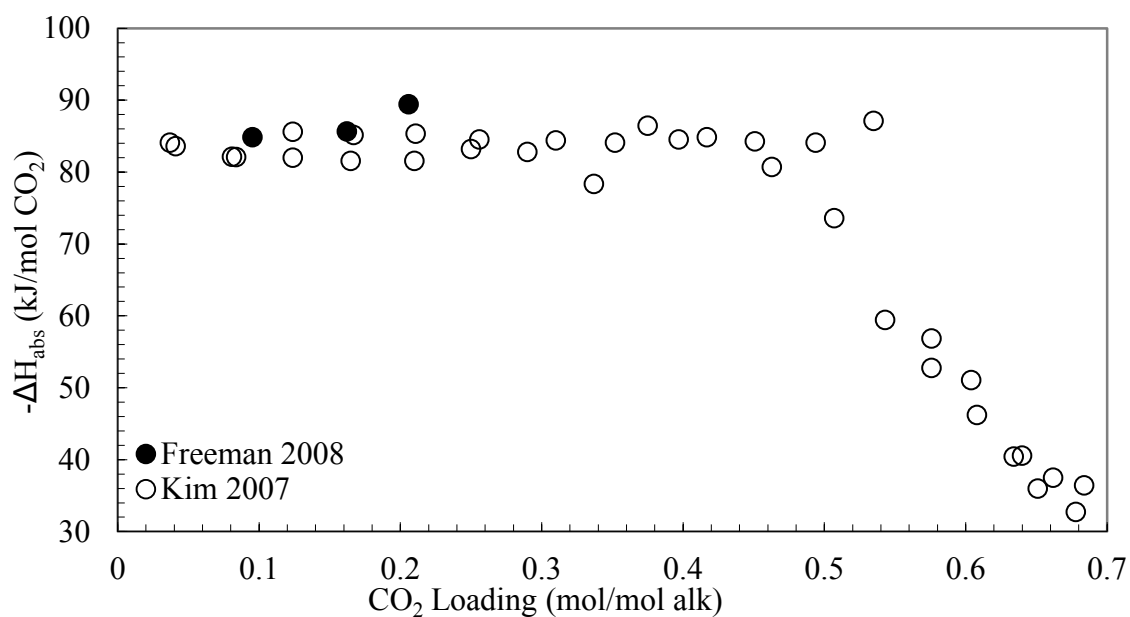


Figure F.2: Heat of absorption of 7 m MEA at 40 °C (Kim and Svendsen, 2007)

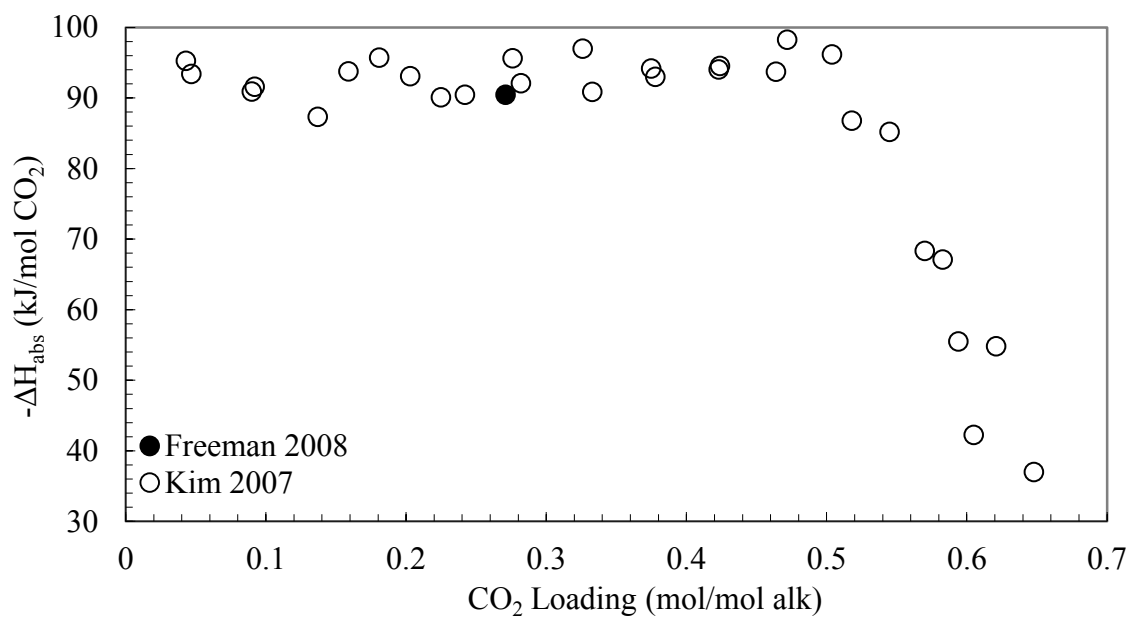


Figure F.3: Heat of absorption of 7 m MEA at 80 °C (Kim and Svendsen, 2007)

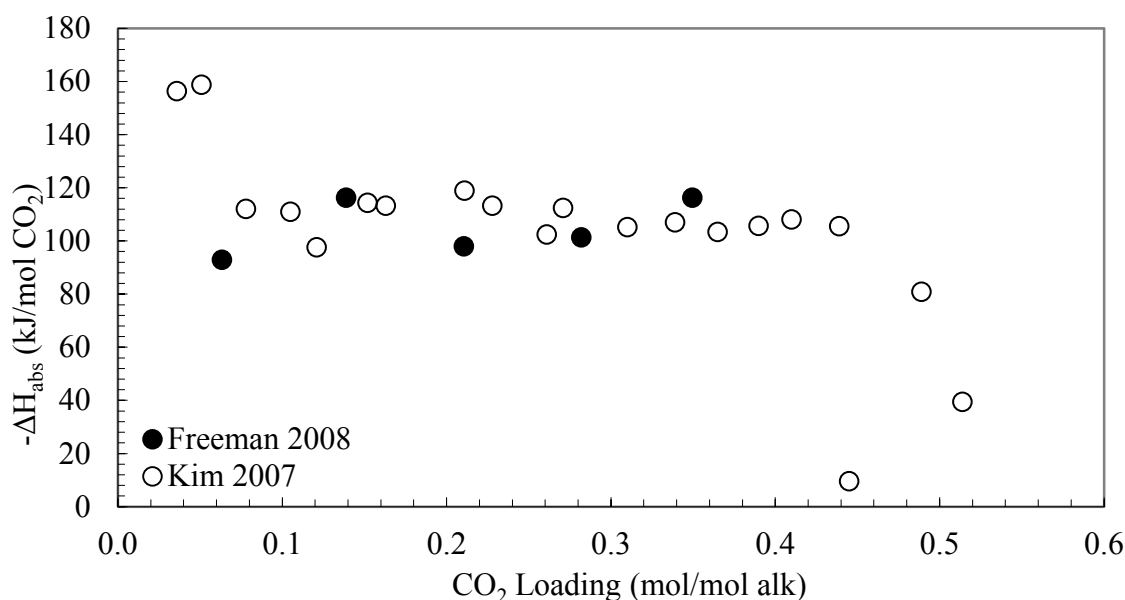


Figure F.4: Heat of absorption of 7 m MEA at 120 °C (Kim and Svendsen, 2007)

After the short tests with MEA, the work with PZ was started. The comparison between my data and that from Hilliard's thesis for 2.4 m PZ at 40 °C is shown below in Figure F.5 (Hilliard, 2008). The experiment performed on 2.4 m PZ took larger differential elements in CO₂ loading so the procedure could be quickly verified by reproducing Hilliard's results. With the exception of the very first point, the new data are close to that of Hilliard, although not within the $\pm 2\%$ error that was reported. The first point was an accident as valve was open and letting CO₂ into the reaction vessel before the test was due to begin. The small amount of CO₂ let into the vessel and the heat released from the reaction was recorded. Since the areas of both were so small, the integration was flawed and not representative of the actual heat of reaction.

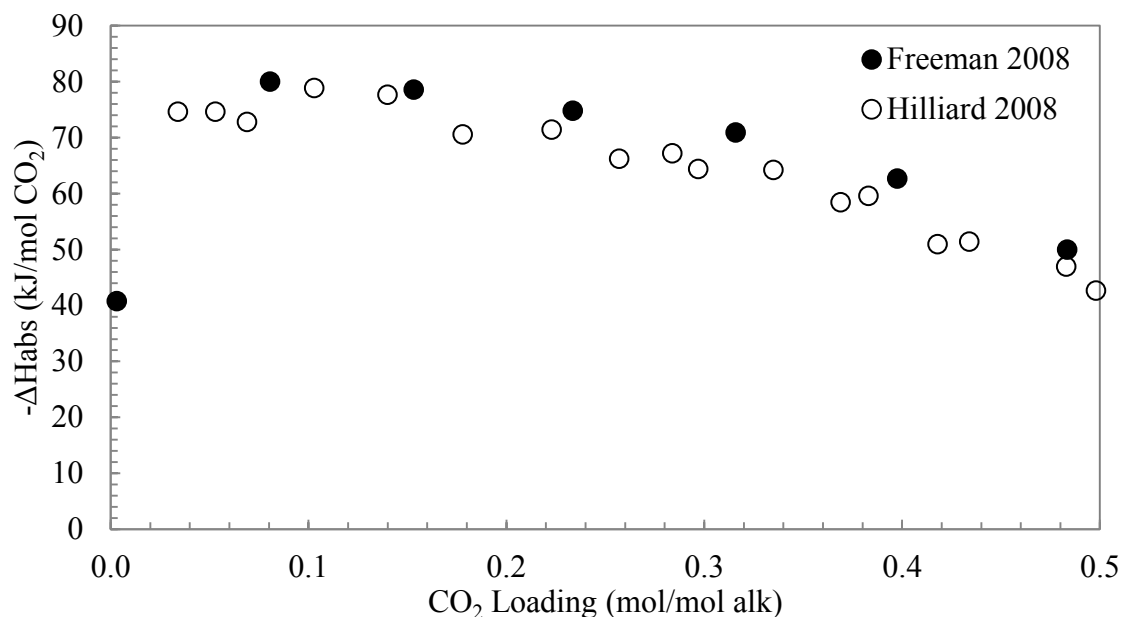


Figure F.5: Heat of absorption of CO₂ in 2.4 m PZ at 40 °C

After it was concluded that the experimental procedure and data analysis matched that of previous experiments, solutions of 8 m PZ were analyzed.

Measurements of the heat of absorption of CO₂ into aqueous 8 m PZ were conducted at 60, 80, 100, and 120 °C. At each temperature, two separate runs were performed and both runs are shown in Figure F.6, Figure F.7, Figure F.8, and Figure F.9 for 60, 80, 100, and 120 °C, respectively.

From the data collected, the cumulative heat of absorption of CO₂ per mole of amine could also be calculated as a function of loading.

$$\Delta H_{\text{abs}} = \frac{\int_0^{a_{\text{final}}} \text{Total Power } (\alpha') d\alpha'}{\text{mol PZ initially fed}}$$

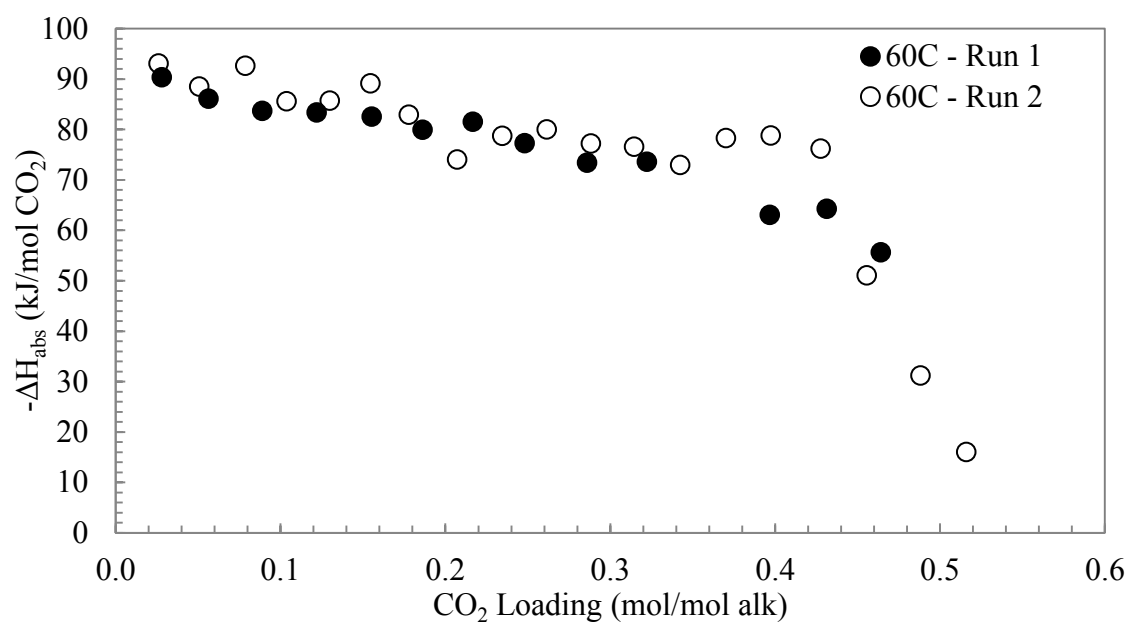


Figure F.6: Heat of absorption of CO₂ in 8 m PZ at 60 °C

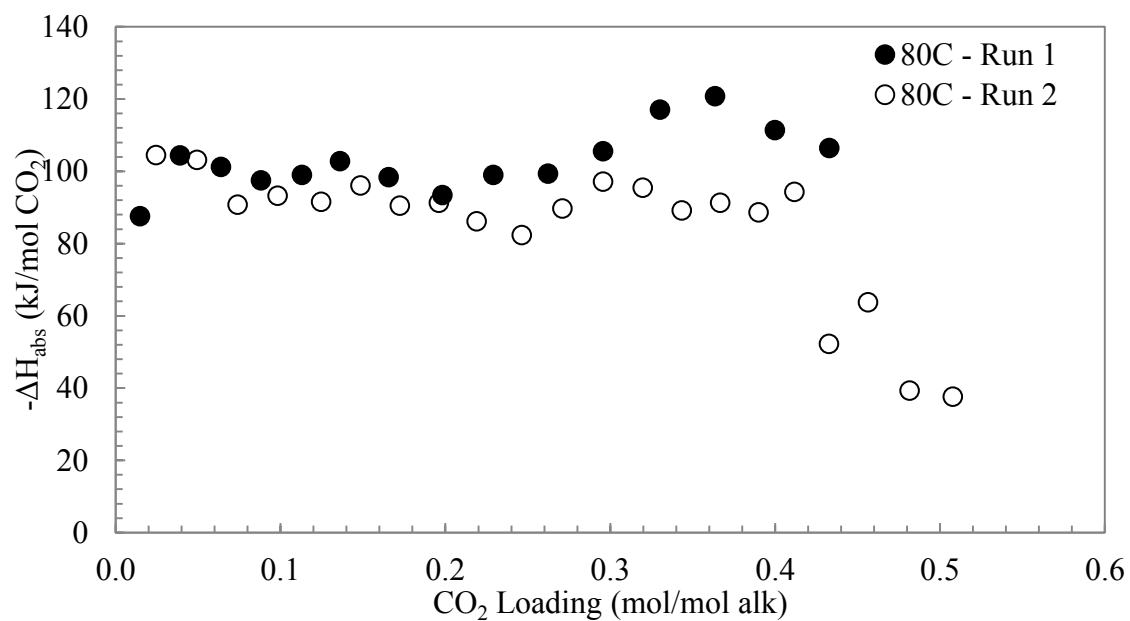


Figure F.7: Heat of absorption of CO₂ in 8 m PZ at 80°C

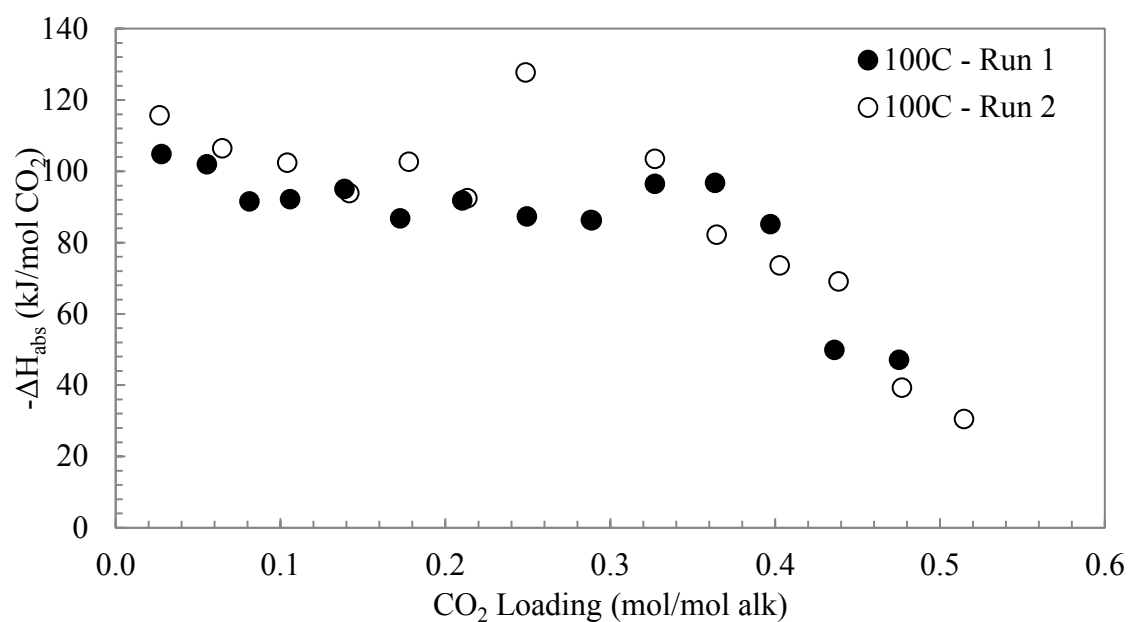


Figure F.8: Heat of absorption of CO₂ in 8 m PZ at 100 °C

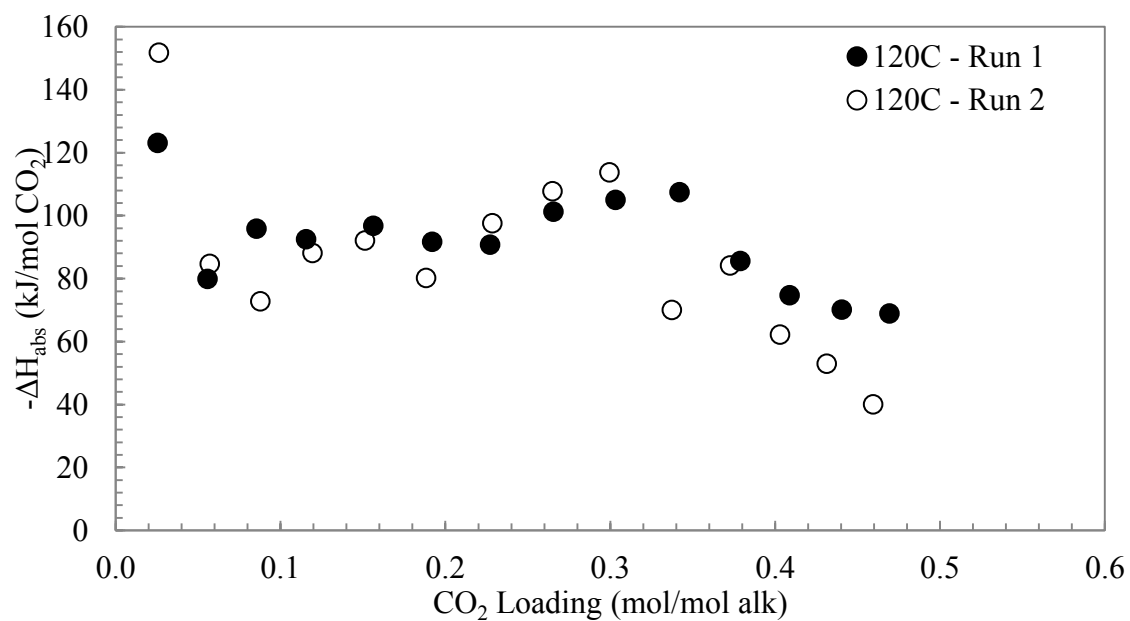


Figure F.9: Heat of absorption of CO₂ in 8 m PZ at 120 °C

The results for all eight runs are shown in Figure F.10. There is a good agreement between the two runs for 60 °C and the 120 °C at low loadings. In the 80 °C runs, the

results are quite separated indicating a lack of repeatability which was also observed in Figure F.7. In the 100 °C runs, the results also seem separated like the 80 °C, but the heat of absorption per mol of CO₂ data in Figure F.10 were much better than that of 80 °C. The 120 °C data fit very well between the two runs from a loading of zero until around 0.3 and then there is a deviation as run2 is lower than run 3. The cause of this deviation is unknown. Overall, the heat of absorption in terms of the total moles of amine does not change significantly with temperature until a loading of above 0.2 to 0.3 is reached. The temperature dependence is significant in the region of higher loading, approximately 0.25 to 0.50, which is the industrially relevant loading region as well.

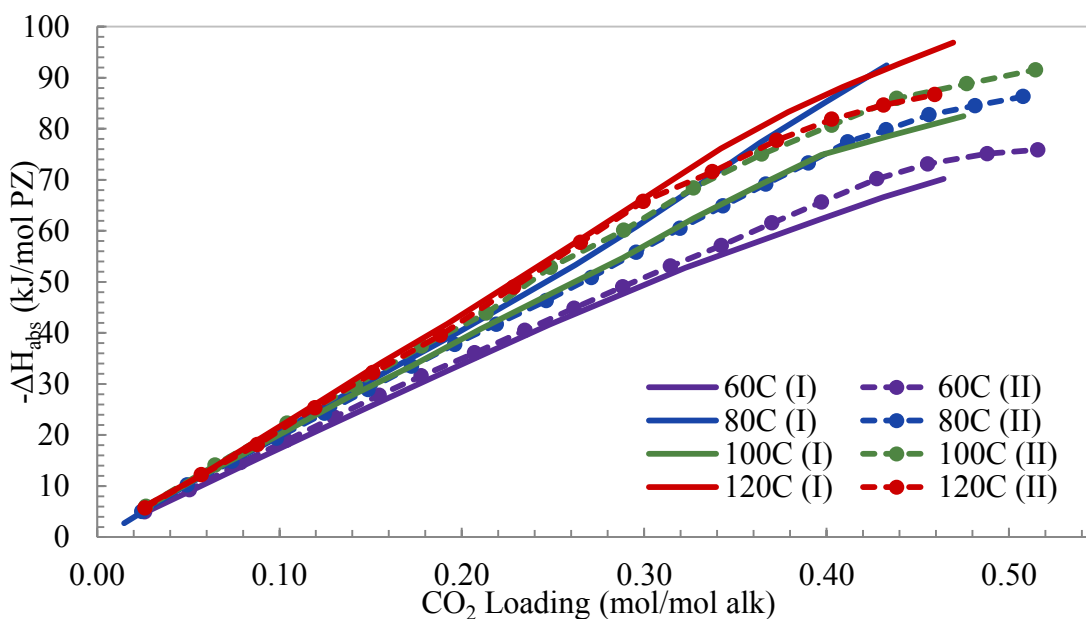


Figure F.10: Heat of absorption per mole of PZ at all temperatures

F.3 COMPLICATIONS WITH THE HEAT OF ABSORPTION MEASUREMENT

The measurement of the heat of absorption for concentrated PZ solutions is very complex because the solutions are not soluble at room temperature while unloaded. The calorimeter is designed so that the vessel is sealed and all solutions must enter through

the designated solvent inlet port. The solutions are loaded via suction created by pulling a vacuum in the reaction vessel prior to solvent loading. In addition, the inlet and outlet tubing is all ¼ inch stainless steel piping and Swagelok[®] valves. These narrow pipes are also highly susceptible to being clogged because of PZ precipitation.

To overcome these obstacles, numerous modifications were required to the original procedure developed at used at NTNU. First of all, the solutions were still prepared unloaded but were kept warm using a water bath maintained between 45 and 50 °C. The first unsuccessful attempt at adding 8 m PZ to the reactor demonstrated that the solvent inlet line needed to be heated to receive the warm solution. Electrical heating tape was wrapped around the entire inlet line with a thermocouple to monitor the temperature of the pipe. The temperature of the heating tape could not be controlled, so the tape was only plugged in a few minutes before loading to ensure that the temperature did not go above 90 °C. This allowed the solution to be successfully added to the reactor.

The first time 8 m PZ was used in the reactor, the temperature in the reactor could not come to equilibrium at 40 °C. The temperature was very slow to respond, slower than had been observed before. The experiment was abandoned and precipitated PZ was found to be clogging the entire outlet line. It was believed that the low temperature of 40°C was not high enough to prevent precipitation under vacuum and the precipitation may have interfered with the temperature sensor in the reactor that was unresponsive. The decision was made to only attempt measurements at 60 °C and above for 8 m PZ solutions.

In addition to heating the inlet line, it was found that warming the entire glass solution loader before attempting to load the solution into the reactor made it much more likely to succeed. After the solution was added to the glass loader, the connection piece was added to the top, the entire bottle was weighed, and then the bottle was ran under

warm water for about 3 minutes. Special attention was made to ensure that the connection piece was warmed before any attempt to load the solution as undertaken. Also, the rest of the bottle was warmed continuously to ensure that the glass did not crack due to thermal shock since some sections were cold after the solvent was added. Warming the connection piece and connecting it to the inlet line warmed by the heating tape ensured that there was not precipitation in the inlet line and that the solution successfully entered the reactor.

F.4 DISCUSSION OF HEAT OF ABSORPTION RESULTS

Two types of heat of absorption data can be measured experimentally, the integral and the differential heats of absorption. The integral heat of absorption is the more standard measurement in literature and is commonly measured using a flow calorimeter.(Carson et al., 2000; Mathonat et al., 1998) In flow calorimeters, two inlet streams of the amine and the CO₂ are fed continuously at defined ratios and the heat released over the course of the apparatus to absorb the CO₂ into the liquid is measured on-line. In this way, the heat need to absorb all of the CO₂ fed is measured. On the other hand, differential calorimetry measures the heat needed to absorb a small, differential amount of CO₂ added to the system. In this way, the same solution is utilized to cover the entire range of CO₂ loadings rather than a separate experiment to obtain each loading point, as with integral heats of absorption. When differential heats are measured, the integral heat can be calculated afterward according to the following equation for each loading point.

$$-\Delta H_{\text{int}} = \int_0^{\alpha} -\Delta H_{\text{diff}}(\alpha') d\alpha'$$

The reverse, calculating differential heats from integral heats is more difficult and usually contains more error. The calorimeter at NTNU is set-up for differential heat of absorption measurements. The integral heats of absorption were calculated from the collected differential heat data and are shown for all eight runs in Figure F.11.

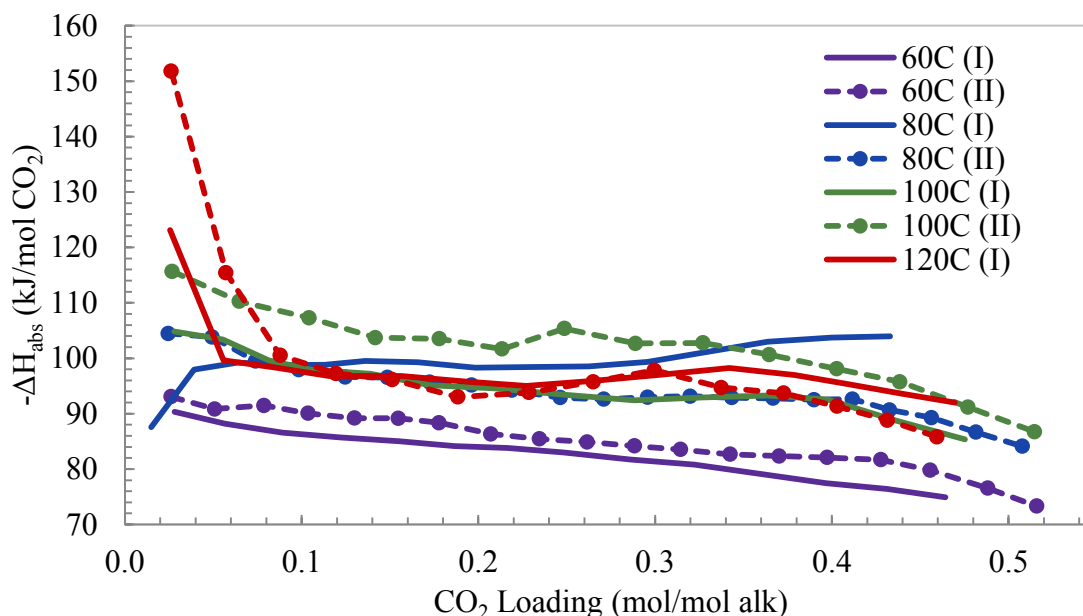


Figure F.11: Integral Heat of Absorption at 60, 80, 100, and 120 °C

As shown in Figure F.11, calculating the integral heats of absorption evens out the differential data and produces easier trends to interpret. Unfortunately, information is lost in performing the integral calculation. As with the heats of absorption in terms of moles of amine (Figure F.10), the data for 80 and 100 °C are quite different between the two runs performed at each temperature. Additionally, the large heat of absorption measured at the first loading for the two runs at 120 °C distort the trends for those runs. As mentioned before, the reason for this larger first measurement is not clear.

The heat of absorption measurements proved to be problematic for 8 m PZ. The data obtained at higher temperatures, primarily 80 and 120 °C, are very scattered within

each individual run and also between the two repeated runs. The cause of the high level of scatter in the higher temperature measurements is not well understood. It was observed that the baseline obtained after each CO₂ pulse was not as steady for the higher temperatures. This unsteady baseline was more difficult to manually integrate and likely resulted in higher errors than in the lower temperature measurements where the baseline was flat and well behaved. The response of the total power measurement over time is shown in Figure F.12 for multiple CO₂ pulses at 60 °C (panel A) and at 120 °C (panel B). This is a representative curve that demonstrates the difficulties encountered while integrating the higher temperature data. The chaotic baselines obtained at higher temperature seem to indicate that the calorimeter had more difficulty keeping a stable temperature, perhaps because of the thermostating oil having too low of a viscosity. All the experiments reported here were conducted with oil with a viscosity of 10 cP, but an oil with 50 cP may have been more able to maintain higher temperatures.



Figure F.12: Comparison of total power baselines for ΔH_{abs} measurements at 60 °C (panel A) and 120 °C (panel B)

The thesis of Hilliard is the only other source of heat of absorption data for aqueous PZ solutions (Hilliard, 2008). His work analyzed 2.4 m PZ and the results for 40, 80 and 120°C are shown below in Figure F.13. As expected, the heat of absorption increased with temperature while, as with other amine solvents, the heat of absorption decreased with increased CO₂ loading. The data at 120°C did not reach as high of a loading as the other data, so the data maintain approximately the same value from a loading of zero to 0.4.

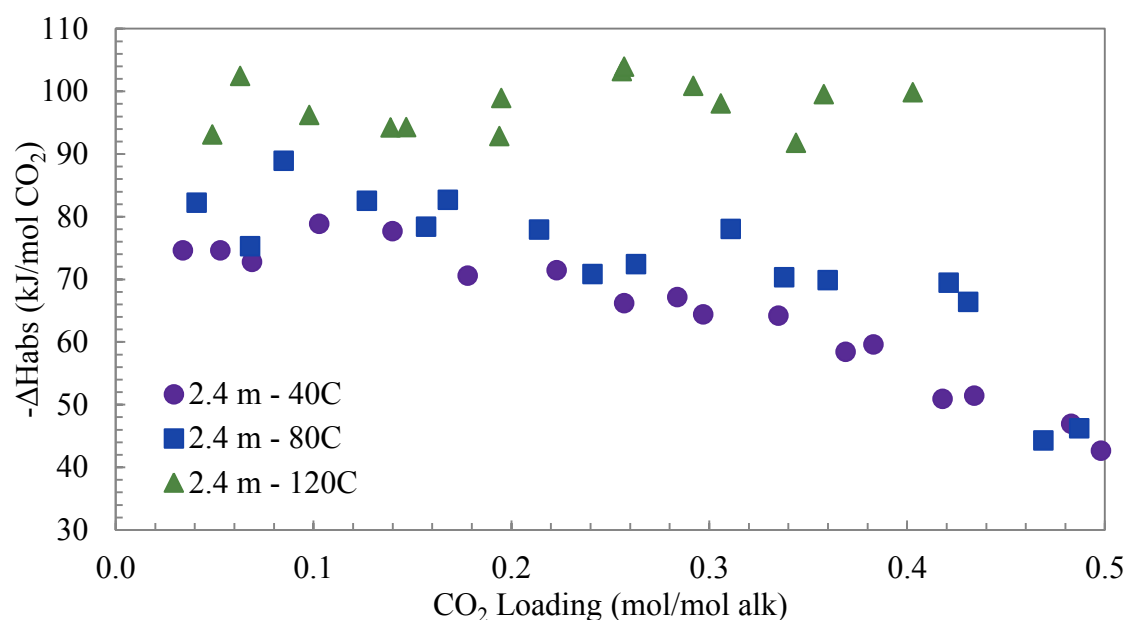


Figure F.13: Heat of absorption of CO₂ for 2.4 m PZ at 40, 80, and 120 °C (Hilliard, 2008)

The data for 8.0 m PZ shown above in the results section demonstrates similar trends, although the quality of data at higher temperatures is still under review.

In this initial phase of experimentation, the addition of lid heating since Kim's previous work was questioned. When the calorimeter was serviced (after the conclusion of most of Kim's work and before that of Hilliard), the lid of the vessel was modified to include an additional metal plate for insulation and a separate lid heating system. The specifics of the lid heating are not known and the control of the small electrical heater in the lid is not integrated with the rest of the calorimeter. Tests with the lid heating apparatus unplugged showed greater similarity with previous data on MEA and PZ so it was determined that lid heating should be abandoned. Calibration points were re-run at the experimental temperatures in the absence of lid heating to ensure complete elimination of the influence of lid heating from the system. Since lid heating was not integrated with the rest of the heat data collected by the calorimeter, it was decided that

this did not adequately reflect the heat of absorption and data collected with lid heating in place most likely had additional error.

F.5 CONCLUSIONS AND RECOMMENDATIONS

The heat of absorption measurements proved difficult due to solubility issues with the PZ and due to the differences in instrument stability at varying temperatures. Overall, the heat of absorption of PZ follows similar trends to other amines, such as MEA and MDEA, in that the heat of absorption trend stays relative constant over a range of low loadings until a threshold loading is reached, when the value decreases rapidly. For PZ, this decreased was observed to begin around a loading of 0.4 mole CO₂ per mole alkalinity or a loading of 0.9 to 1.0 mole CO₂ per mole PZ. In PZ, the data actually decrease slightly until the threshold where in MEA, the data remains quite constant until the threshold of 0.5 mole CO₂ per mole alkalinity is reached. For 8 m PZ at a loading of 0.025 mole CO₂ per mole alkalinity, the heat of absorption was 90.3, 104.5, 115.7, and 123.1 kJ per mole CO₂, respectively, at temperatures of 60, 80, 100, and 120 °C. After the initial loadings, there was little difference in the values for the heat of absorption between 80, 100, and 120 °C.

The nomenclature and abbreviations used throughout this section are summarized in Table F.3.

Table F.3: Nomenclature and abbreviations for heat of absorption calculations

Symbol	Units	Description
a	$\text{m}^3 \text{atm/mol}$	Parameter used in the Peng-Robinson equation of state; function of the gas constant, critical temperature, and critical pressure of a substance.
b	m^3/mol	Parameter used in the Peng-Robinson equation of state; function of the gas constant, critical temperature, and critical pressure of a substance.
BKA	$\text{W}/^\circ\text{C}$	Average total heat transfer between the thermostating media (silicon oil) and the outer reactor jacket, calibrated parameter based on dynamic system response during calibration
Calc_power	W	The power outputted by the recirculator to heat and cool the reactor contents as calculated using the six calibration parameters
CB	$\text{J}/^\circ\text{C}$	Heat capacity of the outer reactor jacket, fixed at 1500 for this calorimeter
CR	$\text{J}/^\circ\text{C}$	Heat capacity of the reactor contents, including the solution, contributions from the stirrer, reactor base, and interior walls; calibrated parameter based on solvent and temperature in use
dF_DT_reactor	$^\circ\text{C}$	Difference in temperature between jacket (taken at the inlet) and the reactor ($T_r - T_j$); recorded variable during calorimeter experiments
dH _{online}	J	Heat exchanged between the circulator and the reactor contents, calculated as the area under a curve of time (s) vs. Total_power (W)
dH _{calc}	J	Heat exchanged between the circulator and the reactor contents, calculated as the area under a curve of time (s) vs. Calc_power (W), used for comparison to dH _{online} and calibration
dT/dt	$^\circ\text{C}/\text{sec}$	Change in reactor temperature with time; recorded variable during calorimeter experiments.
FlowCp	$\text{W}/^\circ\text{C}$	Product of the volumetric flow rate, density, and heat capacity of the thermostating media (silicon oil), usually 600 – 900 $\text{W}/^\circ\text{C}$, calibrated parameter based on temperature
HB_DT_reactor	$^\circ\text{C}$	Temperature difference in silicon oil between entering and exiting the reactor ($T_{j(\text{out})} - T_{j(\text{in})}$); recorded variable during calorimeter experiments

**Table F.3: Nomenclature and abbreviations for heat of absorption calculations
(Continued)**

Symbol	Units	Description
H _{Loss_DT_reactor}	°C	Average temperature gradient across the insulation between the reactor jacket and the outer metal shield ($T_{HL(inner)} - T_{HL(outer)}$); recorded variable during calorimeter experiments
H _{lossC}	W/°C	Heat Conductivity coefficient to characterize heat losses through the thermal shield, usually 1 – 1.4 W/°C, calibrated parameter based on temperature
n	mol	Number of moles
P _C	Bar	Critical pressure
PZ	-	Piperazine (abbreviation)
R	J/mol-K	Universal gas constant
T _C	K	Critical temperature
T _j	°C	Calculated Temperature of the jacket of the calorimeter; function of T _{ref} , BKA, and CB
T _{j(in)}	°C	Temperature of the jacket at the inlet of the thermostating media
T _{j(out)}	°C	Temperature of the jacket at the exit of the thermostating media
T _{j, i}	°C	Temperature of the jacket of the calorimeter at point i
T _{j, (i-1)}	°C	Temperature of the jacket of the calorimeter at point (i-1)
T _r	°C	Temperature of the reactor contents
T _R	K	Reduced temperature, ratio of temperature and the critical temperature of a substance
T _{ref}	°C	Measured temperature of the thermostating media (silicon oil)
Total _{power}	W	The power directly outputted by the recirculator to heat and cool the reactor contents through the silicon oil; recorded variable during calorimeter experiments
V	m ³	Volume, used in Peng-Robinson equation of state
α	-	Parameter used in the Peng-Robinson equation of state; function of temperature and ω, the Pitzer acentric factor
ω	-	Pitzer acentric factor, used for Peng-Robinson equation of state

Appendix G – Details of IC-MS Analysis

An example of the type of details MS work that was done during this project is provided in this appendix. The details of each degraded sample analyzed with IC-MS in this project are not provided anywhere due to space constraints. In this appendix, a full IC-MS analysis is shown for a set of standards and one thermally degraded sample, the final sample of TE12. These are provided as an example of the type of work done to identify degradation products in oxidized and thermally degraded PZ samples.

G.1 IC-MS ANALYSIS OF STANDARDS

PZ derivatives that are suspected degradation products were analyzed with cation IC-MS. IC-MS was used to identify where the compounds would show up on a cation IC chromatogram and what mass-to-charge (m/z) ratios would be shown for each compound. It is expected that each compound would acquire one proton making its m/z equal to the

molecular weight plus one. However, it is possible that each molecule could behave differently than expected. For example, two molecules can attach to the same charge ($m/z = 2 \times MW + 1$) or a molecule attaching to potassium or sodium ion in the system ($m/z = MW + 23$ or 40) to represent their mass differently from expected.

The compounds tested are shown below in Table G.1. The molecular weight and expected m/z for each compound is shown as well as its chemical structure. The cation IC-MS chromatograms for a 1000 ppm solution of each species are shown in Figure G.1 through G.16. In each figure, the top panel is the total MS signal over the course of the chromatographic separation. The bottom panel is the cation IC chromatogram total conductivity signal. The panels are aligned so that they correspond in time.

Table G.1: Summary of PZ Derivatives Analyzed by Cation IC-MS

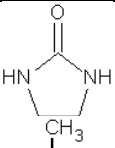
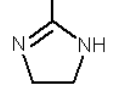
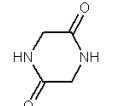
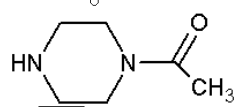
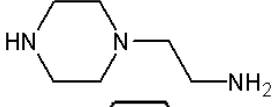
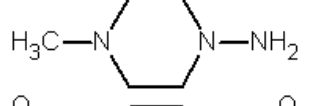
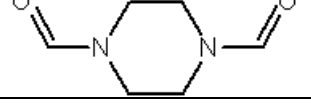
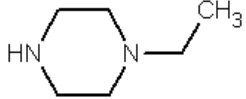
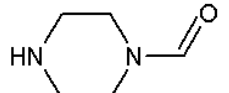
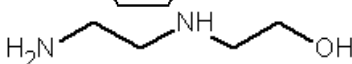
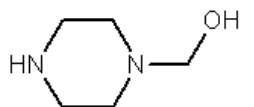
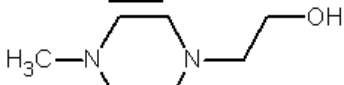
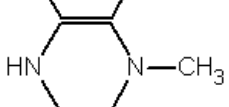
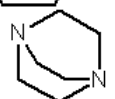
Compound	Abb.	MW (g/mol)	Expected m/z	Chemical Structure
2-Imidazolidone	-	86.1	87.1	
2-Methyl-2-imidazoline	-	84.1	85.1	
2,5-piperazindione	-	114.1	115.1	
N-Acetyl PZ	AcPZ	128.2	129.2	
N-(2-Aminoethyl) PZ	AEPZ	129.2	130.2	
N-Amino-N'-Methyl-PZ	AMPZ	115.2	116.2	
N,N'-Diformyl PZ	DFPZ	142.2	143.2	

Table G.1: Summary of PZ Derivatives Analyzed by Cation IC-MS (Continued)

Compound	Abb.	MW (g/mol)	Expected m/z	Chemical Structure
N,N'-Dimethyl PZ	DMPZ	114.2	115.2	
Ethylenediamine	EDA	60.1	61.1	
N-Ethyl PZ	EPZ	114.2	115.2	
N-Formyl PZ	FPZ	114.2	115.2	
N-(2-Hydroxyethyl) EDA	HEEDA	104.2	105.2	
N-Hydroxyethyl PZ	HEP	130.2	131.2	
N-(2-Hydroxyethyl)-N'-Methyl PZ	HEMP	144.2	145.2	
N-Methyl PZ	1-MPZ	100.2	101.2	
Triethylenediamine	TEDA	112.2	113.2	

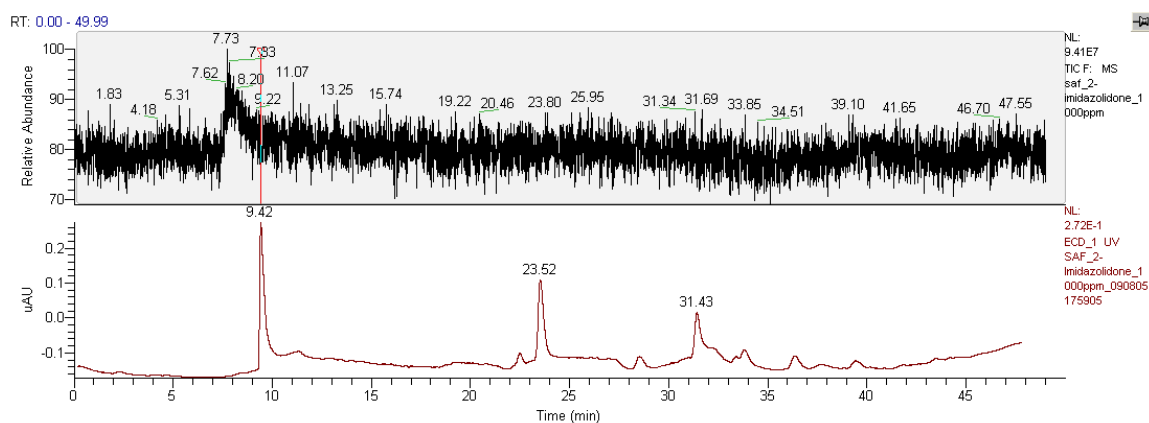


Figure G.1: Cation IC-MS chromatogram for 1000 ppm 2-Imidazolidone (2-Imid)

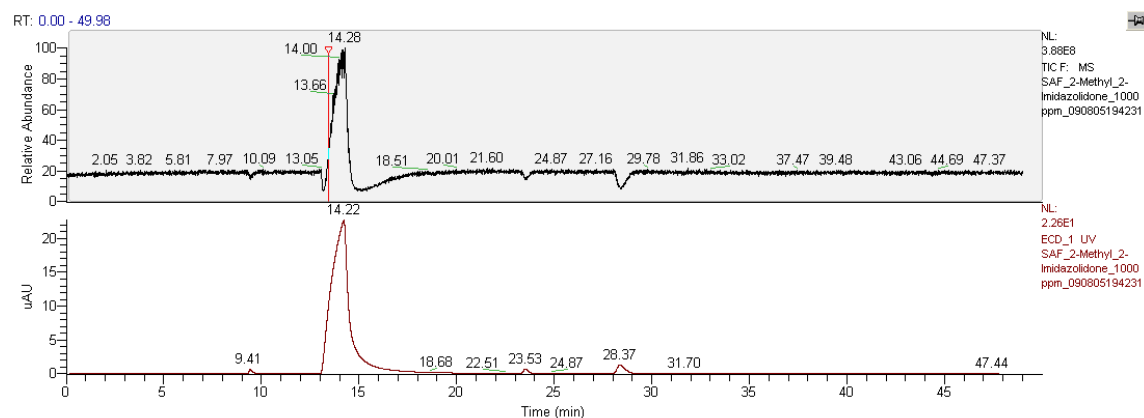


Figure G.2: Cation IC-MS chromatogram for 1000 ppm 2-Methyl-2-Imidazoline

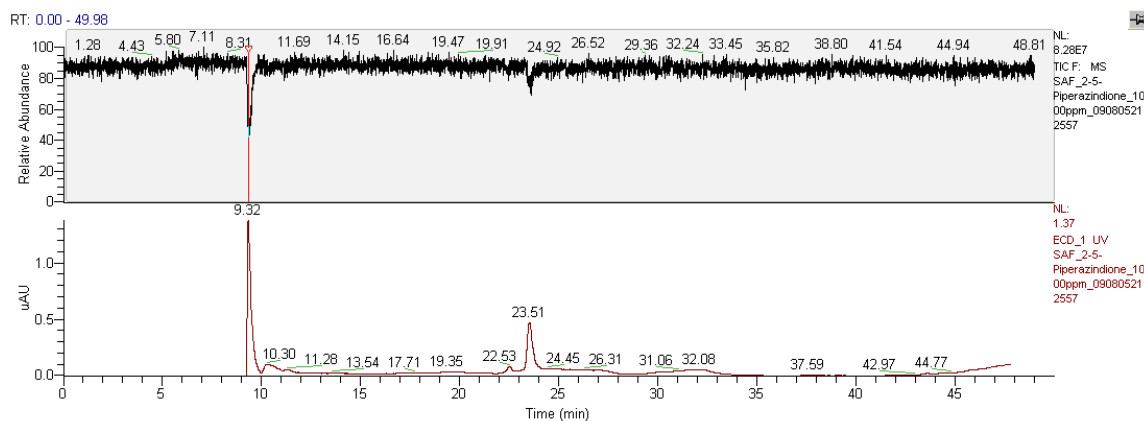


Figure G.3: Cation IC-MS chromatogram for 1000 ppm 2,5-Piperazindione

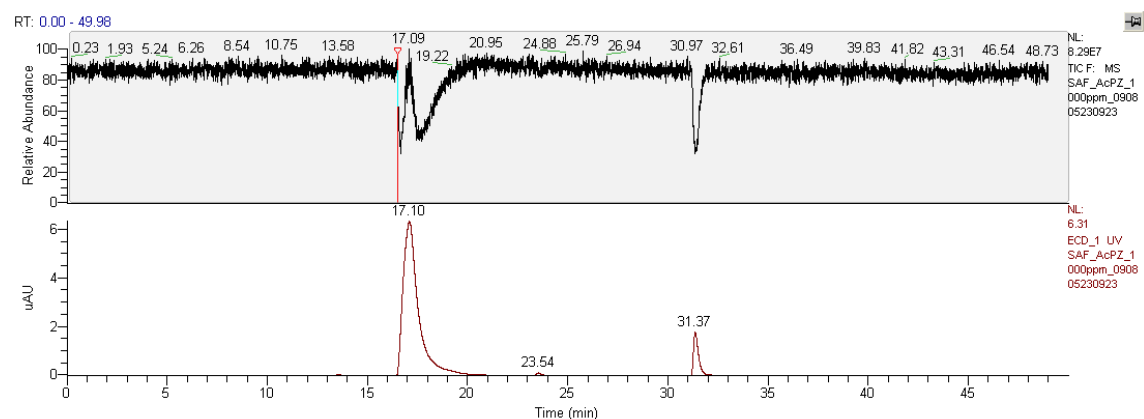


Figure G.4: Cation IC-MS chromatogram for 1000 ppm N-Acetyl PZ (AcPZ)

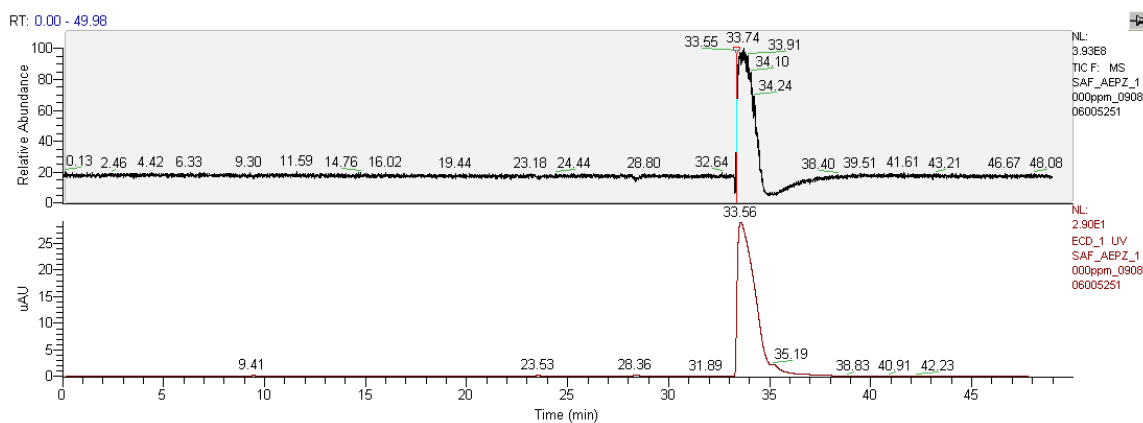


Figure G.5: Cation IC-MS chromatogram for 1000 ppm AEP

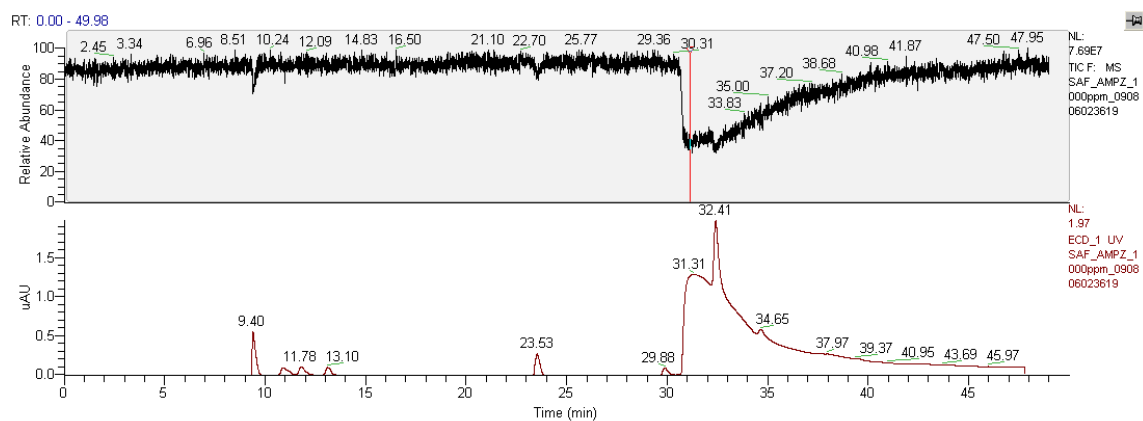


Figure G.6: Cation IC-MS chromatogram for 1000 ppm AMPZ

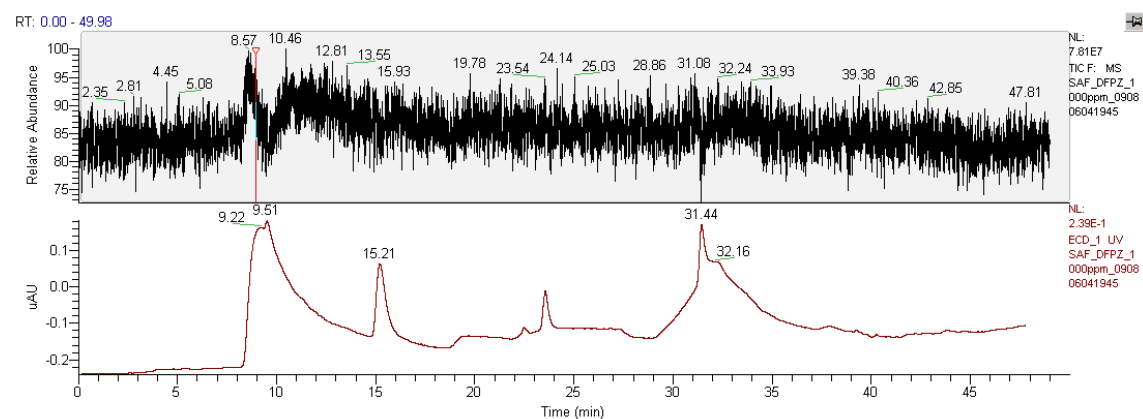


Figure G.7: Cation IC-MS chromatogram for 1000 ppm N,N'-Di-formyl PZ (DFPZ)

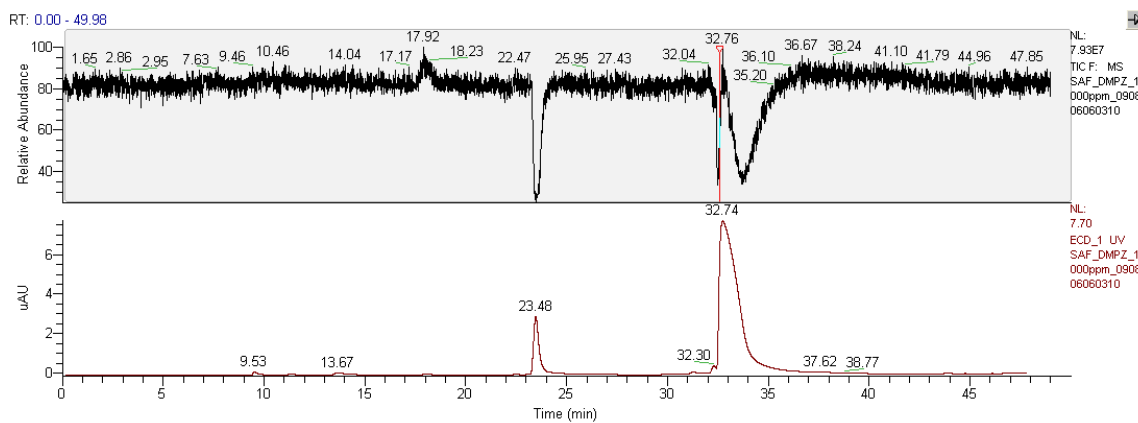


Figure G.8: Cation IC-MS chromatogram for 1000 ppm 1,4-DMPZ

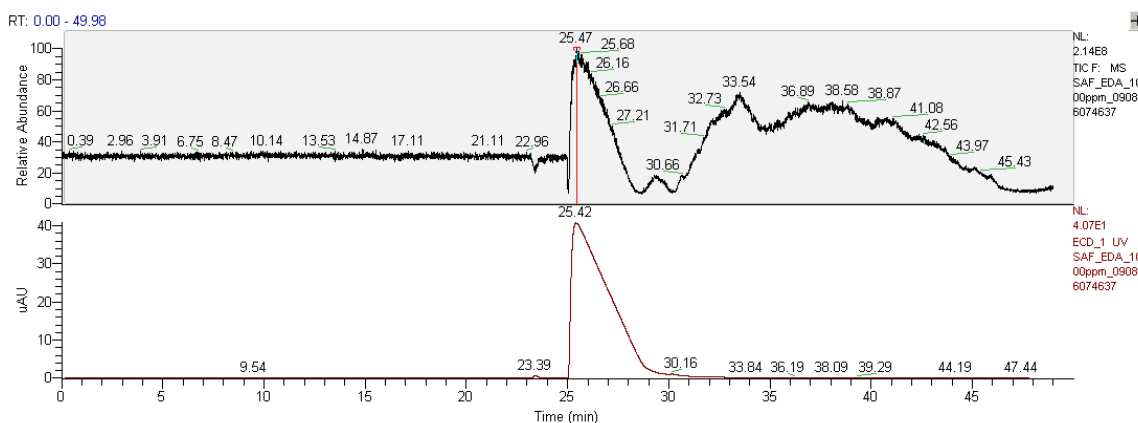


Figure G.9: Cation IC-MS chromatogram for 1000 ppm EDA

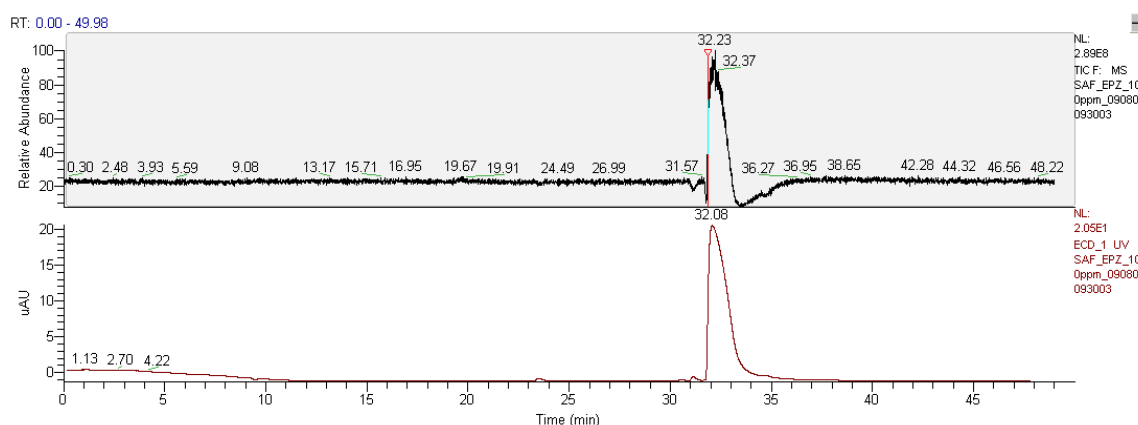


Figure G.10: Cation IC-MS chromatogram for 1000 ppm N-Ethyl PZ (1-EPZ)

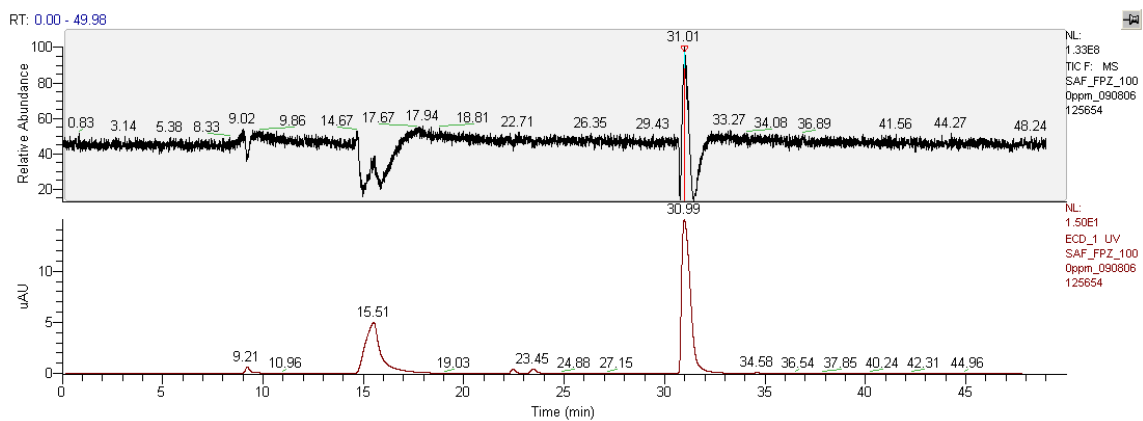


Figure G.11: Cation IC-MS chromatogram for 1000 ppm N-formylpiperazine (FPZ)

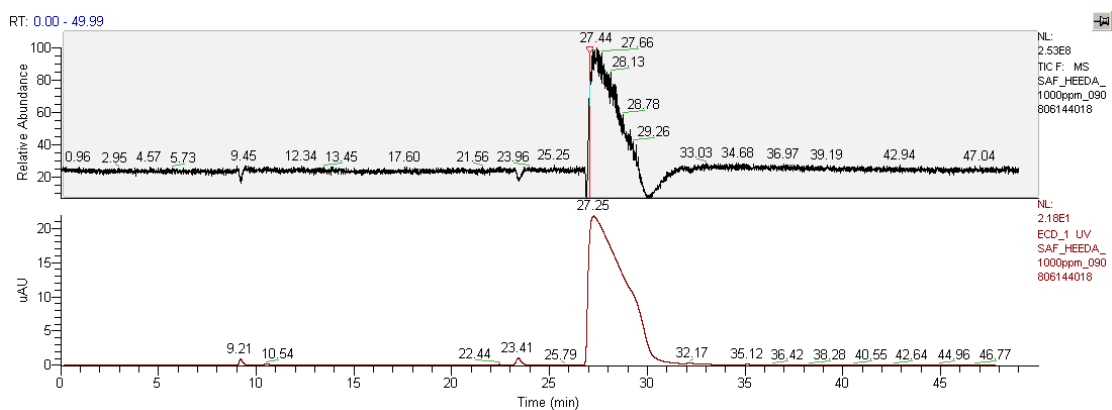


Figure G.12: Cation IC-MS chromatogram for 1000 ppm HEEDA

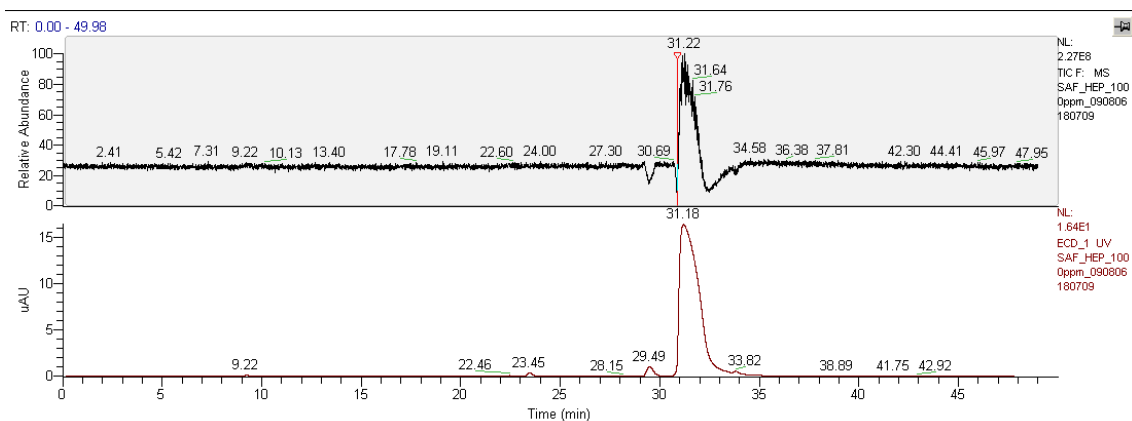


Figure G.13: Cation IC-MS chromatogram for 1000 ppm HEP

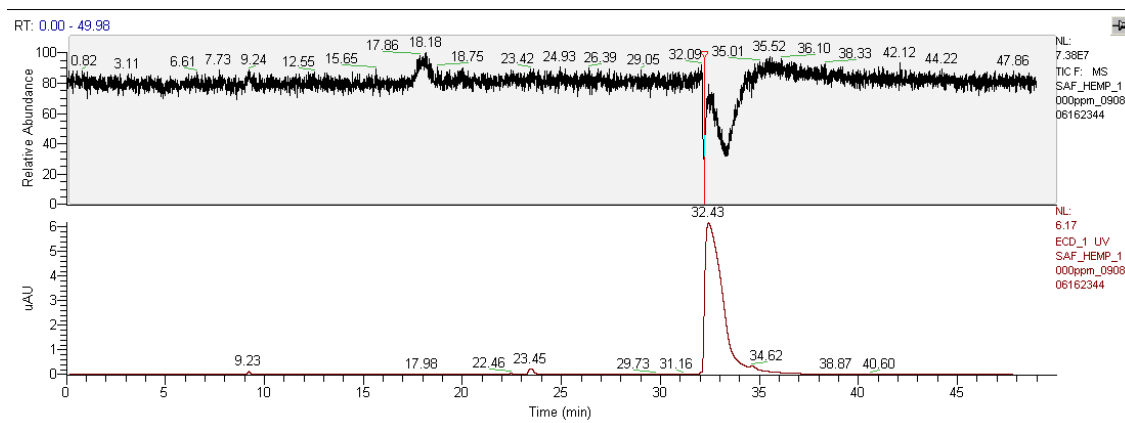


Figure G.14: Cation IC-MS chromatogram for 1000 ppm HEMP

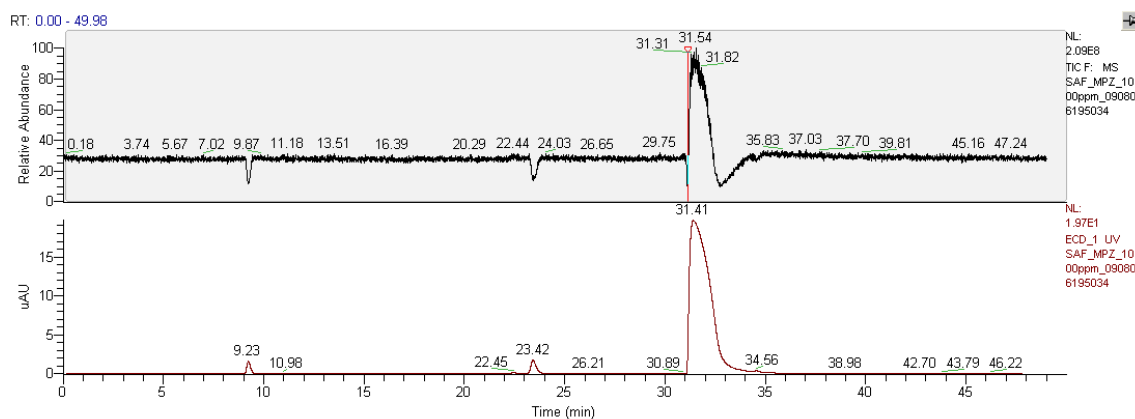


Figure G.15: Cation IC-MS chromatogram for 1000 ppm N-methyl PZ (1-MPZ)

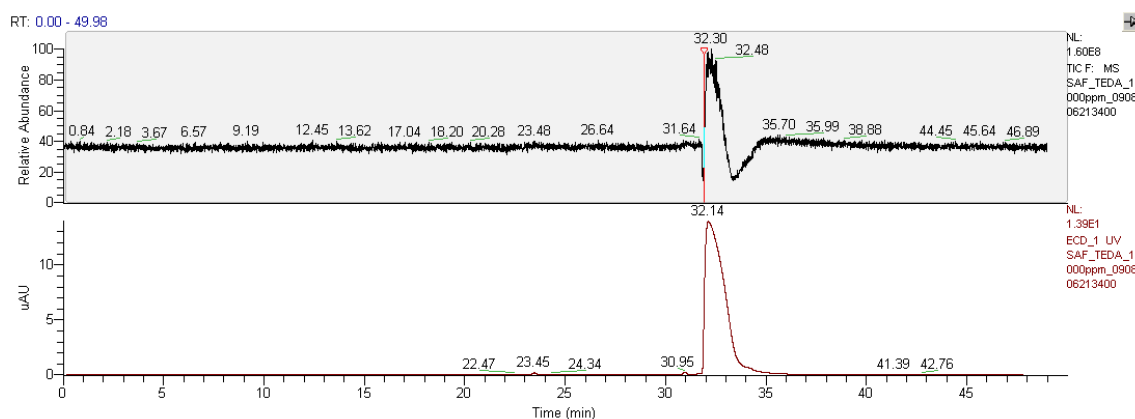


Figure G.16: Cation IC-MS chromatogram for 1000 ppm TEDA

Of the 16 derivatives analyzed by Cation IC-MS, 13 of the species (AcPZ, AEP, AMPZ, DFPZ, 1,4-DMPZ, EDA, 1-EPZ, FPZ, HEEDA, HEP, HEMP, 1-MPZ and TEDA) all gave clear chromatograms with good responses from the primary analyte. Each of these chromatograms had a primary peak that is significantly larger than any secondary peaks and contained the expected m/z value for the given compound. The retention times varied and a few, such as FPZ, had visible PZ contamination peaks. It is not believed that 2-Imid, 2,5-piperazindione, and DFPZ have any significant cation IC response and any peaks shown in the figures above are just background or contaminant species that respond to cation IC.

A comparison of the analytes and their performance on cation IC-MS is shown below in Table G.2. For each analyte, the retention time of the main peak, any other m/z ratios found in that peak, and the maximum signal response of the main peak is shown. The other m/z ratios found in the main peak are indicated because seven of the analytes formed doublets in the main peak (indicated by * in the table). Doublets occur when two analyte molecules attach to one charge, giving a m/z ratio that corresponds to $2 \times MW + 1$. Two analytes, 1,4-DMPZ and 1-EPZ behaved differently as the main secondary m/z in the primary peak corresponded to $2 \times MW - 1$. It is not clear time how this m/z resulted or how the structure of 1,4-DMPZ and 1-EPZ led to this difference. Also, since all the analytes were 1000 ppm, the maximum response gives an indication of the response factor a particular analyte has for the cation IC conductivity detector.

The results shown in Table G.2 reveal important information on where PZ derivatives are expected cation IC chromatograms of degraded PZ samples. First off, the differences in maximum response are very helpful. For the same concentration (1000 ppm), the responses vary from 0.2 to 40. This explains why EDA is one of the most easy degradation products to detect with cation IC. EDA has a retention time separate from

most of the other analytes and has a large response factor. Analytes that have small response factors (AMPZ, and DFPZ) are not likely to be detected in experimental samples unless their concentrations are very high. The retention times also indicate that quite a few analytes overlap and elute at similar times, therefore making it difficult to distinguish between the two (or more) analytes. One set of analytes, HEP, AMPZ, and 1-MPZ, elude within 0.2 minutes of each other. EDA and HEEDA are within 1.8 minutes of each other while are all within only 0.2 minutes. Finally, EPZ, HEMP, and 1,4-DMPZ are all within 0.6 minutes of each other.

Table G.2: Summary of PZ Derivative Cation IC-MS Results

Compound	Abb.	RT (min)	Also in Main Peak (m/z)	Maximum Response (uAU)	Notes
2-Imidazolidone		9.43	105.1	0.2	
2-Methyl-2-imidazoline		14.22	103.1, 205.1	23	+
2,5-piperazindione		9.32	77.0, 129.2	1.4	+
N-Acetyl PZ	AcPZ	17.10	257.2*	6	^
N-(2-Aminoethyl) PZ	AEP	33.56	130.1	28	
N-Amino-N'-Methyl-PZ	AMPZ	~31-32	114.1	2	
N,N'-Diformyl PZ	DFPZ	9.22	161.1	0.2	
N,N'-Dimethyl PZ	1,4-DMPZ	32.74	227.2*	8	
Ethylenediamine	EDA	25.42	121.1*	40	
N-Ethyl PZ	1-EPZ	32.08	227.2*	20	^
N-Formyl PZ	FPZ	15.51	229.1*, 87.1	15	^
N-(2-Hydroxyethyl) EDA	HEEDA	27.25	209.1*	22	
N-Hydroxyethyl PZ	HEP	31.18	129.1	16	
N-(2-Hydroxyethyl)-N'-Methyl PZ	HEMP	32.43	145.1, 287.1*	6	
N-Methyl PZ	1-MPZ	31.41	101.1, 119.1	16	
Triethylenediamine	TEDA	32.14	113.1, 225.2*	15	

* Secondary m/z found in peak is doublet of analyte

+ Primary analyte is not in main peak. Details of main peak are still given.

^ PZ contamination is present at PZ RT of ~30.5 to 31 min

G.2 CONFIRMATION OF PZ CARBAMATE WITH IC-MS

The presence of piperazine carbamate in aqueous, loaded PZ solutions was confirmed using MS with direct injection. This confirmation was made in both positive

and negative ion mode. In positive ion mode, the PZ carbamate exists as its protonated acid form. In negative ion mode, PZ carbamate usually exists as drawn (PZCOO⁻). Both structures are shown in Figure G.17.

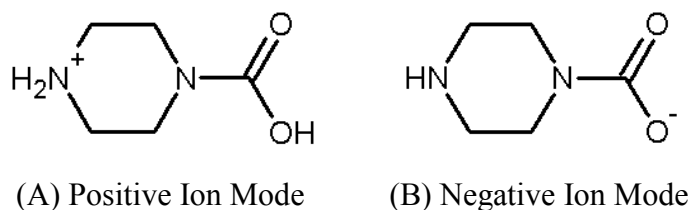


Figure G.17: Structure of PZ carbamate as seen in (A) positive and (B) negative ion modes of the MS

To confirm this species was present, an 8 m PZ solution with a loading of 0.3 mole CO₂ per mole alkalinity was tested on the MS using direct infusion (i.e., not utilizing any chromatographic separation). In positive mode, the species of interest (Figure G.17, panel A) has a mass-to-charge (m/z) ratio of 131.15. In order to verify the molecule, a total scan of m/z of 30 to 150 was done to see the prevalence of 131.2. The peak at 87.1 for PZ was dominant, so collision-induced disassociation (CID) was performed to isolate the molecule of interest. In CID, a filter is applied between the first and second quadrupoles of the instrument that only allows the particular m/z of interest (known as the parent molecule) to reach the second quadrupole. All other masses are deflected to the waste stream. A voltage (0 to 50 eV) is applied to the second quadrupole to induce disassociation of the parent molecule. The fragments then travel to the third quadrupole and are detected.

The CID for m/z 131.2 is shown in Figure G.18 for positive mode of the MS. The parent fragment of 131.2 is clearly visible as well as fragments at 114.3 and 85.3. The

fragment at 114.3 is a loss of 16.9 (~17) which is likely a loss of NH_3 during fragmentation. The fragment at 85.3 is a loss of 45.9 (~46) or a loss of HCOOH .

In negative mode, the same procedure of direct infusion was followed and the m/z of interest was 129.1. The CID for m/z 129.1 is shown in Figure G.19 for negative mode of the MS. The parent fragment of 129.1 is clearly visible as well as primary fragment at 84.8 and a small fragment at 45.2. The fragment at 84.8 is a loss of 44.3 or COO^- .

The fact that 131.2 and 129.1 m/z could be isolated and fragmented in positive and negative mode, respectively, indicates the presence of PZ carbamate in solution. Also, in both modes a dominant fragment was the loss of a carbamate piece of the structure (either -44 or -46). Both allude to the presence of PZ carbamate.

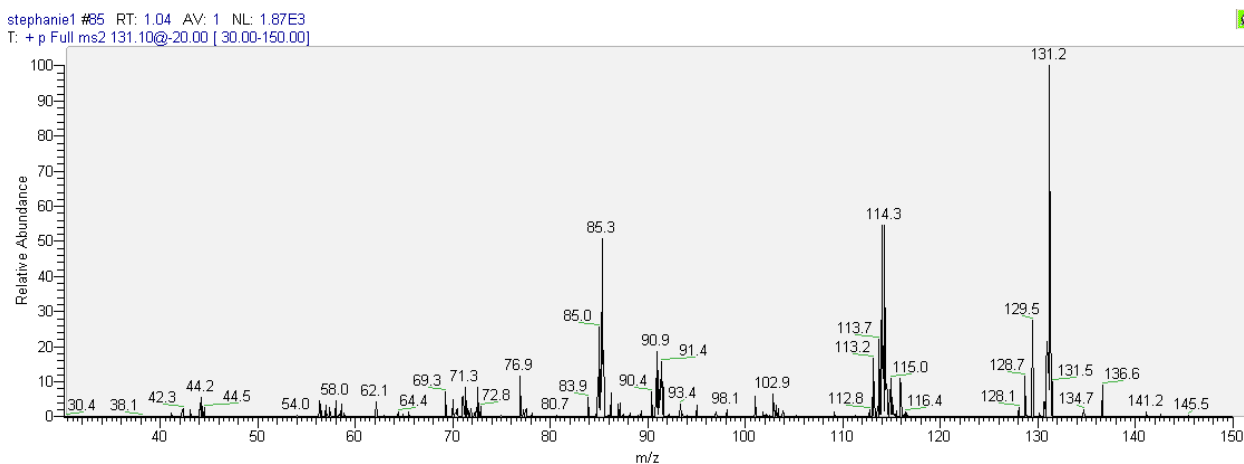


Figure G.18: Total Ion Current (TIC) graph for CID of 131.1 in positive mode

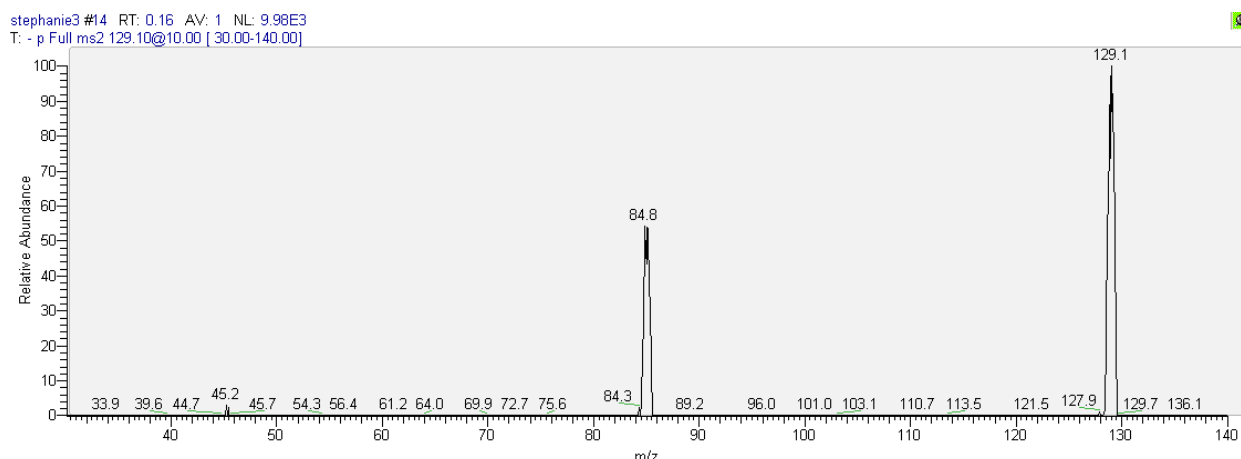


Figure G.19: Total Ion Current (TIC) graph for CID of 129.1 in negative mode

A common m/z ratio that co-elutes with PZ at a retention time of 30.5 minutes was also identified. The m/z of 105.1 is always found with the large PZ peak on the cation IC-MS and has the second highest response in terms of ion current, after PZ. This m/z has been identified as the hydrated form of protonated PZ, or $PZH^+ \cdot H_2O$. During electrospray ionization (ESI), both a PZ and a water molecule are co-coordinated with one proton. The mass of this molecule is 105.1 with one charge, giving a m/z of 105.1. A representation of this molecule is shown below in Figure G.20.

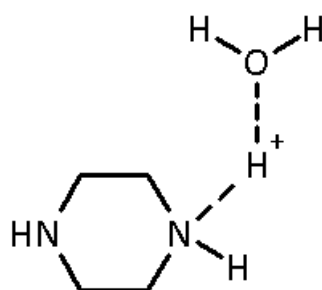


Figure G.20: Representation of $PZH^+ \cdot H_2O$ as it would appear after ESI

G.3 IC-MS ANALYSIS OF THERMALLY DEGRADED PZ (TE12, T=15 WEEKS)

A detailed cation IC-MS analysis was performed for the final sample of TE12. In TE12, 8 m PZ with 0.3 mole CO₂ per mole alkalinity was degraded for 15 weeks. This sample was chosen to represent the most heavily degraded sample and, therefore, most likely to contain all of the important species of interest. This solution was analyzed with cation IC-MS and the resulting data was analyzed for the possible identity of the unknown peaks.

The raw data for the final sample of TE12 (t=15 weeks) is shown in Figure G.21. The top portion of the figure is the Total Ion Current from the MS while the IC chromatograph is shown in the bottom half of the figure. The two signals are adjusted so the timing of the horizontal axis matches. This sample is heavily degraded and there are numerous peaks in both panels. Peaks in the TIC signal sometimes appear with negative deflection if the sample hitting the sensor is relatively small. When higher concentrations of ions hit the sensor, the negative deflection revers to create a positive deflection, as with the PZ peak at 30.86 minutes.

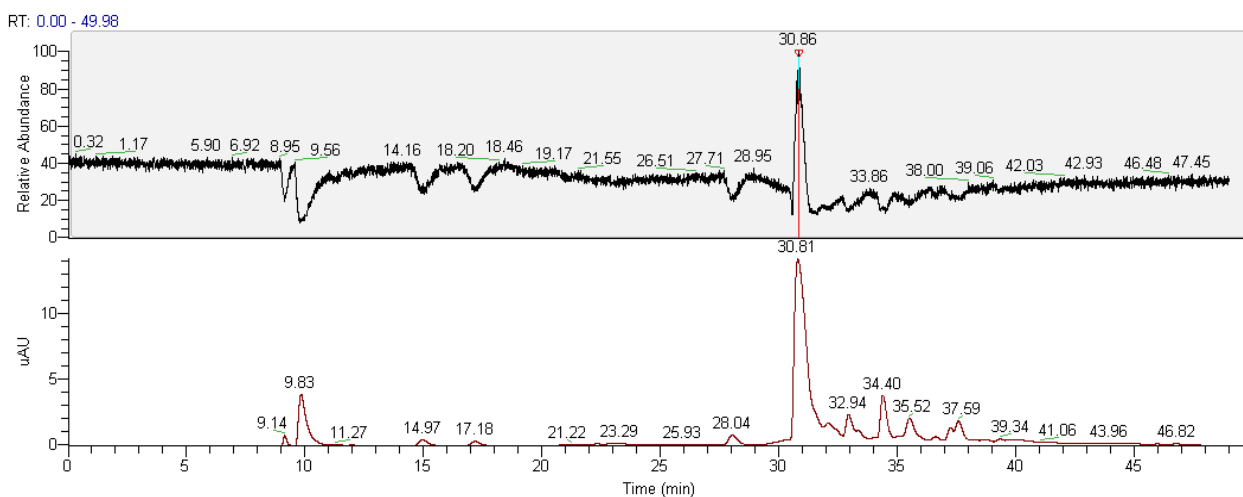


Figure G.21: Total Ion Current for m/z 50.0-300.0 and Cation IC Chromatograph for TE12 t=15 weeks

In the Xcalibur software where data analysis occurs, the TIC signal can be analyzed in two ways. First, the signal can be scanned over time to determine the most abundant m/z values for any given position in the chromatogram. Second, a particular mass range of ions can be isolated to see where a particular ion elutes in relation to the IC chromatogram. This is a powerful way to relate a particular ion of interest to a peak on the IC chromatogram. To demonstrate this technique, Figure G.22 through G.24 show three different isolated m/z or mass ranges.

In G.22, the mass range for PZ (87.1 ± 0.5 m/z) is isolated. The peak corresponding to where PZ elutes is clearly distinguished in both the Total Ion Current and the cation IC. The peak assigned to PZ at a retention time of 30.8 minutes is confirmed to have the expected m/z of 87.1 (MW+1).

For smaller, unknown IC peaks, the next two figures demonstrate the utility of this type of data analysis. In Figure G.23, the mass range of 115.1 ± 0.5 m/z is isolated and three distinct peaks are shown that correspond to smaller peaks on the IC chromatograph. Multiple possible species are suspected with this molecular weight (114 g/mol) including N-formylpiperazine (FPZ), N-ethylpiperazine (1-EPZ), N,N'-dimethylpiperazine (1,4-DMPZ), 2,5-piperazindione, and 2,5-dimethylpiperazine. By matching to the standard curves presented in section G.1, it is clear from Figure G.10 and G.11 that the first and third peaks correspond to FPZ and 1-EPZ, respectively. The retention times are slightly off because of the differences in analysis unrelated to the chromatogram.

In Figure G.24, the mass range of 130.2 ± 0.5 m/z is isolated and it is clear that two peaks on the IC chromatogram have been identified as molecules with a molecular weight of 129.2 g/mol. By matching to Figure G.5, the peak at a retention time of 34.4

minutes corresponds to AEP. The identity of the peak at 17.2 minutes is not know at this time but one strong candidate is 1-(2-aminoethyl)-2-imidazolidone (CAS 6281-42-1).

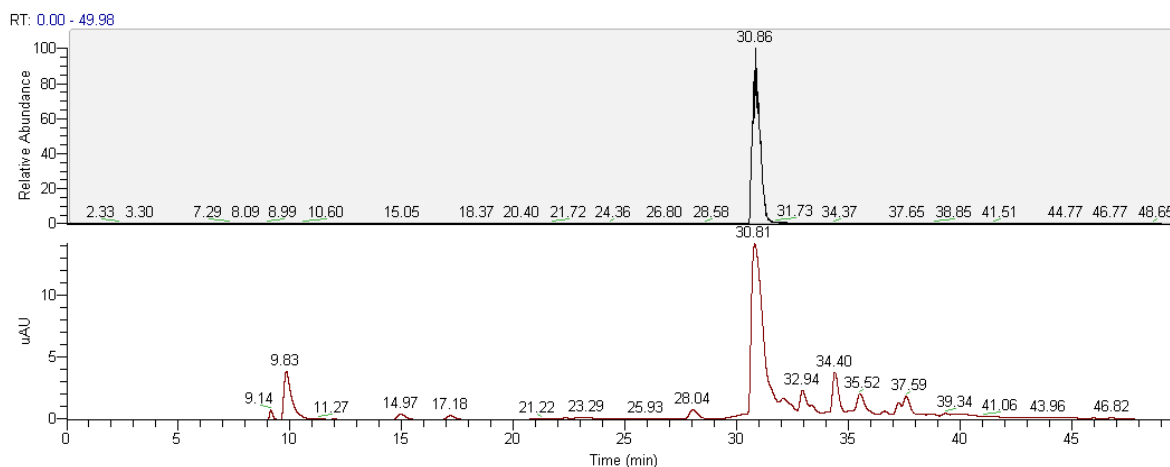


Figure G.22: Total Ion Current for m/z 86.6–87.6 and cation IC chromatograph for TE12 t=15 weeks

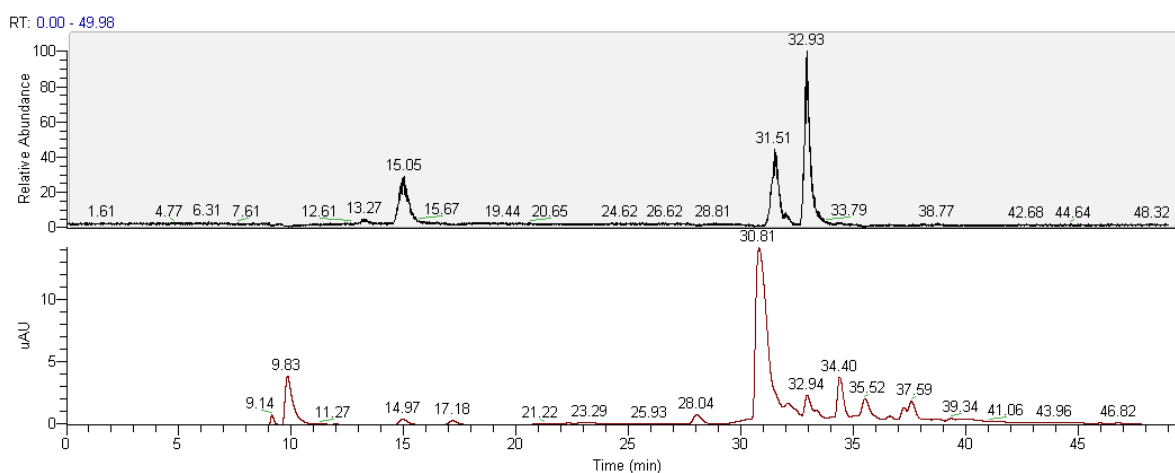


Figure G.23: Total Ion Current for m/z 114.7–115.7 and cation IC chromatograph for TE12 t=15 weeks

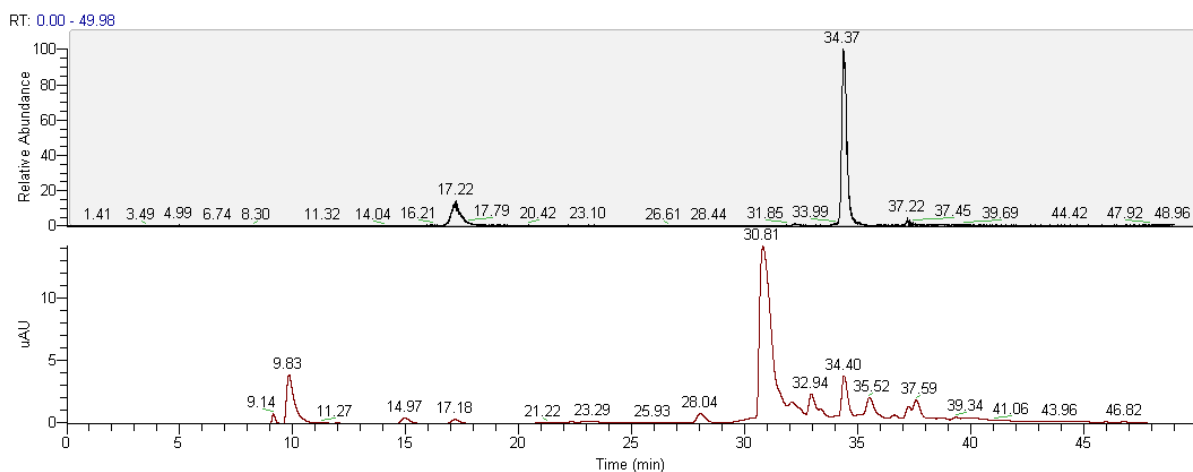


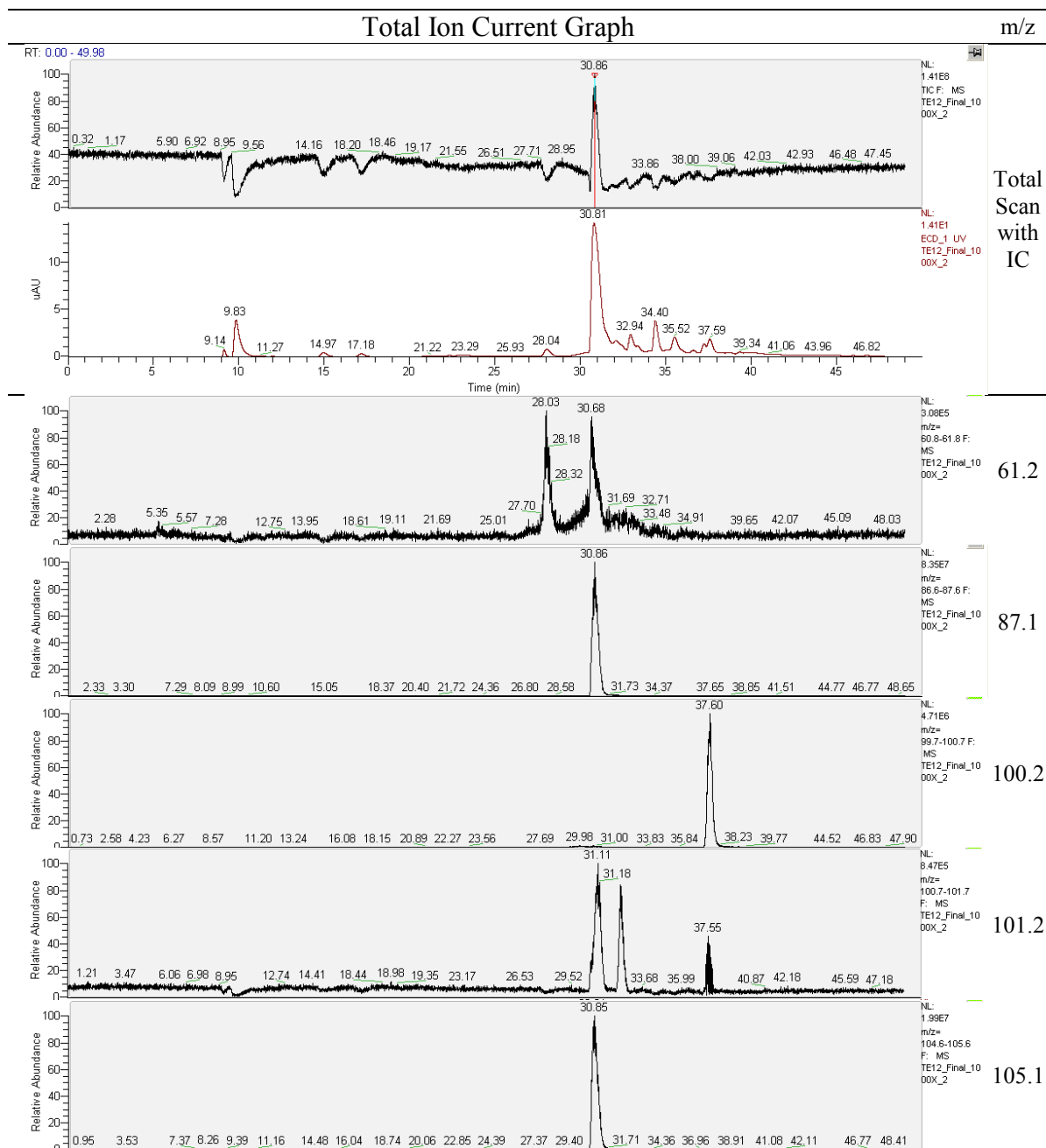
Figure G.24: Total Ion Current for m/z 129.7–130.7 and Cation IC Chromatograph for TE12 $t=15$ weeks

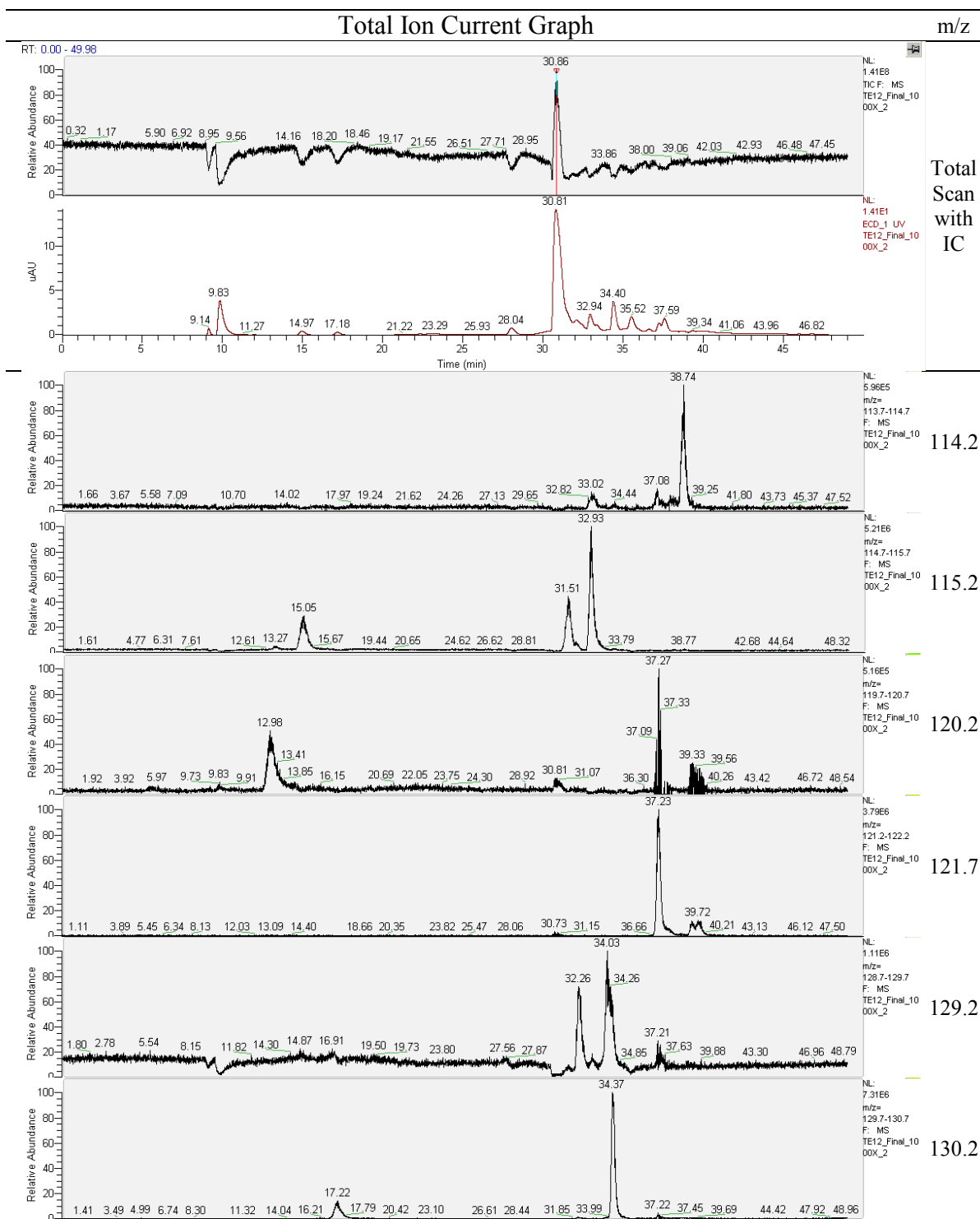
The utility of isolating a specific m/z ratio makes a complicated spectrum more accessible. For degraded PZ solutions, the diamine and triamine section of the cation IC chromatograph will always be complicated as degradation increases. First pass analysis of the raw data determines which m/z values are of interest to isolate. Isolation helps with identification and quantification that would otherwise not be possible in such a crowded part of the IC chromatogram.

This final sample of TE12 is further analyzed below by isolating all of the dominant m/z ratios found any point in the total ion current raw data. The total ion current was isolated for those m/z ratios ± 0.5 m/z to determine the time at which species eluted off the IC column. The isolated total ion current graphs for all of the m/z ratios of interest are compared to the total ion current for 50–300 m/z in Table G.3. This allows the reader to see which molecular weights are co-eluting and which molecular weights are responsible for each of the dominant peaks. The total ion current for 50–300 m/z with the corresponding IC chromatograph is repeated at the top of each page of Table G.3.

A summary of the important m/z ratios is given in Table G.4 along with potential molecules that correspond to the indicated molecular weight.

Table G.3: Isolated m/z ± 0.5 for degradation products of TE12 on Cation IC-MS





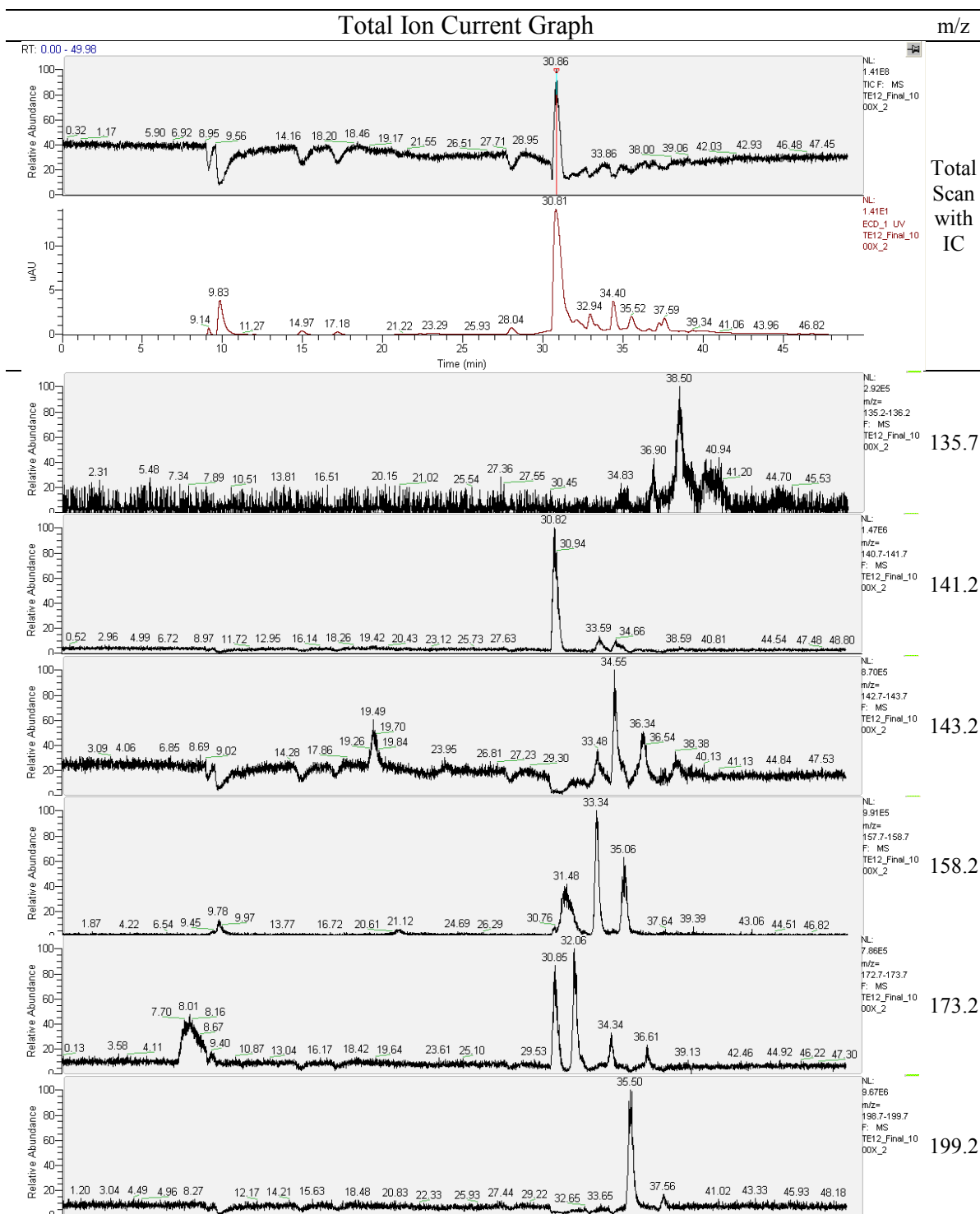


Table G.4: Possible identification of the major peaks from isolated m/z ratios in TE12

m/z	MW	Possible Species (Confirmed) (RT of Standard)	Major Peaks (Dominant)
61.3	60.2	EDA (27.80 mins)	28.0, 30.7
87.1	86.1	PZ (30.9 mins)	30.9
100.2	99.2		37.6
101.2	100.2	N-methyl PZ (31.41 mins) 2-methyl PZ 2-piperazinone	31.1, 32.2, 37.55
105.1	104.1	PZ·H₂O	30.9
114.2	113.1		38.8
115.2	114.2	2,5-piperazinedione N-Formyl PZ (15.5 mins) 1,4-Dimethyl PZ (32.79 mins) 2,5-Dimethyl PZ N-Ethyl PZ (32.08 mins)	15.0, 31.5, 32.9
120.2	119.2	MDEA N1-(2-aminoethyl)-N1-hydroxy-1,2-Ethanediamine	13.0, 37.3
121.7	120.7	N,N'-bis(Hydroxymethyl) urea N,N'-di(hydroxymethyl) EDA	37.2, 39.7
129.2	128.2	N-Acetyl PZ (ruled out due to NaOH treatment)	32.3, 34.0
130.2	129.2	PZCOO ⁻ 1-(2-Aminoethyl)-2-imidazolidone (17.10 min) 1,4,7-Triazacyclononane N-(2-aminoethyl) PZ (33.56 mins)	17.2, 34.4
135.7	134.7		38.5
141.2	140.2		30.8, 33.6, 34.7
143.2	142.2	N,N'-Diethyl PZ N,N'-Diethyl PZ (34.4) (v. small concentration)	19.5, 34.6
158.2	157.2		31.5, 33.3, 35.0
173.2	172.2	PZ(COO ⁻) ₂ 1-[2-[(2-aminoethyl)amino]ethyl] PZ (AEAEPZ) (suspected at 36.6 mins) N,N'-bis(2-aminoethyl) PZ (DAEP)	8.0, 30.9, 32.0, 34.3, 36.6
199.2	198.2	1,1'-carbonylbis-PZ (diPZ urea) Urea of AEAEPZ (suspected at 35.5 mins) 1,1'-(1,2-ethanediyl)bis-PZ (PEP) (suspected at 37.6 mins)	35.5, 37.6
213.2	212.2		23.0, 30.8, 37.0
227.2	226.2	1,1'-(1,2-dioxo-1,2-ethanediyl)bis PZ 1-ethyl-4-[2-(1-piperaziny)ethyl] piperazine	15.0, 26.0, 36.6, 37.6, 40.6
242.2	241.2		30.9, 35.8, 37.2
259.2	258.2		14.7, 17.2, 28.1, 37.5

G.4 MS ANALYSIS OF OXIDATION SAMPLES

The final samples of some oxidation experiments were analyzed by cation IC-MS and the results are shown here to demonstrate the range of IC-MS data obtained. The samples shown range from barely degraded (e.g. OE3, OE5) to fairly heavily degraded (e.g. OE2). The cation IC-MS chromatograms for OE1 through OE10 are shown below in Figure G.25 to Figure G.35. The chromatographs are displayed in the same way as the PZ derivatives panels above (Figure G.1 to Figure G.16) in that the top panel is the total MS signal while the bottom panel is the cation IC chromatogram total conductivity signal. The panels are aligned so that they correspond in time. In each of these chromatographs, peaks that are known to correspond to a particular species are indicated. They all contain PZ, the primary peak at ~30.5 minutes. Other peaks positively identified are EDA and N-Formyl PZ. Contamination from MEA, and MDEA during cation IC analysis was suspected in a few samples. Other peaks with well-established m/z values are shown and tentative identifications of peaks are shown with a question mark. Further analysis of oxidation samples were not performed due to the lack of unidentified peaks of a significant size.

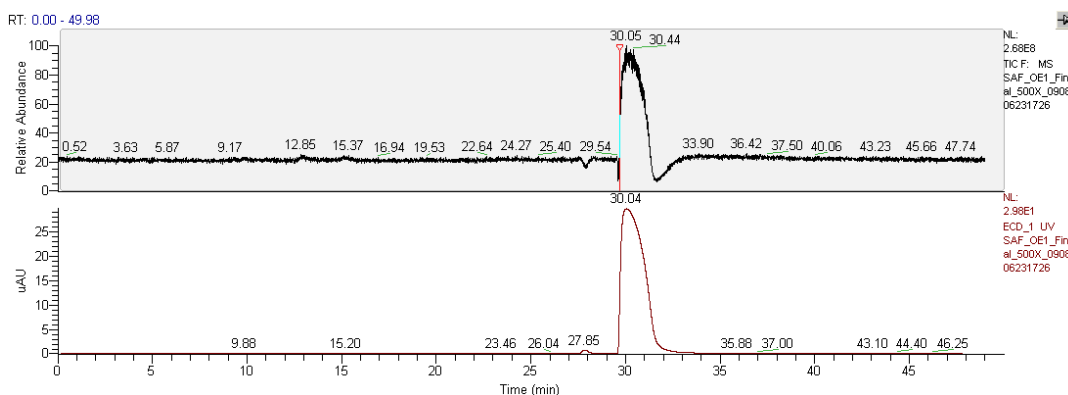


Figure G.25: Cation IC-MS chromatogram for the Final Sample of OE1 (10 m PZ, 55 °C, 2% CO₂, 0.26 mM Fe²⁺, 0.65 mM Cr³⁺, 0.26 mM Ni²⁺)

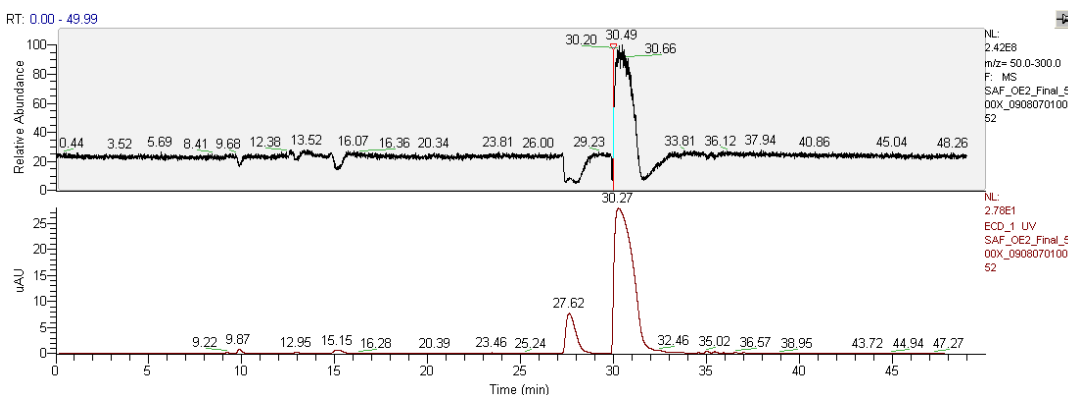


Figure G.26: Cation IC-MS Chromatogram for the Final Sample of OE2 (10 m PZ, 55 °C, 2% CO₂, 4.0 mM Cu²⁺)

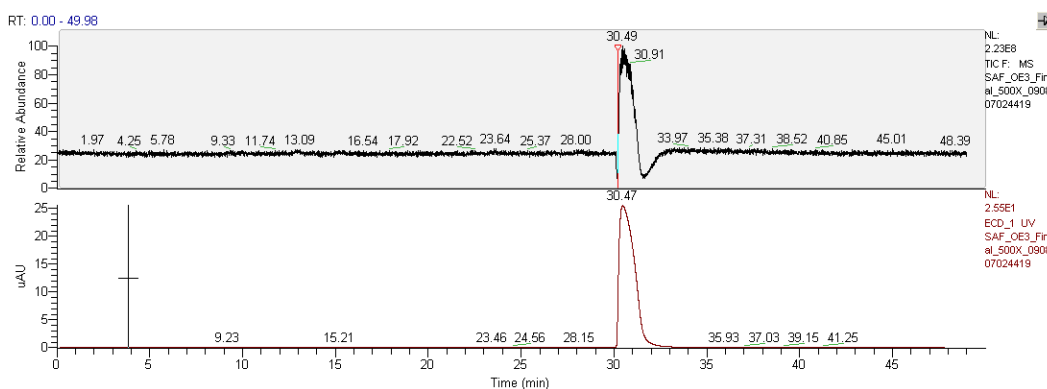


Figure G.27: Cation IC-MS Chromatogram for the Final Sample of OE3 (8 m PZ, 55 °C, 2% CO₂, 0.1 mM Fe²⁺, 0.1 mM V⁵⁺)

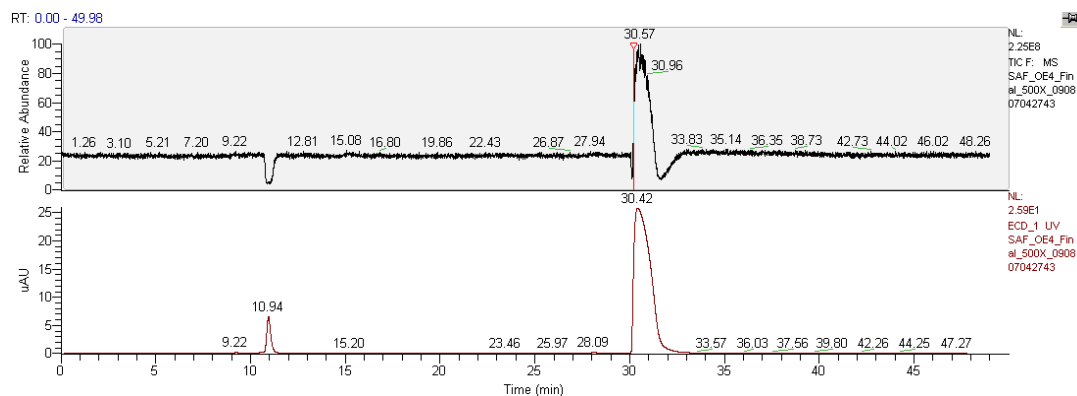


Figure G.28: Cation IC-MS Chromatogram for the Final Sample of OE4 (8 m PZ, 55 °C, 2% CO₂, 5.0 mM Cu²⁺, 0.1 mM Fe²⁺, 100 mM Inhibitor A)

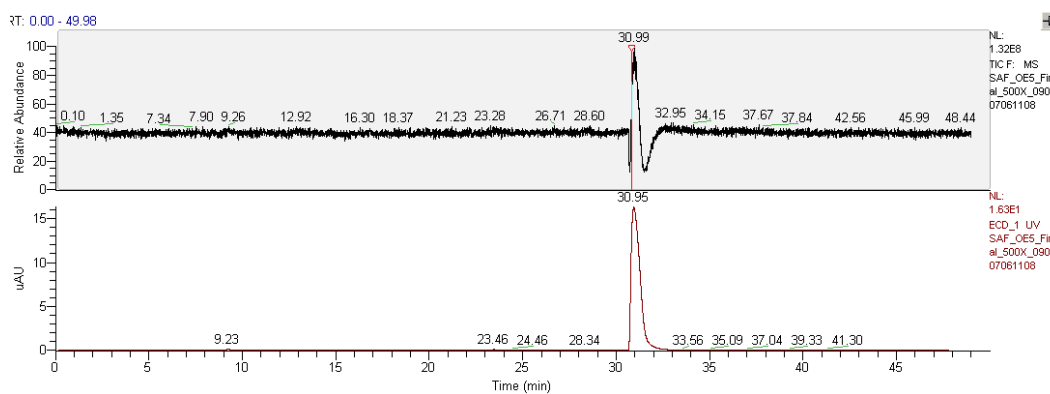


Figure G.29: Cation IC-MS Chromatogram for the Final Sample of OE5B (8 m PZ, 55 °C, 2% CO₂, 1.0 mM Fe²⁺)

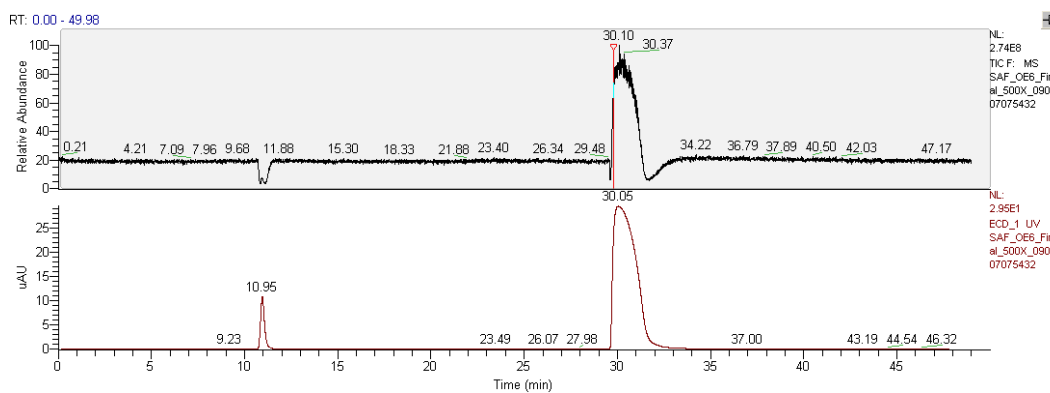


Figure G.30: Cation IC-MS Chromatogram for the Final Sample of OE6B (8 m PZ, 55 °C, 2% CO₂, 1.0 mM Fe²⁺, 100 mM Inhibitor A)

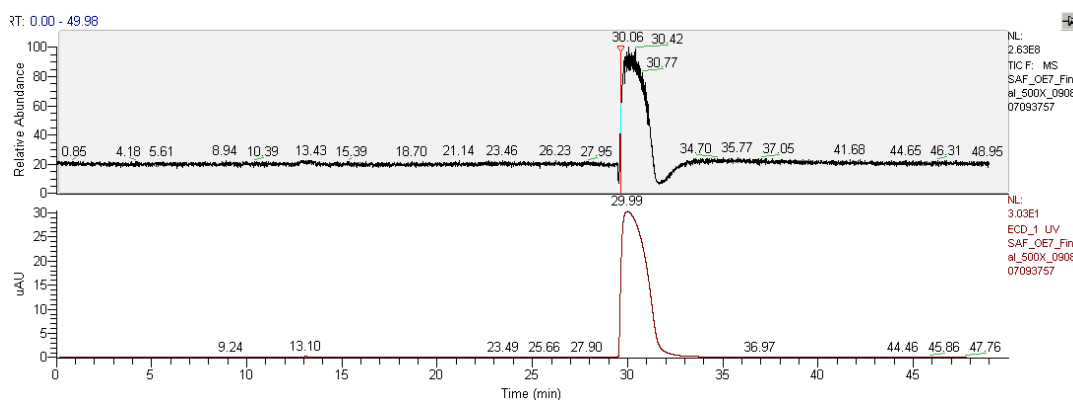


Figure G.31: Cation IC-MS Chromatogram for the Final Sample of OE7 (8 m PZ, 55 °C, 2% CO₂, 1.0 mM Fe²⁺, 20 mM Inhibitor B)

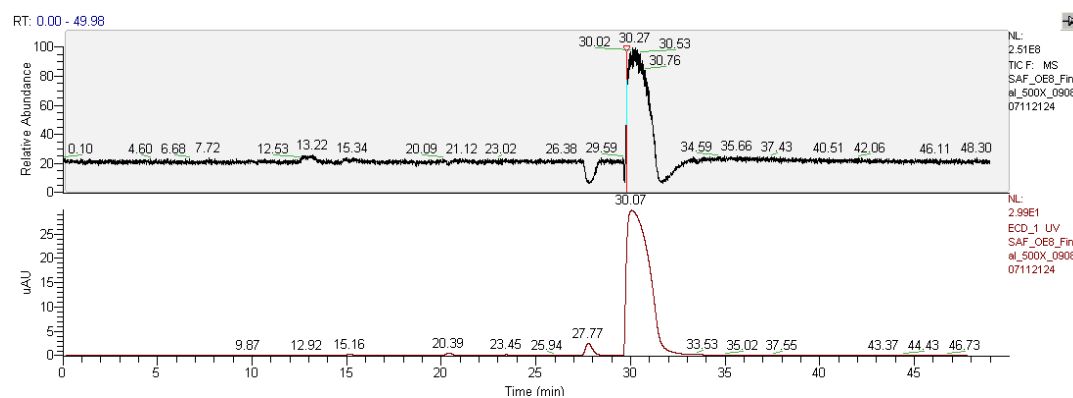


Figure G.32: Cation IC-MS Chromatogram for the Final Sample of OE8 (8 m PZ, 55 °C, 2% CO₂, 1.0 mM Fe²⁺, 30 mM EDTA)

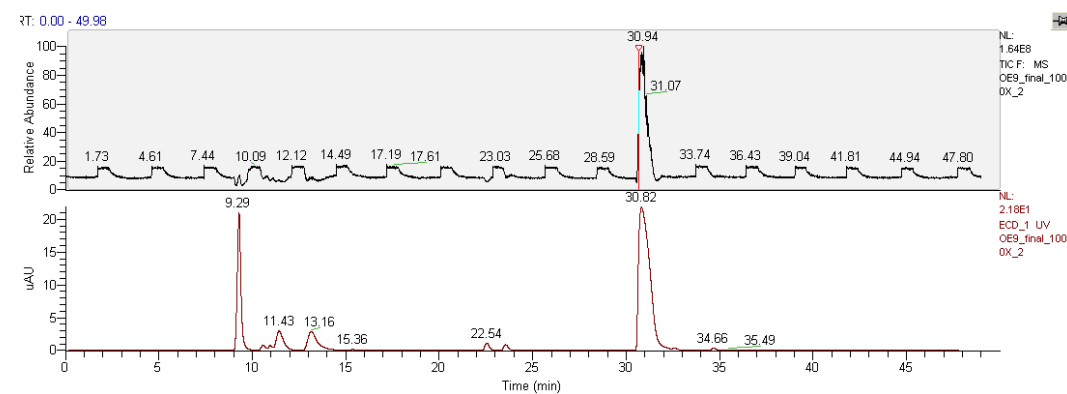


Figure G.33: Cation IC-MS Chromatogram for the Final Sample of OE9 (8 m PZ, 55 °C, 2% CO₂ in N₂)

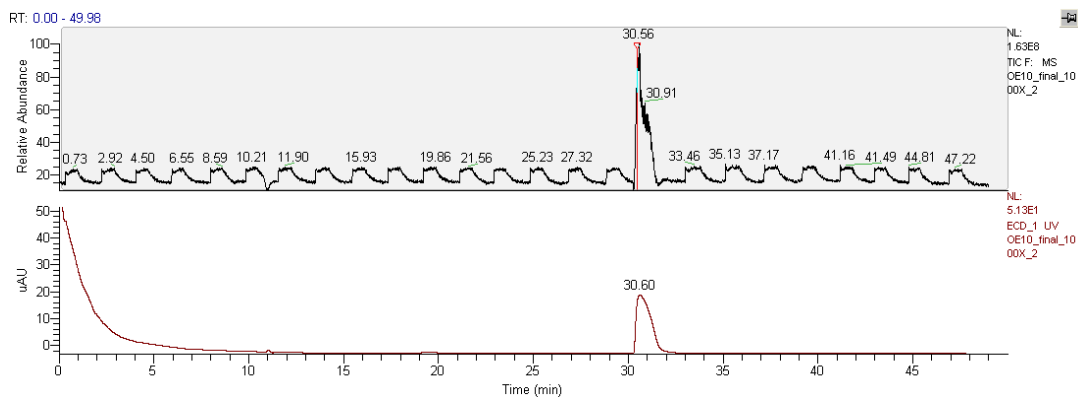


Figure G.34: Cation IC-MS Chromatogram for the Final Sample of OE10 (8 m PZ, 55 °C, 2% CO₂ in N₂)

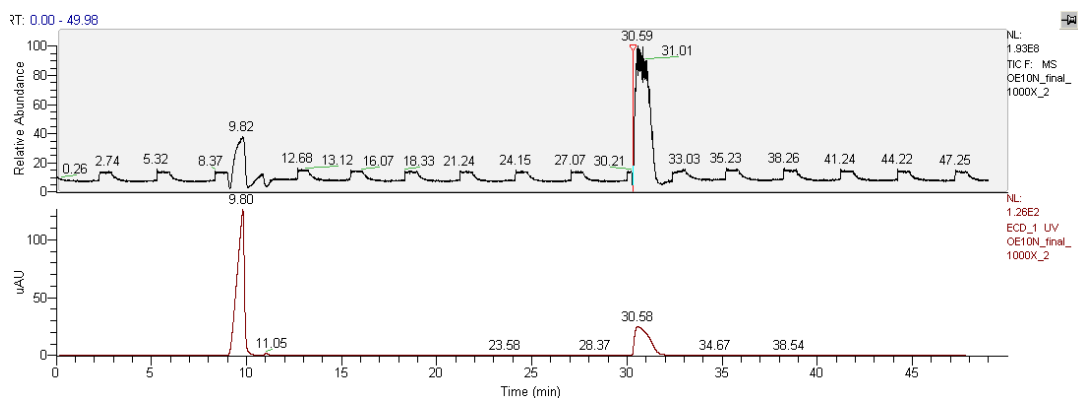


Figure G.35: Cation IC-MS Chromatogram for the Final Sample of OE10 Treated with 5N NaOH (8 m PZ, 55 °C, 2% CO₂ in N₂)

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