THE EFFECT OF MOISTURE ON THE REACTIVITY OF CA(OH)$_2$-BASED SORBENTS FOR FLUE GAS DESULFURIZATION

by

STEPHEN P. BEAUDOIN, B.S.

THESIS
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
MASTER OF SCIENCE IN ENGINEERING

THE UNIVERSITY OF TEXAS AT AUSTIN

August, 1990
(Revised for Distribution)

Abstract

$Ca(OH)_2$-based sorbents were investigated for application in tail-end flue gas desulfurization systems in coal-fired power plants. The effects of free moisture and surface area on sorbent reactivity were studied at 0 to 85% relative humidity and 1000 and 5000 ppm SO_2. In 1000 ppm SO_2 at 60% relative humidity and 60 s reaction, the conversion of sorbent formed by slurrying $Ca(OH)_2$ with Clinch River fly ash was found to increase from 0.15 in the absence of excess moisture (ambient reaction) to 0.3 with 30% free moisture. For the same reaction time and relative humidity, but in 5000 ppm SO_2, the conversion of Mississippi Hydrated Lime increased from 0.12 at ambient conditions to 0.23 with 14% free moisture. The reactions between damp lime/fly ash sorbent (5-50% moisture) and 1000 ppm SO_2 and between damp hydrated lime sorbents and 5000 ppm SO_2 were modelled successfully assuming gas-phase mass transfer of SO_2 to the damp sorbent was rate-limiting. The reaction of damp lime/fly ash with 5000 ppm SO_2 was not gas-phase controlled. During ambient reaction, hydrated lime sorbents of high surface area (74 m^2/g) attained conversions up to 0.30 in 5000 ppm SO_2 during 60 s reaction at 60% relative humidity, compared to 0.12 for low surface area (17 m^2/g) hydrated lime at the same conditions. The reaction in the presence of excess moisture was independent of sorbent surface area.

This work was funded in part by DOE Contract number DE-AC22-88PC8874 through Acurex Subcontract number EC597942, and by the Texas Advanced Technology Program.

Table of Contents

Chapter 1

Introduction

Previous pilot and bench-scale work has determined that $Ca(OH)_2$ and $Ca(OH)_2$-based sorbents have significant potential for application in dry duct-injection SO_2-abatement systems. The effectiveness of these solids can be enhanced by increasing the surface moisture content of the sorbent as a function of the relative humidity of the ductwork, although operational difficulties arise when flue gas is treated with reactive sorbent at high relative humidities. Many processes are therefore limited to tightly controlled conditions of temperature, flue gas moisture content, and duct configuration (Babu et al., 1988; Yoon et al., 1988; Drummond et al., 1988).

Improvements to sorbent reactivity are possible by increasing the surface area of the sorbent and the availability of reactive species which may fix the SO_2 in a condensed state (White et al., 1989; Drummond et al., 1988; Jozewicz and Chang, 1986, 1987; Jorgensen et al., 1987). Even with these enhancements, though, lime-based sorbents do not approach the reactivity of similar lime-based sorbents applied in spray-dryers (Blythe, 1988).

In a spray dryer, reactive sorbent contacts flue gas as a slurry, as a damp sorbent, and as a dry sorbent in equilibrium with flue gas relative humidity (Klingspor, 1986). Duct injection of dried sorbents utilizes only the third stage of spray dryer reactivity, and damp sorbent, which utilizes two of the three stages, presents a significant improvement over equilibrium sorbent at the pilot-plant level (Jozewicz and Chang, 1987). Equilibrium sorbent used in pilot facilities often scavenges liquid water which is present to humidify the gas, and in the presence of this liquid water, the equilibrium sorbent presents a significant improvement over bench scale sorbent which does not scavenge liquid water (Jozewicz and Chang, 1987).

The reactivity of damp sorbent towards SO_2 has not been investigated at the bench scale, and both pilot-scale work and spray dryer work indicate that excess surface moisture significantly enhances the reactivity of lime-based sorbents towards SO_2. It would be beneficial to study the performance of various damp lime-based sorbents at the bench level, in order to investigate the mechanism by which reaction with SO_2 occurs and to quantify the enhancement in reactivity due to the excess moisture. It may be possible to develop a predictive model for the performance of damp sorbents based upon the similarity of the damp sorbent reaction and the reactions which occur in spray dryer or wet slurry scrubbing.

This work investigates the reactivity of several lime-based sorbents towards SO_2 in the presence of equilibrium and excess moisture on the sorbent. Sorbents of varying surface area and surface structure are studied in a differential reactor under conditions of 0 to 90% relative humidity, 1000 to 5000 ppm SO_2 in the flue gas, 70 °C reaction temperature, 3 to 50% initial excess moisture, and 10 to 120 second reaction times.

Chapter 2

Theory

The mechanism of the gas-solid reaction between SO_2 and lime-based sorbents under duct injection conditions has not been established. The key variables which affect the reaction are flue gas relative humidity, sorbent water content, flue gas SO_2 concentration, and sorbent surface structure. Two theoretical models which utilize these parameters to predict SO_2 removal and sorbent reactivity are presented.

It is assumed that in the presence of liquid water, the reaction occurring at the surface of a reactive particle is fast compared to the gas-phase mass transfer of reactants to the particle surface. The reaction is assumed to occur in the adsorbed liquid on the particle surface, with subsequent precipitation of $CaSO_3$ and $CaSO_4$ onto the surface of the particle.

Sorbent containing up to 50% initial moisture, by weight, is referred to as damp sorbent, and the reactivity of sorbent with this quantity of moisture has not been studied. Previous spray dryer studies involved the reactivity of sorbent particles suspended in liquid droplets, which, as they dried, passed through the liquid, damp, and ambient stages of reactivity. In the ambient stage, the particle is assumed to contain surface water in equilibrium with the relative humidity of the flue gas. While the total reactivity of such a solid has been studied, there have been no efforts to decouple these effects.

Mass transfer theory may be applied to the gas-solid reaction system when moisture in excess of the ambient quantity is on the surface of a reactive sorbent. The theoretical models below describe the reaction occurring when a wet solid is drying and relate the evaporative drying and the SO_2 capture mechanisms.

2.1 Assumptions for Theoretical Development

The reaction between damp sorbent and SO_2 is assumed to be fast compared to gas-phase mass transfer of SO_2 to the particle surface, and the transfer is assumed to occur by Knudsen diffusion within the pores of the reactive sorbent. The following assumptions also are used in the development of the model:

1] liquid water present on the damp solid is present predominantly in the pores of the solid,

2] the resistance to mass transfer for both the evaporation process and the SO_2 capture process is controlled by diffusion in the gas phase, and

3] reaction between SO_2 and a damp sorbent which dries during the course of reaction occurs in two separate stages, the effects of which are additive.

The two stages of reaction are; reaction in the presence of excess surface moisture (damp sorbent), and reaction in the presence of ambient moisture (sorbent in equilibrium with flue gas relative humidity).

The final assumption required is:

4] the bulk flow contribution to the overall mass flux of the exchanged species is negligible during pore diffusion.

2.2 Derivation of Additive Model

The evaporation of water from the pores of the solid and the transport of SO_2 through the pores to the gas-liquid interface can be represented by:

$$N_{H2O} = (\mathcal{D}_{H2O})^* \frac{dC_{H2O}}{dx} \tag{2.1}$$

$$N_{SO2} = (\mathcal{D}_{SO2})^* \frac{dC_{SO2}}{dx} \tag{2.2}$$

where:

N_i = molar flux ; [mole i/(area-time)],

x = diffusion distance ; [length],

$\mathcal{D}$ = mass diffusion coefficient; [length^2/time], and

C_i = concentration i ; [mole i/volume].

These expressions are based on a rectangular coordinate system and a one-dimensional concentration gradient. The mechanism assumes that the reaction occurs in a liquid droplet at the bottom of a pore. Since there will be no reaction at the walls of the pore, it is not necessary to model diffusion in the radial direction.

Transport of H_2O and SO_2 are assumed to occur by Knudsen diffusion, which is a valid assumption if the gas/liquid interface is located within small pores in the sorbent. Knudsen diffusion is applicable when the mean free path over which a molecule can travel is greater than the pore diameter through which it is diffusing. The mean free path of a molecule is (Bird et al., 1960):

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 n} \tag{2.3}$$

where:

λ = mean free path; [length],

d = particle *diameter*; [length], and

n = concentration of molecules; [number molecules/volume].

The Knudsen diffusion coefficient is given by (Hines and Mattox, 1985):

$$\mathfrak{D}_{AK} = 97.0\, r \sqrt{\left(\frac{T}{M_A}\right)} \tag{2.4}$$

where:

$\mathfrak{D}_{AK}$ = Knudsen diffusion coefficient; [length^2/time],

r = radius of diffusing particle ; [length],

T = system temperature, and

M_A = diffusing particle molecular weight; [mass].

At typical flue gas conditions, the mean free path of SO_2 is approximately 520 Å, and Knudsen diffusion will occur in pores with diameters significantly lower than this value.

The pore irregularities are traditionally handled using an empirical factor, the tortuosity of a pore, along with the particle porosity. These factors are neglected here as the ratio of the two flux expressions will be taken, and the tortuosities and porosities will cancel from the final expression.

It is now possible to insert the Knudsen diffusion coefficient into the flux expressions and, taking the ratio of the two, the following relationship holds:

$$\frac{N_{SO2}}{N_{H2O}} = \frac{\mathfrak{D}_{SO2K}(dSO_2/dx)}{\mathfrak{D}_{H2OK}(dH_2O/dx)}. \tag{2.5}$$

The relationship between the water evaporated from the solid surface and the SO_2 captured is obtained by integrating this expression, giving:

$$\frac{\Delta SO_2}{\Delta H_2O} = \frac{\mathfrak{D}_{SO2K}(P_{SO2})}{\mathfrak{D}_{H2OK}(P_{H2O}^{*} - P_{H2O})} \tag{2.6}$$

where:

ΔSO_2 = SO_2 captured; [moles],
ΔH_2O = H_2O evaporated; [moles],
P_{SO2} = partial pressure SO_2 in bulk gas; [atm],
P_{H2O} = partial pressure H_2O in bulk gas; [atm], and
P_{H2O}^* = partial pressure H_2O at gas-liquid interface; [atm].

The model allows one to predict the conversion of the porous sorbent as a function of the quantity of water evaporated from the sorbent while in contact with SO_2. This representation does not account for reaction which occurs when the sorbent contains water in equilibrium with the flue gas relative humidity.

When experiments are conducted, the initial weight percent water on the reactive sorbent, the relative humidity of the flue gas, and the SO_2 content of the flue gas are noted. The expression above is modified to predict the Ca utilization of the sorbent based on these parameters. The modified predictive expression is:

$$\frac{\Delta SO_2}{Ca} = \frac{(0.53)(P_{SO2})}{(P_{H2O}^* - P_{H2O})}\left(\frac{\Delta H_2O}{Ca}\right) \qquad (2.7)$$

where:
Ca = Ca content of the sorbent; [moles/gram sorbent].

Figure 2.1 shows the conversion predicted by the model under typical experimental conditions.

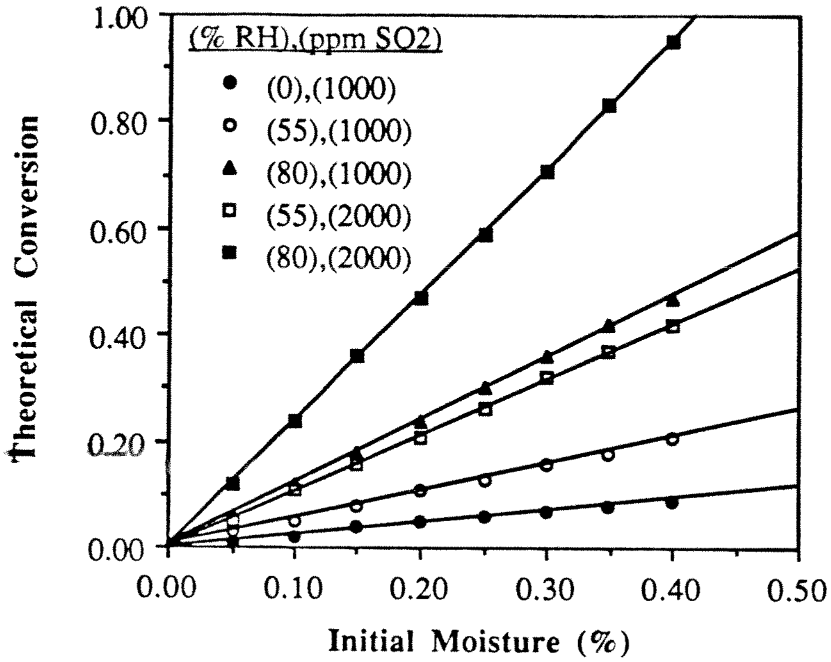

Figure 2.1 Predicted Conversion in the Presence of Liquid H_2O:
(Lime/Fly ash sorbent containing 3.65×10^{-3} moles Ca/g sorbent)

In these results, P_{H2O}^* is set as the saturation partial pressure of H_2O at the dry bulb temperature of the reaction system, as it is believed that heat transfer occurs through the damp sorbent itself and not by convective transport through the pores. It also is assumed that all moisture present on the sorbent surface evaporates during reaction. The results shown do not include reaction with SO_2 in the absence of excess moisture on the sorbent surface.

The accuracy of this model will be studied using damp hydrated lime and hydrated lime/fly ash sorbents with flue gas of varying SO_2 concentration and relative humidity. Hydrated lime sorbents of varying surface area and porosity will be studied to determine the effects of surface properties on the sorbent reactivity, although the model indicates that the reaction with damp sorbent should be independent of the sorbent surface properties. The surface area effects will be observed when the reactive sorbent contains ambient moisture, and such effects will be reflected by a changing y-intercept in the plot above.

When the model is applied to predict the conversion of a damp sorbent, the conversion attained by that sorbent with no excess moisture present will be required to predict the total conversion. Tests will be done to determine the conversion of sorbent which is in equilibrium with flue gas relative humidity during reaction. The conversion observed in these tests will vary with time and relative humidity, and the conversions noted in these tests will be added to the conversions predicted as a function of initial moisture to obtain the total expected conversion of damp sorbent which dries as it reacts. If there is no interaction between the wet reaction and the reaction when the sorbent contains moisture in equilibrium with the flue gas relative humidity, this combination, referred to as the Additive Model, will accurately predict the total conversion of damp sorbent which is dried as it reacts.

2.3 Effects of Reaction with Ambient Moisture

It is possible that the effects of the wet reaction and the reaction occurring in the presence of ambient moisture are not additive, but rather that the presence of liquid moisture on the sorbent surface affects the reaction with equilibrium moisture. Excess moisture on the surface of the sorbent occupies surface area otherwise available for reaction due to ambient moisture. If the conversion observed with ambient moisture is significant, the conversion attained in the combined wet/ambient-moisture system will be lower than a linear combination of the expected results for the independent wet and ambient-moisture systems.

It is believed that the conversion predicted as a function of excess moisture on the surface of the sorbent is correct, but that the magnitude of the contribution of the ambient-moisture reaction may require adjustment from that given in the Additive Model to reach a correct total conversion. To calculate the conversion which will occur by the ambient-moisture reaction, the results of ambient-moisture reaction studies will be analyzed to determine the rate of sorbent conversion by the ambient mechanism as a function of reaction time. For each experiment to be modelled, the conversion expected due to wet reaction will be noted, and the time required to achieve this conversion by the ambient-moisture reaction will be noted. The ambient reaction will be assumed to proceed at the ambient conversion rate corresponding to this reaction time. If it is assumed that the excess moisture on the sorbent surface will evaporate instantly during reaction, the differential expression for conversion due to reaction in the presence of ambient moisture must be integrated over the entire reaction time. The resulting conversion predicted due to reaction in the presence of ambient moisture will be added to the conversion expected due to wet reaction in order to determine the total conversion of the sorbent.

2.4 Derivation of Interactive Model

The expression which predicts sorbent conversion due to excess moisture is shown above in Equation 2.7. The expression for total sorbent conversion is:

$$\text{Pred. Conversion} = f_{H2O} + g_{EQ} \tag{2.8}$$

where:

f_{H2O} = conversion due to excess H_2O: [mole SO_2/mole Ca], and

g_{EQ} = equilibrium-moisture conversion; [moles SO_2/mole Ca].

The conversion due to excess moisture (f_{H2O}) is described in Equation 2.7.

It is possible to evaluate g_{EQ} as follows:

$$g_{EQ} = h_{EQ}(t + t_o) - f_{H2O} \tag{2.9}$$

where:

t_o = time required to achieve f_{H2O} conversion by the equilibrium-moisture mechanism; [s],

t = time available for equilibrium-moisture reaction; [s], and

$h_{EQ}(t + t_o)$ = conversion by equilibrium-moisture mechanism evaluated at $(t + t_o)$; [(moles S/mole Ca)/(s)].

When the ambient-moisture portion of the total conversion is predicted using this method, the model will be referred to as the Interactive Model.

Chapter 3

Apparatus and Procedures

The experimental equipment used to perform this study consisted primarily of a flue gas preparation/delivery system and a fixed-bed reactor. It was similar to that used by other researchers at the University of Texas at Austin (White, 1989; Peterson, et al., 1987).

3.1 Flue Gas Preparation and Delivery System

The flue gas preparation/delivery system is shown in Figure 3.1. This apparatus included:

1] 4 mass flow controllers, which were used to maintain constant flowrates of the various gases used in the simulated flue gas,
2] a furnace and evaporator, to evaporate water and mix the steam into the flue gas,
3] a pressure control valve, to set the flue gas relative humidity after the water and gas flowrates were established,
4] a constant-rate syringe pump, to provide water to the evaporator,
5] a water bath and several heat exchangers, to maintain the flue gas and reactor at a constant temperature during reaction,
6] a scrubber, to remove any unreacted SO_2 from the gas stream, and
7] an analyzer, to determine the SO_2 concentration in the gas.

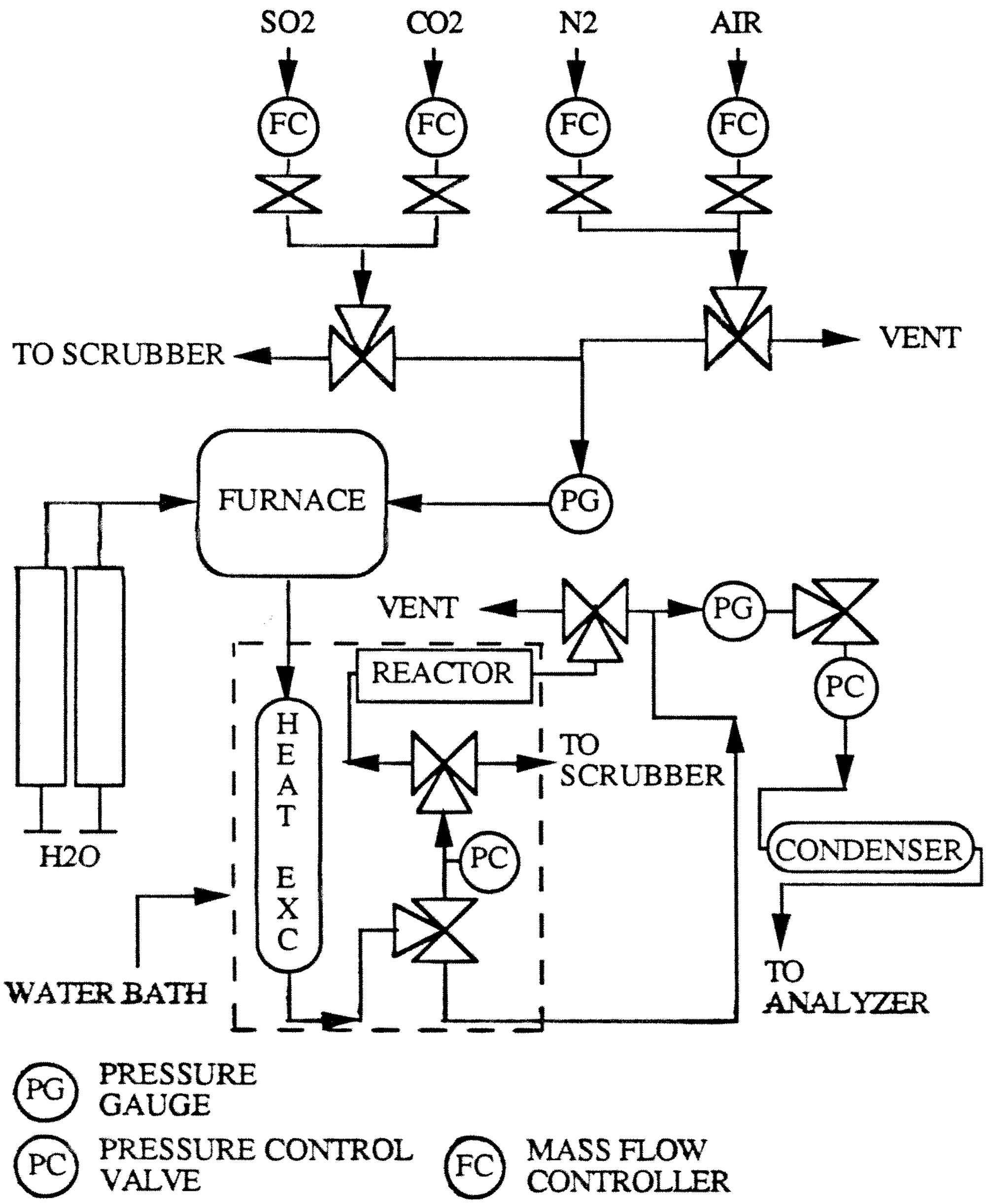

Figure 3.1 Flue Gas Preparation/Delivery System

House air, N_2, CO_2, and a mixture of 1% SO_2 in N_2 were metered through Brooks Series 5580 Mass Flow Controllers, marked "FC" in Figure 3.1, to provide a flue gas of accurately known composition. CO_2 was drawn from a gas cylinder of pure CO_2, while N_2 was drawn from a cylinder of liquid N_2.

The SO_2/N_2 mixture and the CO_2 were provided by either Wilson Oxygen of Austin, TX or Big Three Industrial Gases of Houston, TX. The N_2 was provided by the Cryogenics Lab at The University of Texas at Austin.

The flue gas was a mixture of N_2, CO_2, air, and the SO_2/N_2 gas mixture, and after the flue gas was formed, steam was injected to achieve a desired water content in the gas. The steam was generated and injected within an evaporator housed in the furnace (Not shown in Figure 3.1). Water was fed into the evaporator, and thus into the flue gas, at a constant rate of 0.03 ± 0.002 mol/min with a single-speed pump, labelled "H2O" in Figure 3.1. The water injection system is discussed in detail in Section 3.1.1: Water Injection System.

3.1.1 Water Injection System

Water was delivered to the flue gas system by a constant-speed pump made by Kemisk Teknologi of Sweden and two plastic syringes manufactured by Becton-Dickinson and Co. of Rutherford, NJ. The pump was designed to provide constant pressure on the syringes, and when two 60 cm^3 plastic syringes were attached, the liquid flowrate out of the pump was 0.54 cm^3/min (0.03 mol H_2O/min). After leaving the pump, the water was evaporated in a glass evaporator manufactured in the Glassblowing Shop at The University of Texas at Austin, which was itself housed in a furnace provided by Tracor Co. (Stone Furnace model FD-1).

The evaporator consisted of a narrow glass tube wrapped around a large contacting barrel containing glass beads, as shown in Figure 3.2, below. The flue gas entered the top of the evaporator while the water was forced into the outer tube, beginning at the bottom of the evaporator. The water evaporated as it travelled through the tube, so that the steam exited the top of the tube and entered the mixing chamber, where it mixed with the flue gas. The humid flue gas left the bottom of the evaporator after passing through the glass beads, to guarantee adequate mixing. The furnace was typically run at temperatures ranging from 200 to 250 °C.

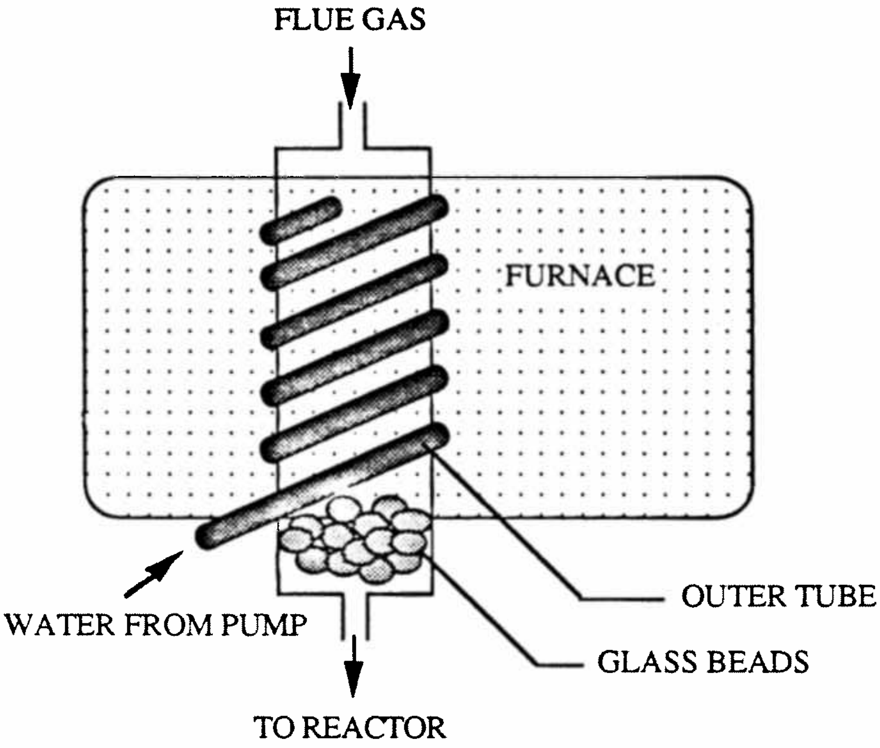

Figure 3.2 Evaporator

For the constant water flow rate, the flue gas relative humidity was controlled by changing the total flowrate of the flue gas and adjusting the pressure of the gas stream using the pressure control valves labelled "PC" in Figure 3.1. The total overall gas flowrates, considering the flowrates of the individual gases in the flue gas on a dry basis, are presented in Table 3.1, below. The gas flowrates were set to achieve a desired relative humidity at a pressure of 2 psig.

Table 3.1 Experimental Gas Flowrates

SO_2 content (ppm)	flue gas RH (%)	total gas flow (slpm)	CO_2 content (vol %)	O_2 content (vol %)
1000	55-68	4.1	10	12
1000	55-68	4.6	9	10
2000	80-93	2.5	10	11
2000	80-93	2.8	9	10
5000	55-68	4.1	10	12
1000, 2000, or 5000	0	4.1	10	12

3.1.2 SO_2 Analyzer

The SO_2 content of the flue gas was measured using a Columbia Scientific Industries ambient-level flame photometric SO_2 analyzer (model SA285E). The SO_2 concentration was determined prior to the onset of reaction by bypassing the fixed-bed reactor unit and sending the simulated flue gas to the analyzer.

The analyzer was calibrated with a calibration gas mixture of approximately 1000 ppm (by volume) SO_2 in N_2, which was provided by either Wilson Oxygen or Big Three Industrial Gases. The SO_2 content of the calibration gas always was known, although several cylinders of calibration gas were used, each with a slightly different SO_2 content.

The analyzer operated in the 1 ppb range, so it was necessary to dilute both the calibration gas and the flue gas to this level prior to analysis. The dilution was accomplished by metering house air (dilution air) through a rotameter (Matheson model 7630-C) into the analyzed gas. When calibrating, house air was introduced so that the analyzer output for the 1000 ppm calibration gas was at either 90 or 45% of full-scale. If experiments were to be conducted using 2000 ppm SO_2 in the flue gas, the dilution air rate was set so that the analyzer read 45% of full scale when the 1000 ppm calibration gas was being analyzed, while if 1000 ppm flue gas was to be used in the experiments, the dilution air flowrate was set so that the analyzer read 90% of full-scale during calibration.

When the simulated flue gas was being prepared, the same flowrate of dilution air was used as as during the calibration step. After the carrier gas flowrate was set, the flowrate of the SO_2-N_2 mixture into the carrier gas was modified so that the analyzer read either 90 or 45% of full-scale, depending on the calibrated value. For example, to accurately attain flue gas SO_2 levels of 2000 ppm, the analyzer was calibrated so that the 1000 ppm calibration gas read 45% of full-scale, then the carrier gas and SO_2 flowrates were set so that, with the same flowrate of dilution air as in the calibration, the analyzer read 90% of full-scale. In all cases, the flue gas concentration was within 100 ppm of the desired level, with the exception of the 5000 ppm experiments.

When experiments were conducted using 5000 ppm SO_2 in the flue gas, the SO_2 content of the flue gas could not be checked with the analyzer because of the great quantities of dilution air required to dilute the 5000 ppm SO_2 into the functional range of the analyzer. At this high dilution air flowrate, dilution air penetrated upstream into the flue gas delivery system, causing unmanageable pressure fluctuations and inhibiting the operation of the mass flow controllers. An alternative method was developed to set the flue gas SO_2 concentration at 5000 ppm.

To operate the reaction system with 5000 ppm SO_2 in the flue gas, a mass flow controller was inserted between the SO_2/N_2 cylinder and the delivery system. The flowrates of the Air, N_2, CO_2, and SO_2/N_2 streams were adjusted, based on the mass ratios determined by the flow controllers, to obtain 5000 ppm SO_2 in the flue gas while maintaining the O_2 and CO_2 levels and preserving the overall total gas flowrate required to achieve the desired relative humidity in the flue gas. When the system was operated in this manner, it is estimated that the flue gas SO_2 content ranged from 4800 to 5200 ppm SO_2.

3.2 Fixed-Bed Reactor

The fixed-bed reactor is presented in Figure 3.3. This system was inserted into the flue gas line in the space marked "REACTOR" shown in Figure 3.1.

The fixed-bed reactor was composed of three individual reactor units, with common intake and outlet manifolds. The individual reactors were isolated from each other and the manifolds by stainless steel ball valves, and the interior volume of each of the three reactors was approximately 5.7 cm^3. The reactors were constructed from 1/2" stainless steel tubing with Swagelok® fittings and ball valves mounted on each end of the individual reactor chambers. The inlet and outlet manifolds were constructed of 1/4" stainless steel tubing and Swagelok® fittings. The reactor unit was rigid, and the steel construction was airtight and allowed for excellent heat transfer. The design allowed for three experiments to be run consecutively under the same conditions of temperature, gas-phase SO_2 content, and sorbent H_2O content.

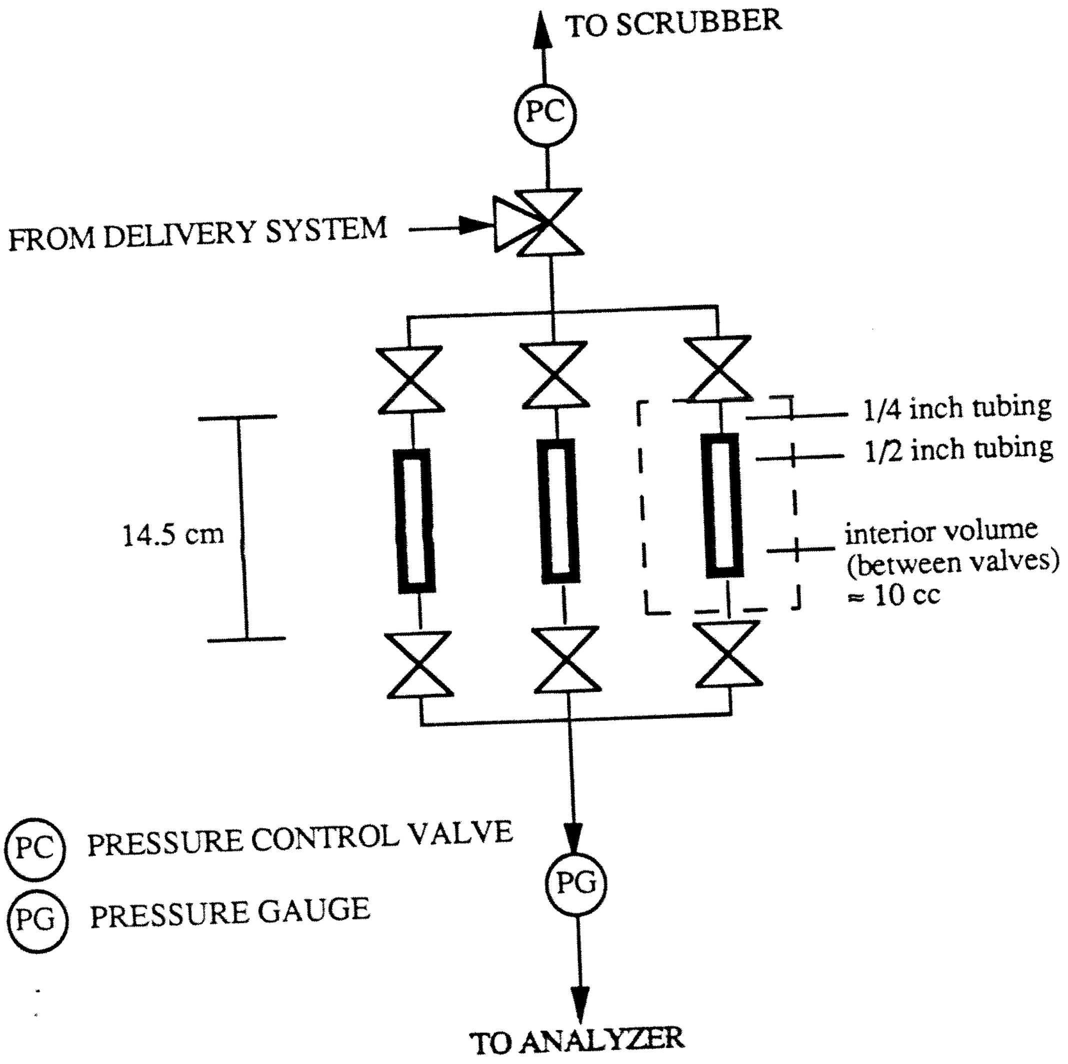

Figure 3.3 Fixed-Bed Reactor

Wet sorbents which were loaded into the three reactors were equilibrated to the reaction temperature without being exposed to hot, unsaturated (to H_2O) flue gas. As a result, while the water evaporated from the sorbent to saturate the vapor space of each individual reactor unit, the sorbents still retained a significant quantity of their initial surface moisture until reaction was initiated. The interior volume of each reactor was accurately known, making it possible to quantify the amount of H_2O which would evaporate from the wet sorbent prior to reaction.

Using this reactor design, three experiments could be run consecutively at nearly identical conditions of sorbent H_2O content, relative humidity, and SO_2 concentration. The most variation between consecutive experiments arose as a function of the density of the wet sorbent/sand mixture packed in the three reactors. During different experiments, pressure changes through the different individual reactor housings ranged from 2 to 5 psig, altering the relative humidity condition from one experiment to the next. In all cases, the relative humidity during an experiment was known accurately as a function of the H_2O and gas flowrates and the reactor pressure, measured as a change in the pressure upstream of the reactor.

3.3 Wet Sorbent Preparation

Wet sorbents were prepared by weighing approximately 2.5 g of sorbent and H_2O into a small glass vial (approximately 15 cm^3) which accepted a screw-on cap. The sorbents and H_2O were mixed using a stainless steel spatula, and a sample of damp sorbent was removed. The sample was weighed immediately to determine its mass while wet, and then oven-dried at approximately 100°C. The initial H_2O content of the sample was determined by weight difference.

The vial containing the wet sorbent was capped and stored in a refrigerator at approximately 50 °F. When wet sorbent was required for experiment, two samples were extracted. One was placed in the reactor and the other was weighed, dried, and reweighed to determine the initial moisture content of the reacted sample.

3.4 Reaction Procedure

To begin an experiment, supported wet sorbent was loaded into each of the three reactor units in the fixed-bed reactor and the units were sealed and inserted into the flue gas delivery system. The fixed-bed reactor was allowed to equilibrate to the reaction temperature in the water bath for approximately 10 minutes prior to the introduction of flue gas. The supported wet sorbent was prepared by adding approximately 3 g of 60 mesh silica sand and two small (≈0.25 cm dia.) glass beads to each of three vials, and then adding a weighed quantity of wet sorbent from the refrigerated storage vial. Prior to the onset of experimentation, the sand was acid-washed with dilute HCl and rinsed with water to remove any Ca-containing species. The sand/sorbent vials were capped and shaken vigorously to break any agglomerates of reactive material, and then the mixtures were poured into the reactor assemblies, which were immediately sealed. One vial of sand/sorbent mixture was placed into each reactor unit, so that approximately 10 mg of wet sorbent were used in each experiment, supported by approximately 3 g of sand.

It was assumed that H_2O evaporation from the sorbent occurred during the mixing with the sand. This evaporation was assumed to saturate the interior vapor space of the mixing vial. An estimate of the interior volume of the mixing vials was made to account for this H_2O loss. It also was assumed that evaporation occurred from the sorbents to saturate the interior vapor space of the reactor units, but that no additional H_2O loss from the reactive sorbents occurred. As stated previously, the interior volume of each reactor unit was known, so that all evaporative losses could be calculated. In total, a maximum loss of 0.0012 g of H_2O from the sorbent was expected due to evaporation during the mixing, loading, and equilibration processes.

After the reactor was loaded, it was inserted into the flue gas delivery system and allowed to equilibrate to the reaction temperature. During the equilibration step, flue gas flow bypassed the reactor. To initiate an experiment, flue gas was directed into the reactor housing, and one reactor unit was opened by opening its two ball valves. The pressure in the flue gas line during the reactions was controlled by both the pressure-control valve downstream of the reactor outlet and the pressure drop inherent in the reactor packing. The pressure was monitored, upstream of the reactor, throughout the course of reaction, so that the relative humidity during reaction was known.

The reaction was stopped by directing flue gas flow away from the reactor and closing the ball valves on each end of the reactor, sealing it from the flue gas. The reactor itself was of sufficiently small interior volume that any residual flue gas remaining inside after the reaction was stopped would not significantly alter the outcome of an experiment. For each experiment, the ball valves for one of the three reactors were opened while the remaining two reactors remained isolated and sealed. This mode of operation allowed accurate control of the flue gas relative humidity and composition prior to the start of each reaction while thermally equilibrating, but otherwise not affecting, the wet sorbents in the other reactors. This procedure also allowed multiple reactions to be performed in rapid succession.

3.5 Analytical Procedure

To determine the sulfate, calcium, and carbonate contents of a reacted sorbent, the sorbent and sand first were stirred for several hours in a 50 ml mixture of approximately 47 ml H_2O, 1.5 ml of 30% H_2O_2 in H_2O, and 1.5 ml of 0.07 M HCl. The H_2O_2 was added to the solution to ensure that all of the captured SO_2 was oxidized to sulfate, while the HCl was added to guarantee complete dissolution of all of the calcium-based species. When carbonate analyses were performed, the flask containing the dissolved samples was sealed with a rubber septum cap during the stirring step, but if carbonate analysis was not to be performed, the flask was sealed with "Parafilm M" during the stirring step.

After the sorbents were completely dissolved in the liquid, a 1.0 ml gas-tight syringe (Hamilton Co.) was used to extract a sample of the clear liquid for inorganic carbon (carbonate) analysis. After the inorganic carbon analysis was complete, the solutions were filtered to remove any particulate matter, which was either indigestible fly ash or the sand and glass beads which supported the sorbent in the reactor. If the inorganic carbon analysis was not attempted, the solutions were filtered immediately after the stirring was complete.

The mother liquor from the filtration process was mixed with water in a 100 ml volumetric flask to make a 100 ml stock solution, which is referred to later in this document as the undiluted stock solution. This solution was diluted by withdrawing a 5 ml aliquot and adding it to 45 ml of H_2O in a 50 ml volumetric flask. The diluted liquid was injected into a Dionex Ion Chromatograph (IC) to determine sulfate content. A second 5 ml aliquot was removed from the stock solution, and it was added to 5 ml of 1 M NaCl and 40 ml of H_2O in a second 50 ml volumetric flask. This second diluted sample was used in a Varian Atomic Absorption Spectrophotometer (AA) to determine Ca content.

3.6 Analytical Equipment

3.6.1 Ion Chromatograph

Three analytical devices were used to perform this study. The first was an Ion Chromatograph, model 2000i/SP, manufactured by Dionex Corp., which was attached to a Hewlett-Packard 3390A reporting integrator. The following are the operating conditions used with the IC:

1] separator column; Dionex HPIC-AS4A; p/n 037041,
2] guard column; Dionex HPIC-AS4A; p/n 037042,
3] eluant; 0.75 mM $NaHCO_3$, 2 mM Na_2CO_3 in H_2O,
4] cation suppressor solution; 0.005 M H_2SO_4,
5] suppressor module; Dionex Anion Micro Membrane Suppressor, p/n 038019, and
6] output conductivity range; 30 µs (microsiemens).

The integrator was operated at the following settings:

1] attenuation 2; 10,
2] peak width; 0.04,
3] threshold; 4, and
4] area rejection; 0.

During operation, the IC first was calibrated with two standard solutions, after which the solutions of unknown sulfate content were analyzed. The standards were 0.05 mM Na_2SO_4 and 0.001 or 0.002 mM Na_2SO_4. In this concentration range, the IC responded in a linear fashion to concentration differences in the analyzed solution, and a least-squares fit to the two standards outputs and an assumed zero output for a sulfate-free solution was used to determine the concentration of sulfate in the unknown samples. With the operating conditions presented above, the sulfate peak was eluted from the column after slightly less than 6 minutes.

3.6.2 Atomic Absorption Apparatus

To determine the calcium content of sorbent samples, a Varian Atomic Absorption Spectrophotometer, model number AA-1475, was used. Gases to operate the AA were supplied by Wilson Oxygen of Austin, Tx. The following gases were used;

1] acetylene, AA grade, and
2] nitrous oxide, medical grade.

The AA was operated at the following settings:

1] lamp mode; double beam,
2] wavelength monitored; 422.7 nm,
3] slit width; 0.5 nm, and
4] lamp current; 10 mA.

A reducing flame (high fuel:oxidant ratio) was employed during operation, and three standard solutions were used to calibrate this device, a distilled water standard, a standard containing 2 ppm calcium, and a standard containing 4 ppm calcium. The instrument was operated by setting the machine output to "concentration mode", combusting the three standards, and setting the resulting output to correspond to the three standards' values. After performing this procedure the machine output is provided in ppm calcium, corresponding to the 0 to 4 ppm range used in the calibration. In this calibrated range, the AA responds in a linear fashion to changes in the calcium content of analyzed solutions. Slight deviations from the calibration occurred, so that after the calibration was complete, the standards were re-analyzed, and a least-squares fit to the machine output for the three standard solutions was constructed. This calibration curve was used to interpret the output of the unknown samples.

3.6.3 Total Carbon Analyzer

To determine the inorganic carbon contained in the sorbent samples, an Oceanographic Total Carbon Analyzer (TCA) was used. The following conditions were employed during operation of the TCA;

1] acid source; 15% H_3PO_4 in H_2O,
2] carrier gas; N_2,
3] water sorbent; $Mg(ClO_4)_2$,

4] integrating device; Horiba PIR-2000 Infrared CO_2 Analyzer,

5] CO_2 standard; 0.1 M $NaHCO_3$, and

6] injection volume of unknown; 1 ml.

An oxidation furnace was not employed, as the only carbon species of interest were those present in the solid as carbonate/bicarbonate.

The Integrator output was an integer value, which reflected the magnitude of the absorption of infrared light by CO_2. When operating this analyzer, three standard solutions were used to provide a calibration curve within the linear operating range of the instrument. To calibrate the device, 1.0, 3.0, and 5.0 µl of a 0.1 M $NaHCO_3$ standard solution, containing 0.1, 0.3, and 0.5 µM of CO_2, respectively, were injected with a 10 µl Hamilton gas-tight syringe (Hamilton, no. 701) The machine output was linear over this range of CO_2 content.

3.6.4 SO_2 Sorbents

Several different sorbents were utilized in this study. Their properties are presented in Table 3.2. These sorbents were selected for use in this study for three reasons. First, they are representative of the type of sorbent most frequently considered for application in duct-injection technologies. Second, the properties of two of the sorbents are known and their reactivities towards SO_2 under conditions similar to those proposed here have been well-documented. Finally, it was expected that all of these sorbents would show significant changes in their reactivity over the range of conditions considered.

Table 3.2 Sorbent Properties

Sorbent Name	Surface Area (m^2/g)	Porosity (cm^3/g)	Formation Conditions
Lime/Fly Ash*	16	0.21	3:1 ratio Clinch River Fly Ash:Miss. Hydrated Lime slurried at 90°C for 12 hours
Mississippi Hydrated Lime**	17	0.19	
Hydrated Lime "A"@	74	0.47	hydrated (alcohol present) at 74 °C for 50 min., N_2 blanket for 41 min.
Hydrated Lime "B"@	51	0.25	hydrated (alcohol present) at 74 °C for 35 min., N_2 blanket for 26 min.

(*Borgwardt and Rochelle, 1989;@Acurex,unpublished document 1990;**Acurex, 1989b)

The reactivities of Mississippi Hydrated Lime and the lime/fly ash material have been studied by previous researchers at The University of Texas at Austin (Peterson et al., 1987; White, 1989, Trempel,1989). The other two sorbents, which are made from Mississippi lime which has been hydrated in the presence of alcohol to promote the formation of high surface area, high porosity $Ca(OH)_2$, were selected to determine the effects of surface area and porosity on the reaction with SO_2. All of the sorbents used in this study were provided by Acurex Corp, with the exception of the Mississippi Hydrated Lime (17 m^2/g), which was provided by the Mississippi Lime Co.

Chapter 4

Results and Conclusions

The experimental work was performed in two stages. In the first stage, sorbents containing moisture in equilibrium with laboratory relative humidity (~ 50%) were exposed to flue gas of varying relative humidity and SO_2 content. In the second stage, water was added to the sorbent so that its water content was above that attained through equilibrium with the room humidity. Four sorbents of varying surface properties and chemical composition were used, and the SO_2 concentration and relative humidity were varied during both stages of testing. The properties of the sorbents are presented in Table 3.2 of Section 3.6.4: SO_2 Sorbents.

In this work, two different gas-phase SO_2 concentrations were utilized, 1000 and 5000 ppm. At 1000 ppm, it was expected that measurable $Ca(OH)_2$-conversion could be achieved in the lime/fly ash sorbent when both ambient moisture and excess moisture were present on the sorbent surface. The hydrated lime sorbents were not expected to achieve high conversions with 1000 ppm SO_2 in the presence of ambient moisture and the effect of excess moisture on hydrated lime sorbent with 1000 ppm SO_2 was expected to be small. As a result, only lime/fly ash sorbent was studied at 1000 ppm SO_2.

With 5000 ppm SO_2, it was expected that significant $Ca(OH)_2$-conversion would be attained in all of the sorbents (lime/fly ash and hydrated limes) independent of sorbent moisture content, and both classes of sorbent were studied at this condition. The lime/fly ash sorbent was expected to approach 100% $Ca(OH)_2$-utilization if significant quantities of moisture were present with 5000 ppm, so the amount of water added to this sorbent was limited during this testing.

4.1 Results: Stage 1; Sorbent with Ambient Moisture

Table 4.1 presents the test plan followed to investigate the reactivity of sorbent containing ambient moisture.

Table 4.1 Test Plan: Stage 1. Sorbent with Ambient Moisture

Sorbent Type	Initial Moisture (%)	Flue Gas SO_2 content (ppm)	Reaction Time (s)	Flue Gas RH (%)
Lime/Fly Ash	3.5	1000	10,60,120	0,55,80
	3.5	5000	10,60,120	0,55
Miss. Hydrate	1.0	5000	10,60,120	55
Promoted Lime Hydrate "A"	1.0	5000	10,60,120	55
Promoted Lime Hydrate "B"	1.0	5000	10,60,120	55

The results with lime/fly ash sorbent containing ambient moisture are presented in Figure 4.1. At the ambient condition, the sorbent initially contained moisture in equilibrium with the laboratory relative humidity, but when the flue gas was introduced into the reactors, the moisture content of the sorbents shifted to approach equilibrium with the flue gas relative humidity. It was expected that the magnitude of the change in the surface moisture content of the sorbent was negligible during this process.

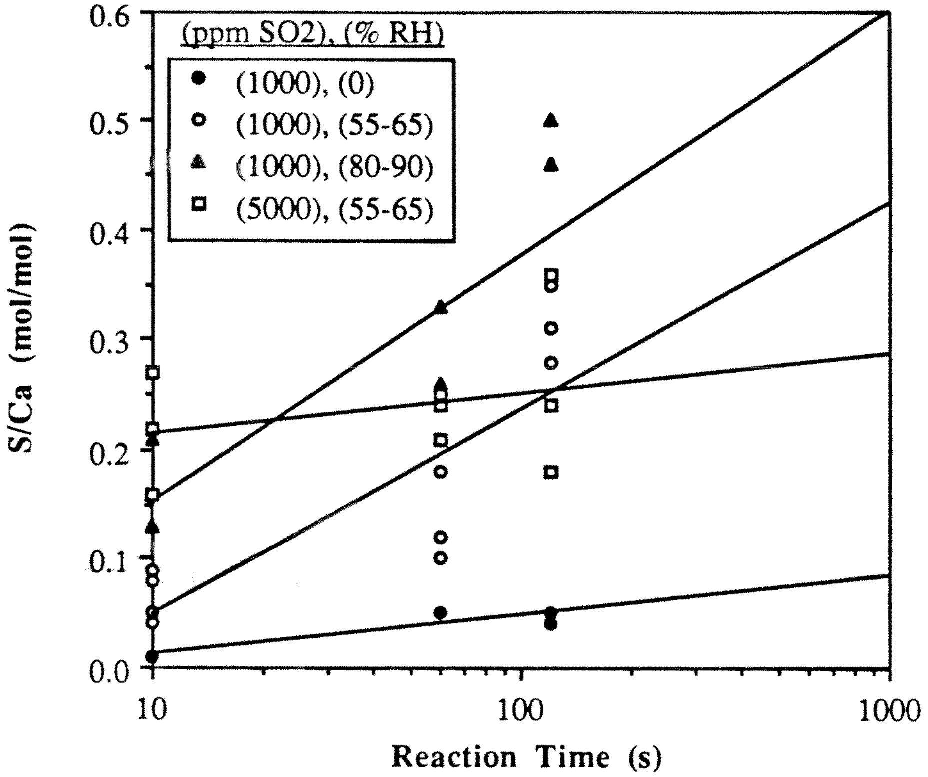

Figure 4.1 **Conversion of Lime/Fly Ash Sorbent Containing Ambient Moisture:** (70 °C, 3.5% initial moisture)

It can be seen in Figure 4.1 that increasing the relative humidity of the flue gas and increasing the gas-sorbent contact time enhance the conversion (moles S captured/mol Ca) of the lime/fly ash sorbent. At the higher relative humidities, conversions reach 0.50 and 0.20 for 120 and 10 s reactions, while the average sorbent conversion for 120 s gas/solid contact time is 0.30 at approximately 60% RH. The increase in sorbent conversion with increasing reaction time is not as significant at the lower relative humidity as at the higher relative humidity, implying that for a given reaction time, the greater the surface moisture content of the sorbent, the greater the conversion.

The conversion of the lime/fly ash sorbent increases more significantly with reaction time with 1000 ppm SO_2 than with 5000 ppm SO_2. The conversion of the lime/fly ash sorbent is approximately the same at 120 s for the different SO_2 concentrations, although the 10 and 60 s reactions provide significantly higher conversion in the presence of the 5000 ppm SO_2 than in the presence of the 1000 ppm SO_2. It appears that, with 5000 ppm SO_2 in the flue gas, the conversion occurring during the short time reactions is the dominant conversion, with only incremental reaction occurring at longer times.

In Figure 4.2, data from the current work using ambient lime/fly ash sorbent with 1000 and 5000 ppm SO_2 at 55-64% relative humidity is compared with results obtained by White (1989) using the same sorbent with 450 and 1800 ppm SO_2 and 51-58% relative humidity.

It can be seen that the results from the present work using 1000 ppm SO_2 are approximately the same as those obtained by White using 450 ppm SO_2 and lower than those obtained by White using 1800 ppm SO_2. At short times, the conversion from the present work with 5000 ppm SO_2 is greater than the obtained by White with either 450 or 1800 ppm SO_2, but at long times the differences are small. The results of White show a smaller effect of SO_2 than the current work at short times. At long times, the White results retain the dependence on SO_2, while the results of the current work do not show this effect.

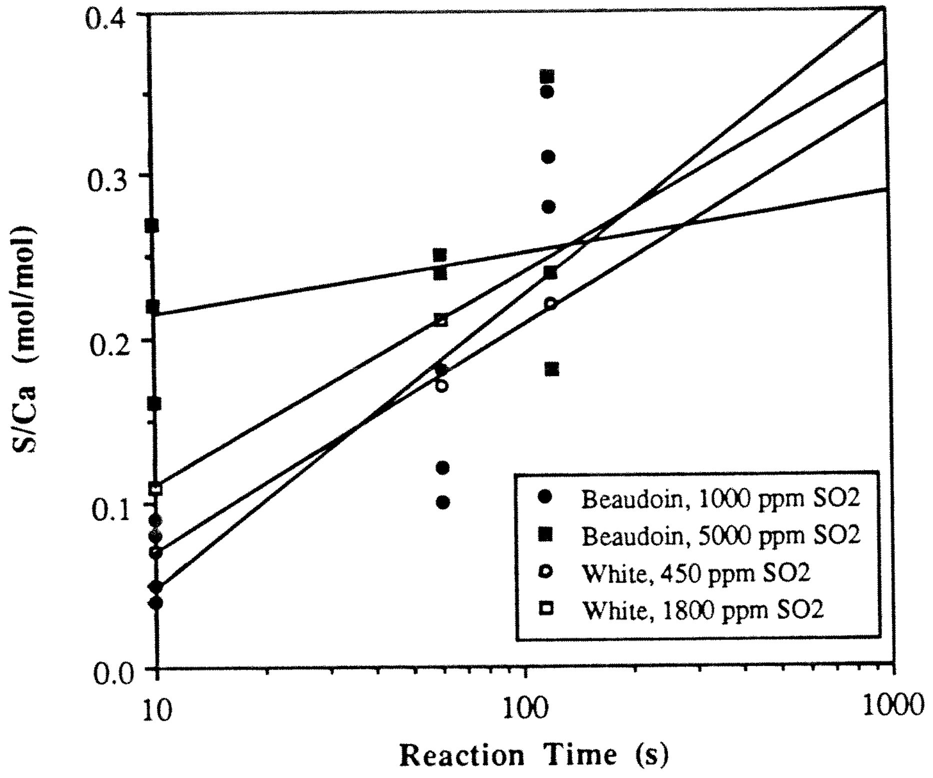

Figure 4.2 Effect of SO_2 Concentration on Lime/Fly Ash Sorbent Containing Ambient Moisture: (Comparison with White (1989);, 70 °C, 3.5% initial moisture, 51-64% relative humidity)

The experimental work performed with hydrated lime sorbents containing ambient moisture is presented in Figure 4.3. The data for the high surface area hydrated limes are labelled according to their BET surface area.

As in Figure 4.1, the sorbents initially contained moisture in equilibrium with the laboratory relative humidity, but when the flue gas was introduced into the reactors, the moisture content of the sorbents shifted to approach equilibrium with the flue gas relative humidity.

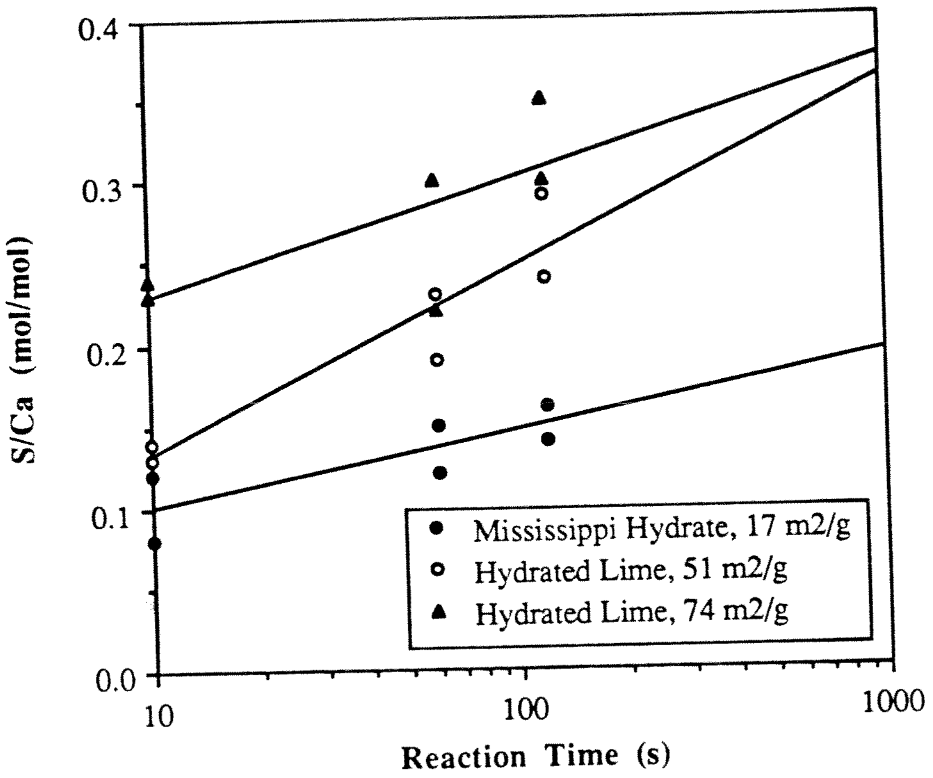

Figure 4.3 **Conversion of Hydrated Lime Sorbents Containing Ambient Moisture:** (5000 ppm SO_2, 70 °C, 1.0% initial moisture, 58 to 67% relative humidity)

The ambient conversion of the hydrated lime sorbents increases with increasing sorbent surface area, and the conversion of lower surface area sorbents does not approach that of the high surface area sorbents at short or long times. The conversion of the hydrated lime sorbents increases slightly with increasing reaction time, although the effect is not as significant as for the lime/fly ash sorbent in the 1000 ppm flue gas (Figure 4.1).

Significant conversion of the hydrated lime sorbents occurs, ranging up to approximately 0.22 and 0.33 for 10 and 120 s reactions at approximately 61% relative humidity with the high surface area hydrated lime. The high surface area provides adequate space for instantaneous reaction, but the formation and precipitation of product on the particle surface limits additional conversion.

Comparing Figures 4.3 and 4.1, the conversion of the lime/fly ash sorbent at 5000 ppm SO_2 was greater than that of the Mississippi Hydrate (17 m^2/g) at all reaction times, although the surface area of the two sorbents is similar. The conversion of the high surface area hydrated lime and the lime/fly ash sorbent is approximately the same at all conditions, implying that the ambient sorbent conversion is controlled by the dispersion of Ca throughout the sorbent surface area.

Figure 4.4 compares the results obtained by White (1989), using Mississippi Hydrated Lime containing ambient moisture at 450 and 1800 ppm SO_2, with results obtained in the current work using the same Mississippi Hydrated Lime sorbent as well as the high surface area hydrated limes. The results from the current work were obtained with ambient moisture and 5000 ppm SO_2. The White results are at 51-58% relative humidity, while the results from the current work are at 58 to 67% relative humidity.

The results for all of the hydrated limes at 5000 ppm SO_2 are greater than those obtained by White using Mississippi Hydrated Lime at either 450 or 1800 ppm SO_2. The effect of SO_2 content is not noticeable within the White results (450-1800 ppm), while the higher SO_2 content appears to have influenced the conversion attained in the present work. The effect of reaction time on sorbent conversion is approximately the same between the White results and the results for the Mississippi Hydrated Lime from the current work.

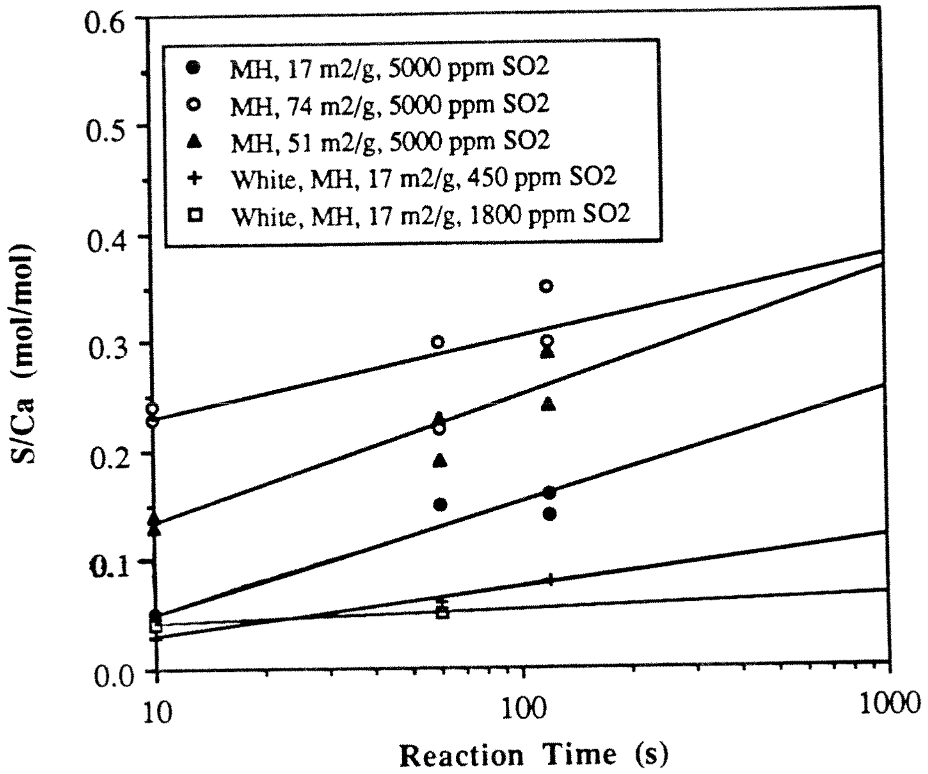

Figure 4.4 **Effect of SO_2 Concentration on Hydrated Lime Sorbents Containing Ambient Moisture:** (70 °C, 1.0% initial moisture, 58 to 67% relative humidity)

Table 4.2 presents the mathematical expressions for the best-fit lines to the conversion vs. time data shown in Figures 4.1 and 4.3. This information is required by the Interactive Model in order to predict sorbent conversion as a function of the initial sorbent moisture content, relative humidity, reaction time, and SO_2 concentration.

Table 4.2 **Expressions for Sorbent Conversion with Ambient Moisture:** (for use in Interactive Model)
Form: S/Ca = (intercept) + (slope)(Log time(s))

Sorbent Type	ppm SO_2 in flue gas	RH (%)	value of slope	value of intercept
Lime/Fly Ash	1000	0	3.62×10^{-2}	-2.36×10^{-2}
Lime/Fly Ash	1000	51-64	0.19	-0.14
Lime/Fly Ash	1000	80-90	0.26	-0.11
Lime/Fly Ash	5000	51-64	3.64×10^{-2}	0.18
Hydrate "A"	5000	58-67	7.32×10^{-2}	0.15
Hydrate "B"	5000	58-67	0.12	1.61×10^{-2}
Miss. Hydrate	5000	58-67	4.61×10^{-2}	5.38×10^{-2}

As stated above, Ca-dispersion over sorbent surface area may have a major effect on ambient sorbent conversion. Figure 4.5 presents a correlation of sorbent conversion with surface area per g $Ca(OH)_2$ in 5000 ppm SO_2. The lime/fly ash and hydrated lime sorbents fall approximately on the same curve. The data taken by Chu (1986) follow the same trends as the data taken from the current work, although the Chu data were taken at 500 ppm SO_2 and 54% relative humidity for 3600 s. In general, the results suggest that the reaction between $Ca(OH)_2$-based sorbent containing ambient moisture and SO_2 is can be maximized by effectively dispersing the $Ca(OH)_2$.

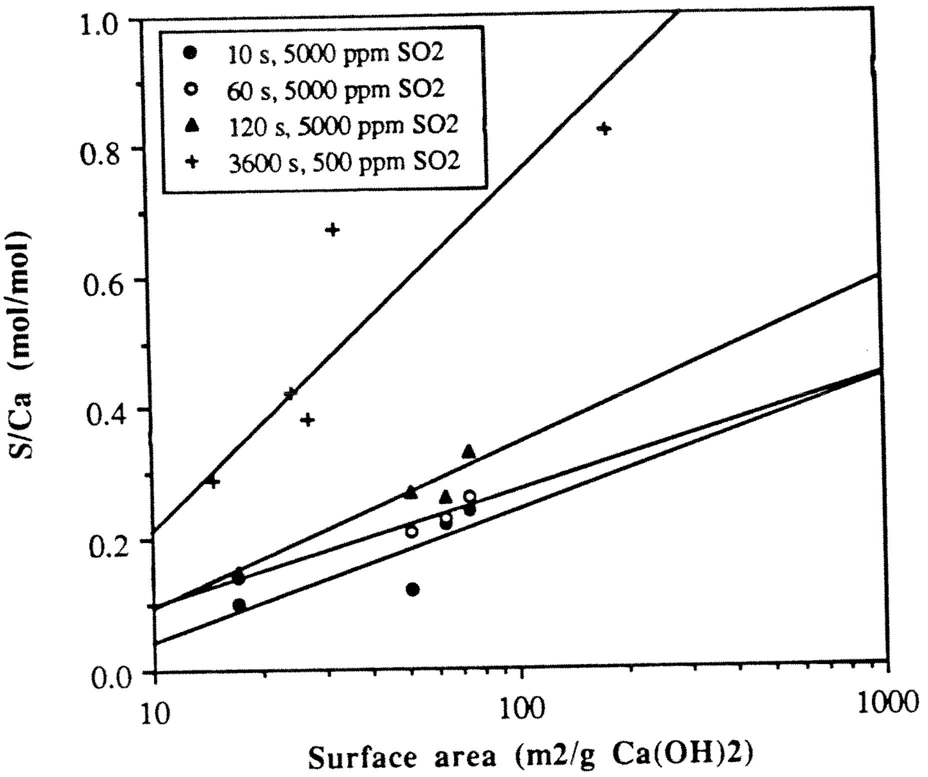

Figure 4.5 **Effect of Ca Dispersion on Sorbent Conversion:** (5000 ppm SO_2 in flue gas, 70 °C, 1.0% initial moisture on Miss. Hydrate, 3.5% on Lime/Fly Ash, 60 to 67% RH in flue gas,
[54% relative humidity for data at 3600 s from Chu (1986)
Chu data for lime/fly ash formed by slurrying 0.5 g $Ca(OH)_2$: 8.15 g San Miguel Fly Ash])

4.2 Results: Stage 2; Reaction of Damp Sorbents

Table 4.3 presents the test plan followed to investigate the effect of excess moisture on sorbent reactivity.

Table 4.3 Test Plan: Stage 2. Sorbent with Excess Moisture

Sorbent Type	Initial Moisture (%)	Flue Gas SO_2 Content (ppm)	Reaction Time (sec)	Flue Gas RH (%)
Lime/Fly ash	15, 30	1000	10, 60, 120	0, 55, 80
	15, 30	5000	10, 60, 120	0, 55
Miss. Hydrate	15	5000	10, 60, 120	55
Hydrated Lime 74 m^2/g	15	5000	10, 60, 120	55
Hydrated Lime 51 m^2/g	15	5000	10,60,120	55

It was expected that lime/fly ash sorbent could hold up to 30% initial moisture (by mass), and still remain free-flowing. Water in excess of this amount would result in agglomerated sorbent which could show inhibited reactivity towards SO_2. The hydrated lime sorbents were expected to lose their free-flowing nature in the presence of quantities of moisture exceeding 10 to 15% (by mass). For both sorbent types, the amount of moisture present on the sorbent during experimental work was limited so that the sorbents remained free-flowing, although a limited number of experiments were performed utilizing sorbents containing moisture in excess of these levels.

4.2.1 Damp Lime/Fly Ash Sorbent in 1000 ppm SO_2

Figures 4.6, 4.7, and 4.8 show the conversion attained for 10, 60, and 120 s reactions using lime/fly ash sorbent in 1000 ppm SO_2 at 0, 54-64, and 80-91% relative humidity. The predictions generated from the Interactive and Additive models are presented with the experimentally observed results.

For all cases shown, the sorbent conversion increases with increasing moisture content and increasing flue gas relative humidity. At 0% relative humidity for all reaction times, the sorbent conversion is not high, so that while the beneficial effect of excess moisture is clearly visible, the slope of the increase is less certain than it appears on the plots. At the intermediate relative humidity, the effect of excess moisture can be seen to level off above ~25% initial moisture in the 60 s plot and, with the exception of some anomalous data, in the 10 s plot as well. At ~60% relative humidity in the 120 s plot, it is unlikely that the conversion of sorbent containing 3.5% moisture is as great as the data present, and the conversion attained at the higher moisture content is approximately independent of the moisture content. At high relative humidity, the sorbent conversion increases greatly with increasing initial moisture content for all reaction times.

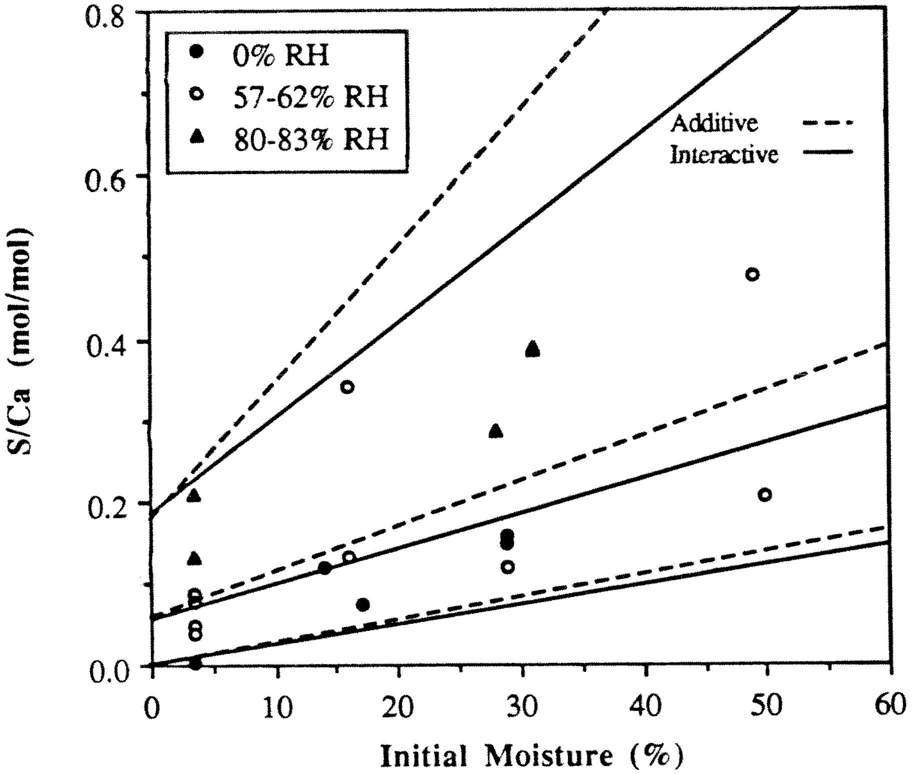

Figure 4.6 Conversion of Damp Lime/Fly Ash Sorbent: (1000 ppm SO_2, 70 °C, 10 s reaction)

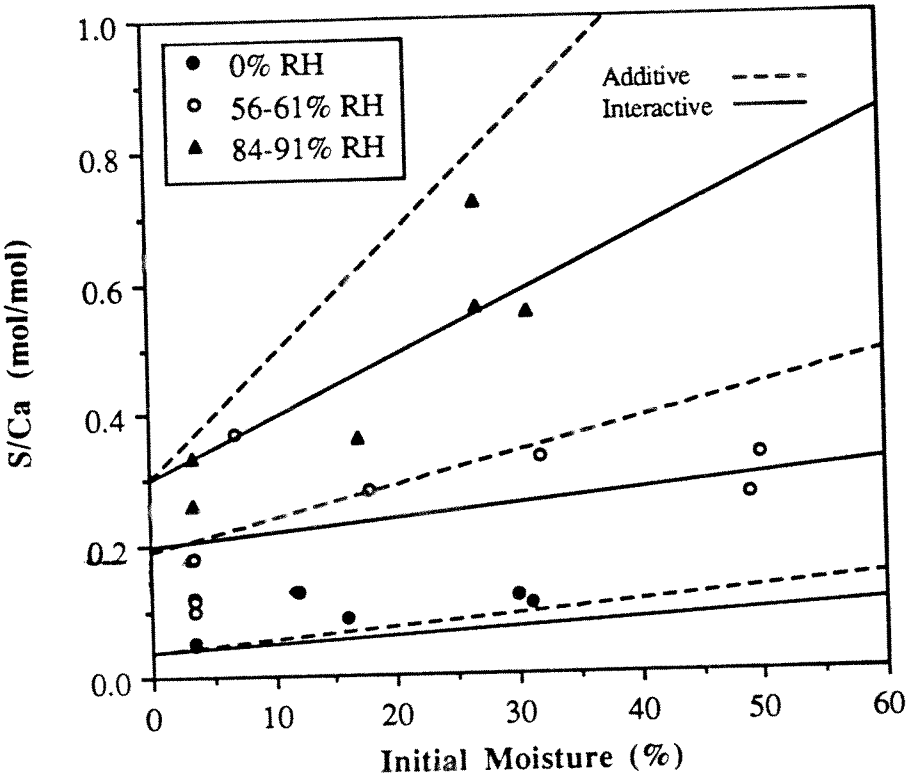

Figure 4.7 **Conversion of Damp Lime/Fly Ash Sorbent:** (1000 ppm SO_2, 70 °C, 60 s reaction)

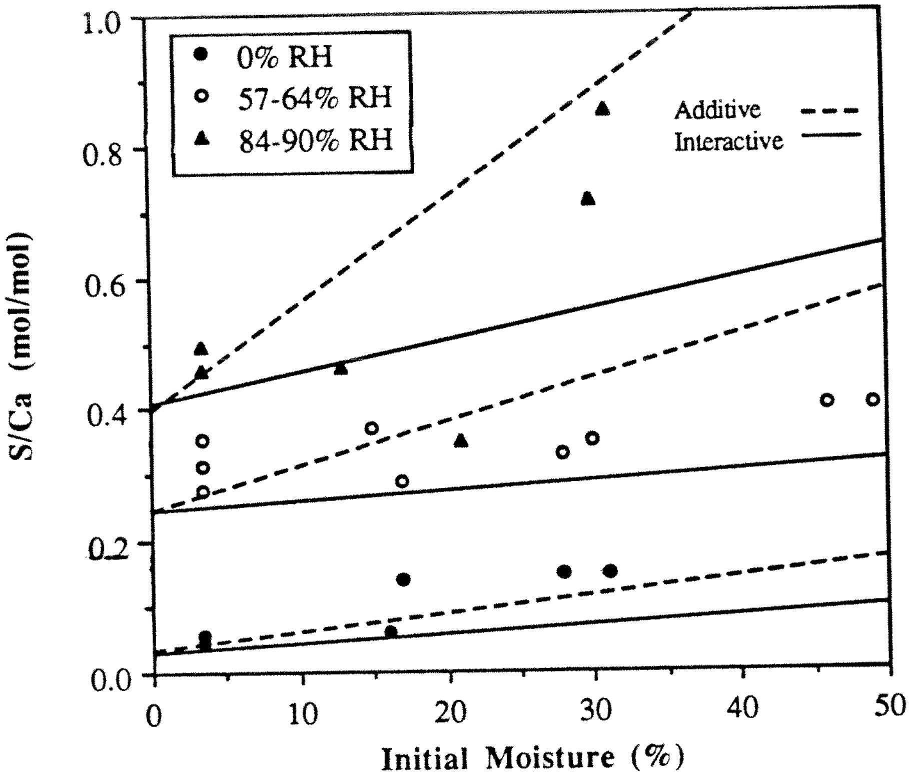

Figure 4.8 **Conversion of Damp Lime/Fly Ash Sorbent:** (1000 ppm SO_2, 70 °C, 120 s reaction)

It was expected that sorbents with high moisture content would not dry completely in the short (10 s) reaction time, negating the beneficial effect of the excess moisture. The increase in sorbent conversion with increasing initial moisture at the 10 s reaction time is significant for all relative humidities, though, indicating that the excess moisture promoted sorbent reactivity. At high moisture content, it was expected that moisture would be lost from the sorbent surface and would adsorb onto the sand during the sorbent preparation process. The results at 55-65% relative humidity contain points where this water loss may have been encountered (~50% initial moisture). Loss of moisture prior to the onset of reaction could explain why the increase in sorbent conversion is not as significant at the high moisture content as at the lower levels, although the intermediate-moisture results support the conclusion that conversion levels off with increasing moisture.

Relative humidity has a significant effect on the reaction in the presence of excess moisture. At all reaction times, the high relative humidity provides a major, non-linear enhancement to the wet reaction.

This is probably the result of increased drying time for the sorbents, which would increase greatly with increasing relative humidity of the flue gas.

In Chapter 2: Theory, an expression describing the effect of excess moisture on the conversion of damp sorbent is presented. Appendix A: Calculations illustrates how this expression is used to predict the conversion of a particular sorbent as a function of the flue gas relative humidity, the initial sorbent moisture content, the Ca content of the sample, and the flue gas SO_2 concentration. The predictive expression (Equation 2.7) is shown here:

$$\frac{\Delta SO_2}{Ca} = \frac{\mathfrak{D}_{SO2} K (P_{SO2})}{\mathfrak{D}_{H2O} K (P_{H2O}^{*} - P_{H2O})} \left(\frac{\Delta H_2O}{Ca}\right) \tag{4.1}$$

The total conversion of the sorbent is the combination of reaction occurring due to the moisture in excess of the ambient quantity and the reaction occurring due to the presence of ambient moisture on the sorbent surface. The Additive Model presented in Chapter 2: Theory assumes that the presence of excess moisture on the sorbent does not interfere with the ambient-moisture reaction. In order to predict the total conversion of the sorbent with the Additive Model, conversion values from ambient-moisture studies must be added to the conversion predicted due to the excess moisture on the sorbent.

Values of the conversion attained by ambient lime/fly ash sorbent when reacted in 1000 ppm SO_2 at 0, 55-65, and 80-90% relative humidity for 10, 60, and 120 s are presented in Table 4.4. In the Additive Model, these values are added to the conversion predicted due to wet reaction. The values are grouped according to the approximate relative humidities of each experiment.

Table 4.4 Contribution of Ambient Reaction to Total Conversion of Lime/Fly Ash Sorbent (Additive Model): (1000 ppm SO_2 in flue gas, 70 °C)

Reaction Time (s)	RH	Equilibrium-Moisture Conversion (add to pred. value)
10	0	0
10	55-68	0.07
10	80-93	0.14
60	0	0.03
60	55-68	0.17
60	80-93	0.24
120	0	0.04
120	55-68	0.27
120	80-93	0.34

The Additive Model slightly underpredicts the conversion of the lime/fly ash sorbent at 0% relative humidity in 1000 ppm SO_2 flue gas for the 10, 60, and 120 s reactions, while generally overpredicting sorbent conversion at the same conditions (reaction time and SO_2 concentration) for ~60% and ~85% relative humidity.

At 0% relative humidity, the magnitude of the ambient reaction in the absence of wet reaction is small. As a result, the contribution of the ambient reaction to the overall Additive Model conversion will be very small at 0% relative humidity, and the predicted conversion will be essentially the conversion predicted by the wet expression. The Additive Model slightly underpredicts sorbent conversion at this condition, suggesting that the predictive expression for the wet conversion of lime/fly ash is a reasonable approximation.

The Additive Model reasonably approximates the observed conversions at 3.5% initial moisture with 1000 ppm SO_2 in the flue gas and lime/fly ash sorbent. At low moisture content, the Additive Model is essentially the ambient moisture conversion. With this consideration, it is not surprising that the data are correctly modelled in this regime.

Considering the results at high moisture content, where the Additive Model overpredicts sorbent conversion, the overpredictions are usually less than the magnitude of the ambient-moisture contribution to the overall predicted conversion. This implies that the effect of excess moisture is correctly approximated, but the effect of the wet reaction on the ambient-moisture reaction is not correctly handled.

The Interactive Model uses the same expression to account for sorbent conversion in the presence of excess moisture as the Additive Model. The difference between the two lies in the relationship between the ambient-moisture mechanism and the wet sorbent mechanism. In both models, the predictions accounting for the wet- and ambient-moisture effects are additive, although the Additive Model assumes that the presence of excess moisture does not alter the extent of reaction occurring by the ambient-moisture pathway, while the Interactive Model assumes that the ambient-moisture reaction is limited by the wet reaction. The Interactive Model also assumes that the rate of sorbent conversion by the ambient-moisture mechanism is a function of the amount of product present on the sorbent surface.

The Interactive Model requires expressions for the rate of conversion by the ambient-moisture mechanism as a function of reaction time. These expressions are taken from Figures 4.1 and 4.3, and are presented in Table 4.2.

To use the Interactive Model, the conversion attained by the wet reaction mechanism is noted and the expressions presented in Table 4.2 are manipulated to determine the time required to attain this conversion by the ambient-moisture mechanism alone (t_o). It is then assumed that the excess moisture evaporates instantly from the sorbent surface upon introduction of the flue gas, so that the time available for reaction by the ambient-moisture mechanism is approximately the original reaction time (t). The rate expressions presented in Table 4.6 are evaluated twice, at time = (t_o + t) and time = (t_o). The conversion expected at t_o is then subtracted from that expected at t_o + t to determine the conversion occurring by the ambient-moisture mechanism after the wet reaction is complete.

The Interactive Model underpredicts system performance for all reaction times at 0% relative humidity and 1000 ppm SO_2 in the flue gas. At this condition the contribution of ambient reaction is relatively insignificant, although the overall magnitude of the sorbent conversion is small. The model also underpredicts lime/fly ash conversion with 1000 ppm SO_2 in the flue gas at long times.

At the long times, the ambient-moisture conversion is significant. The Additive Model overpredicted the system performance at these conditions, while the Interactive Model, which incorporates a significantly lower contribution due to the ambient-moisture reaction, underpredicts system performance. This implies that the wet reaction influences the ambient-moisture reaction and that the model has overcompensated for this effect.

At moderate moisture content, the Interactive Model generally slightly underpredicts sorbent conversion, while the Additive Model overpredicted conversion. At the highest moisture content, the Interactive Model more accurately represented the data, although deviations below the observed conversion were frequent. These results further support the theory that the wet reaction inhibits the ambient reaction, and that the Interactive Model has overcompensated for this effect.

The Interactive Model inaccuracy may be attributed to inaccuracy in determining expressions for sorbent conversion by the ambient mechanism as a function of reaction time. In Figures 4.1 and 4.3, the best-fit lines do not always represent the data accurately. Errors in the projected slopes of these lines will propagate into the expected ambient-moisture conversion used in the Interactive Model.

4.2.2 Results: Damp Sorbent in 5000 ppm SO_2

Figures 4.9 to 4.11 present the results with damp lime/fly ash sorbents in 5000 ppm SO_2. As shown in Table 4.2, the desired flue gas relative humidity during this work was 55%, although some deviations from the target relative humidity did occur. The results predicted by the Interactive and Additive Models are presented with the experimental data.

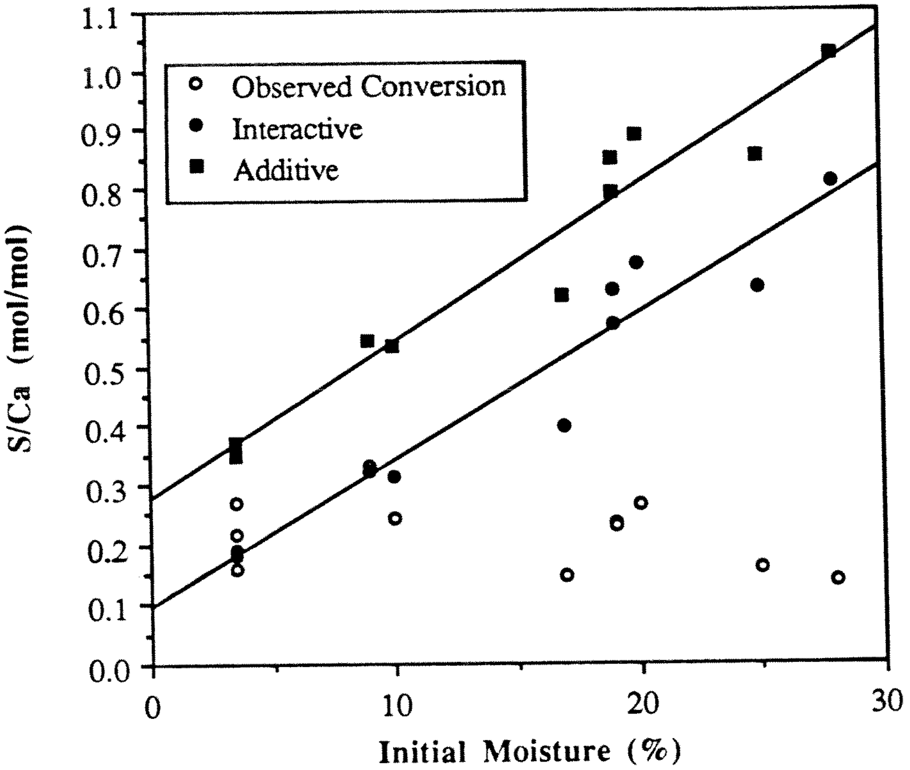

Figure 4.9 **Conversion of Damp Lime/Fly Ash Sorbent:** (5000 ppm SO_2 in flue gas, 70 °C, 10 s reaction, 57-63% RH)

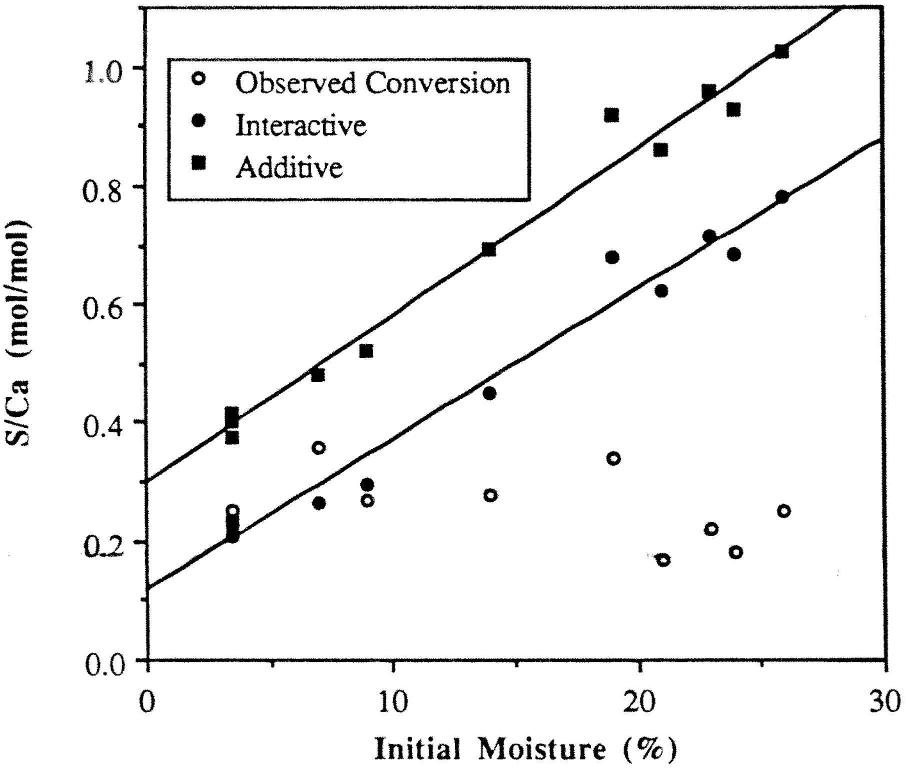

Figure 4.10 Conversion of Damp Lime/Fly Ash Sorbent: (5000 ppm SO_2 in flue gas, 70 °C, 60 s reaction, 58-68% RH)

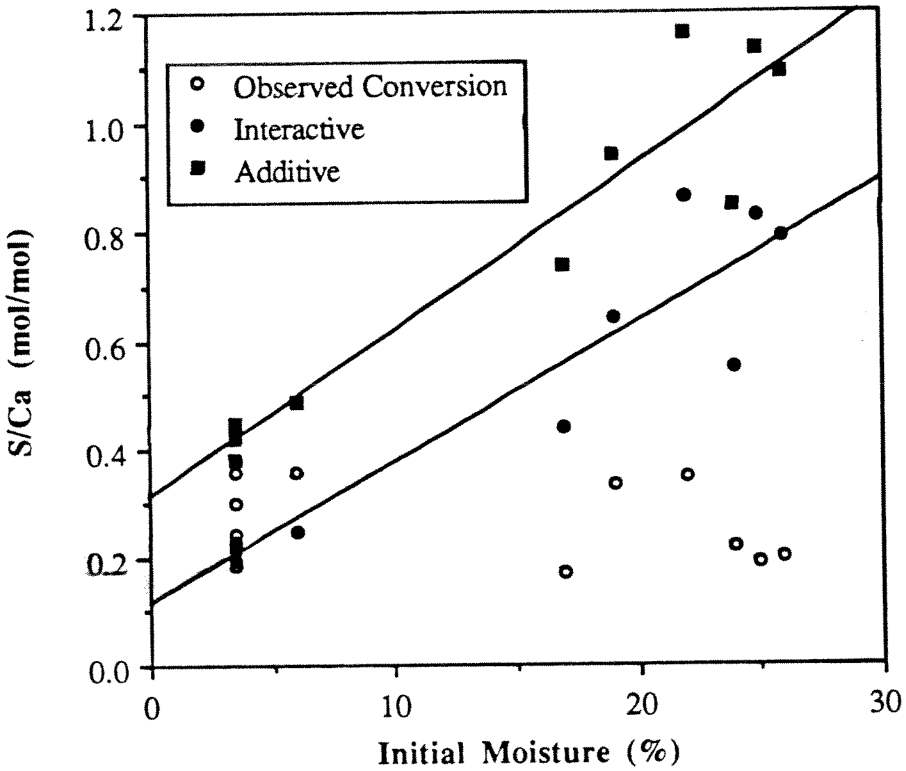

Figure 4.11 Conversion of Damp Lime/Fly Ash Sorbent: (5000 ppm SO_2 in flue gas, 70 °C, 120 s reaction, 58-62% RH)

The lime/fly ash sorbent reacting in 5000 ppm flue gas did not show a significant increase in conversion with increasing moisture content. For this sorbent, the conversion at low moisture content is significantly greater with 5000 ppm SO_2 than with 1000 ppm SO_2 for both the 10 and 60 s reactions. The conversion at higher sorbent moisture content is approximately the same for 5000 and 1000 ppm SO_2. It appears that there is a fixed extent of reaction occurring with 5000 ppm SO_2 and upon completion of this reaction, additional reaction, with increasing reaction time or increasing moisture content, provides only incremental additional conversion. In the presence of 1000 ppm SO_2, the initial reaction is not as significant, so that significant additional conversion can be accomplished by increasing the reaction time or moisture content of the sorbent.

The ambient-reaction portions of the Additive Model for the 5000 ppm work are presented in Table 4.5, below. Using these parameters, the Additive Model consistently overpredicts the lime/fly ash conversion at all sorbent moisture contents. For the 1000 ppm SO_2 work shown earlier, the Additive Model overpredicted the lime/fly ash conversion at high moisture content, but the magnitude of this overprediction was less than the contribution of the ambient reaction. The results of the 5000 ppm study with damp lime/fly ash sorbent do not fall into this category. The model grossly overpredicts the sorbent utilization at all moisture contents, implying that the effect of wet reaction is not correctly predicted in the model.

The Interactive Model overpredicts the conversion attained using lime/fly ash sorbent with high moisture content in 5000 ppm SO_2 flue gas, although it accurately predicts sorbent conversion at low moisture content. The effects of wet reaction and of ambient reaction are correctly noted by the Interactive Model when the wet reaction is gas-phase mass transfer limited, as has been shown earlier. At the high moisture content in 5000 ppm SO_2, the Interactive model grossly overpredicts sorbent conversion, implying that the effect of wet reaction is incorrectly approximated and confirming that the reaction between wet lime/fly ash sorbent and 5000 ppm SO_2 is not gas-phase mass-transfer controlled.

Table 4.5 Contribution of Equilibrium Reaction to Total Conversion of Lime/Fly Ash and Hydrated Lime Sorbents (Additive Model): (5000 ppm SO_2 in flue gas, 70 °C)

Reaction Time (s)	Sorbent Type*	RH (%)	Equilibrium-Moisture Conversion (add to pred. value)
10	MH	56-63	0.08
10	A	58-66	0.21
10	B	58-60	0.10
10	L/FA	57-63	0.22
60	MH	60-67	0.13
60	A	62-67	0.24
60	B	58-69	0.14
60	L/FA	58-68	0.24
120	MH	58-62	0.15
120	A	58-63	0.35
120	B	58-64	0.29
120	L/FA	58-68	0.30

*[MH = Mississippi Hydrated Lime, A = Mississippi Hydrated Lime (74 m2/g), B = Mississippi Hydrated Lime (51 m2/g), L/FA = Lime/Fly Ash]

The results presented in Figures 4.12 to 4.14 are for work done with damp hydrated lime sorbents in 5000 ppm SO_2.

The hydrated lime sorbents reacting in 5000 ppm flue gas did not show a significant increase in conversion with increasing moisture content, and within the spread of the data, the conversion can be considered constant with increasing initial moisture content for the moderate surface area hydrated lime. The conversion of all of the hydrated lime sorbents is approximately the same when large quantities of initial moisture are added, independent of sorbent surface area. Conversion of the highest surface area hydrated lime is seen to decrease with increasing initial moisture content of the sorbent, while for the low surface area hydrated lime the conversion increases with increasing initial moisture content.

There are two possible explanations for these phenomena. First, the excess moisture may promote recrystallization of the high surface area limes, reducing the ambient conversion by reducing the surface area available for reaction. Second, the products of the wet reaction may interfere with the ambient reaction to a greater degree than the products of the ambient reaction. Both of these hypotheses suggest that the effect of moisture on the ambient reaction for the hydrated limes is important. In the high surface area limes, the loss of ambient conversion is significant, while in the low surface area limes, where the ambient conversion is low, the loss of ambient conversion is overshadowed by the wet reaction.

The contributions of the ambient reaction to the Additive Model for hydrated lime conversion in 5000 ppm SO_2 are presented in Table 4.4, above. For the hydrated lime sorbents, the Additive Model correctly predicts or slightly overpredicts the sorbent conversion at low moisture content, where contribution of the wet reaction to the overall conversion is small compared to the ambient conversion. As seen with the lime/fly ash in 1000 ppm SO_2, when the wet reaction is not significant, the Additive Model is accurate.

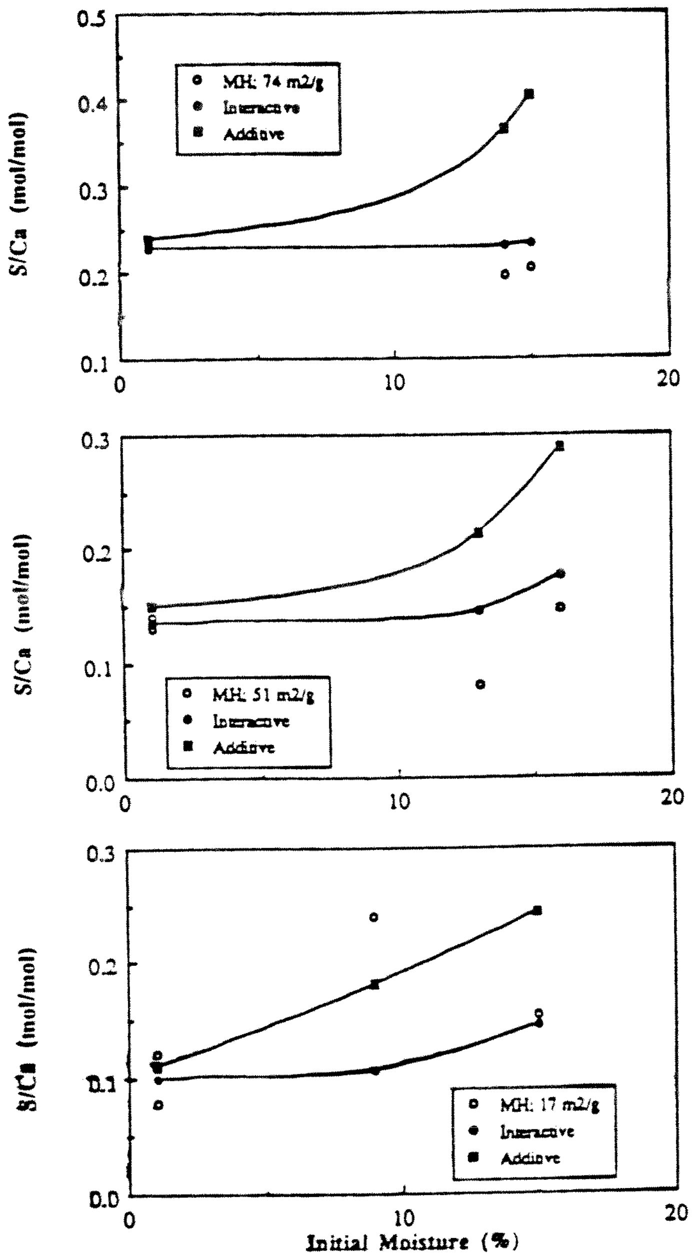

Figure 4.12 Conversion of Damp Hydrated Lime Sorbents: (5000 ppm SO_2 in flue gas, 70 °C, 10 s reaction, 56-66% RH)

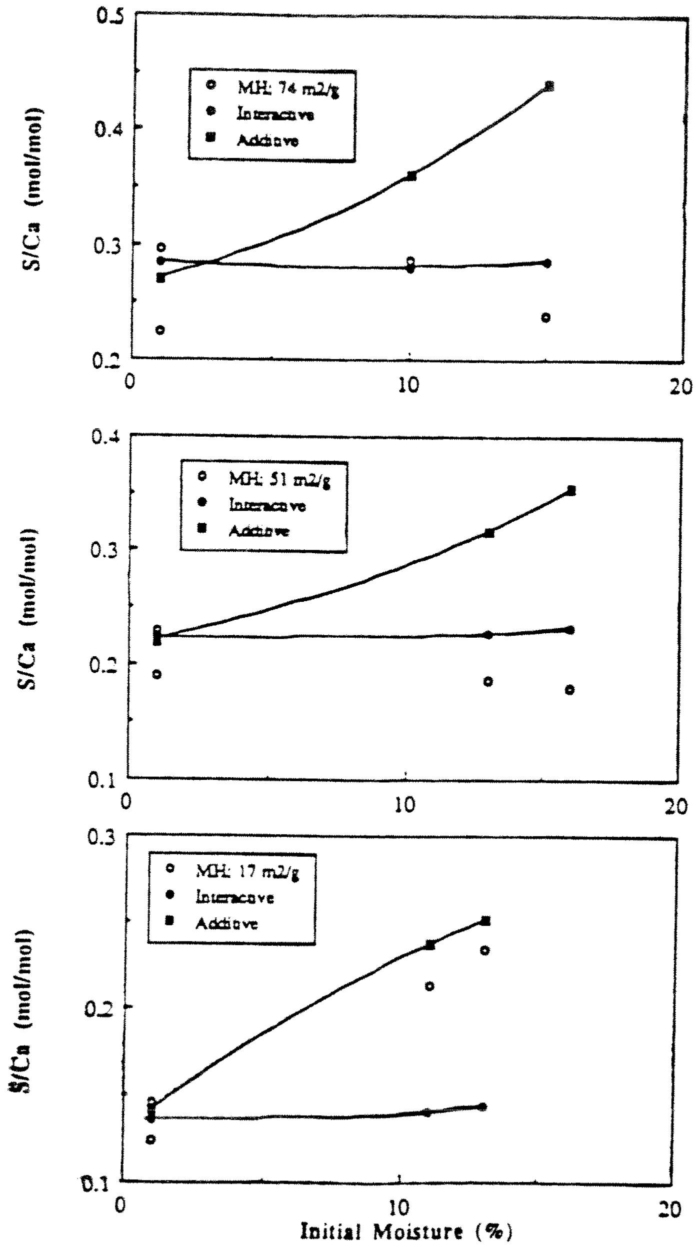

Figure 4.13 Conversion of Damp Hydrated Lime Sorbents: (5000 ppm SO_2 in flue gas, 70 °C, 60 s reaction, 58-69% RH)

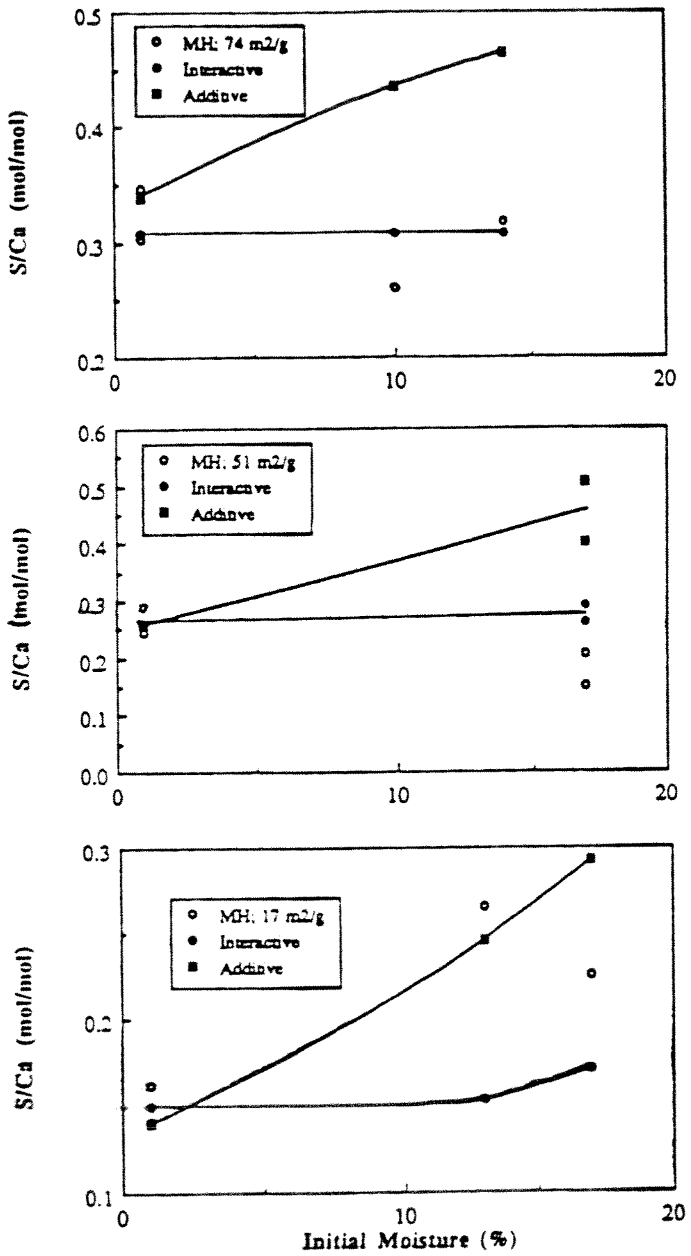

Figure 4.14 Conversion of Damp Hydrated Lime Sorbents: (5000 ppm SO_2 in flue gas, 70 °C, 120 s reaction, 58-69% RH)

At the high moisture content for the hydrated lime sorbents, the Interactive Model generally slightly underpredicts system performance, as it did with the 1000 ppm lime/fly ash results, although it correctly predicts sorbent conversions at low moisture content.

The fits of both models to the damp hydrated lime results in 5000 ppm SO_2 follow the same trends as for the lime/fly ash in 1000 ppm SO_2. In both of these cases, the wet reaction is accurately predicted by the gas-phase controlled expression, and the deviations are encountered when incorporating the effects of ambient reaction on the overall conversion.

4.3 Conversion of Lime/Fly Ash Sorbent by Reaction with CO_2

The results presented in Figure 4.15 below show the conversion of damp lime/fly ash sorbent by CO_2. These results are from studies conducted with 10-12% CO_2 and 1000 ppm SO_2 in the flue gas

The lime/fly ash sorbent contained CO_2 in the form of carbonate, prior to reaction with the 1000 ppm SO_2, 10% CO_2 flue gas. The initial carbonate content of the sorbent was 2×10^{-4} moles CO_2/mol Ca. Significant additional CO_2 capture was not found for short or long time reactions in the presence of excess moisture on the sorbent suface. Within the ability to experimentally determine CO_2 capture on the sorbent, no CO_2 capture occurred, and more importantly, the magnitude of Ca-conversion by CO_2 is several orders of magnitude lower than for conversion by SO_2 with 10% CO_2 and 1000 ppm SO_2 in the flue gas.

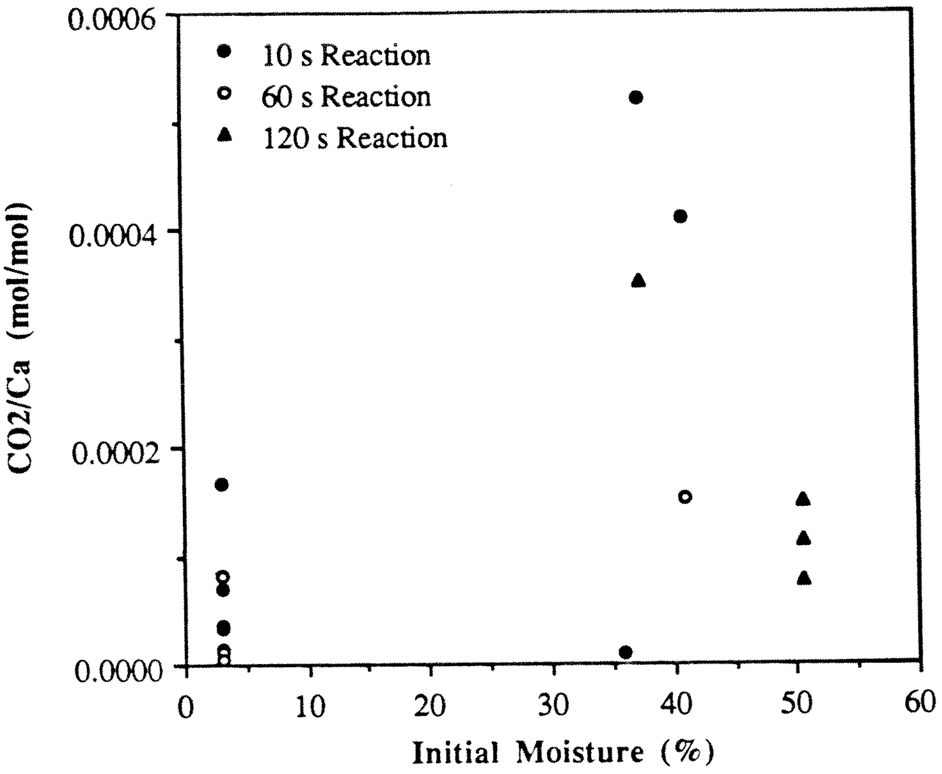

Figure 4.15 **Reaction of Lime/Fly Ash Sorbent with CO_2**:(1000 ppm SO_2 in flue gas, 70 °C, 55-65% RH)

4.4 Conclusions

Based on the results presented above several conclusions may be drawn.

1] In the presence of 1000 ppm SO_2, the addition of excess moisture to lime/fly ash sorbents significantly increases their conversion over that attained in the absence of excess moisture.

2] In the presence of 5000 ppm SO_2, the addition of excess moisture to lime/fly ash sorbents does not increase significantly, and may decrease slightly, the sorbent conversion in comparison with that attained in the absence of excess moisture.

3] The conversion of low surface area hydrated lime increases with increasing initial moisture content of the sorbent , while the conversion of high surface area hydrated lime remains the same or decreases slightly with the addition of excess moisture.

4] The reaction between damp lime/fly ash sorbent and low concentrations of SO_2 is gas-phase mass-transfer controlled until the moisture has evaporated from the sorbent surface.

5] The reaction between damp hydrated lime sorbent and high concentrations of SO_2 is gas-phase mass-transfer controlled until the moisture has evaporated from the sorbent surface.

6] The reaction between damp lime/fly ash sorbent and high concentrations of SO_2 is not gas-phase mass-transfer controlled.

7] Sorbent conversion due to wet reaction is not a strong function of sorbent surface area.

8] Overall damp lime/fly ash conversion at times ranging from 10 to 120 s is a stronger function of relative humidity (sorbent drying time) than of SO_2 content in the flue gas.

9] The reaction occurring between lime/fly ash and hydrated lime sorbents in the presence of excess free moisture is a combination of the equilibrium-moisture reaction and the wet reaction.

10] The conversion of the hydrated lime and lime/fly ash sorbents due to wet reactions affects the surface properties of the sorbents and the extent of ambient-moisture conversion which occurs upon evaporation of the free moisture.

11] The ambient-moisture conversion of the hydrated lime and lime/fly ash sorbents increases with increasing surface area/g $Ca(OH)_2$ of the sorbent.

12] Sorbents which attain high conversions due to equilibrium-moisture reaction do not show increased reactivity at long times in the presence of excess moisture, although the wet reaction occurs much more quickly than the equilibrium-moisture reaction.

13] Reaction occurring between damp lime/fly ash and low-concentration SO_2 and damp hydrated lime sorbents and high-concentration SO_2 can be adequately modelled assuming the wet reaction is gas-phase mass-transfer controlled and the products of the wet reaction affect the progress of the ambient-moisture reaction.

14] Damp hydrated limes and lime/fly ash sorbents can be prepared, loaded and reacted with SO_2 without losing their initial moisture and without agglomerating.

15] With up to 10% CO_2 in flue gas containing 1000 ppm SO_2, damp lime/fly ash does react measurably with CO_2.

Appendix A

Calculations

Sample calculations of the SO_2 and CO_2 capture obtained by reacted sorbent and calculation of the amount of Ca present in each reacted sample are presented here.

A.1 Sorbent Sulfur Content

As indicated in Chapter 3: Experimental Apparatus, a Dionex Ion Chromatograph was used to determine the SO_2 content (as SO_4^{-2}) of the sorbents studied. The sorbents were dissolved into acidic, oxidizing solutions, which were diluted and injected into the IC for analysis. The IC outputs were numerical values corresponding to the magnitude of the SO_4^{-2} concentration in the injected solution, and these values were output to two different locations, a digital display located on the control panel of the IC itself and a Hewlett-Packard (HP) Integrator. The output on the control panel was a direct report of the measured conductivity change, presented in units of microsiemens $(\text{microohms})^{-1}$, while the Integrator output an integer value corresponding to the magnitude of the conductivity change.

Typically, the conductivity of the analyzed solution began at a background level corresponding to the characteristic conductivity of the eluant solution. The conductivity rose to a maximum value when a portion of the eluant containing ions with electrical properties unlike those of the eluant passed through the conductivity cell, returning to the background level after the ions had passed. The digital output on the front of the device changed very rapidly as the conductivity of the solution changed, and the maximum value of the conductivity was the only value which could be noted. The integrator received a continuous voltage output corresponding to the instantaneous conductivity within the cell. The integrator plotted a peak, reporting a calculated peak area and a ratio of peak height to peak area, based on the magnitude of the conductivity change from the background level. The values of the peak areas were utilized in this project, as these were the most convenient measurements with which to work.

To interpret the peaks reported for the analyzed solutions, the peak areas corresponding to the SO_4^{-2} ion were compared to peak areas generated by the injection of standard solutions of SO_4^{-2} ions. As stated above, the solid material to be analyzed was dissolved in an acidic, oxidizing solution, which subsequently was diluted. The diluted solution was analyzed in the IC, and after the SO_4^{-2} concentration of this analyzed solution was determined, it was necessary to calculate the S content of the original solid sample from the dilution ratios.

As reported previously, reacted sorbent was dissolved in 100 ml of an acid solution containing H_2O_2, and 5 ml of this solution were added to 45 ml of H_2O. The resulting 5:50 solution was analyzed for SO_4^{-2} content.

To determine the SO_4^{-2} content of the original solution, a calibration equation was constructed based on the peak areas of the standards:

$$[\text{READING}] = b[SO_4^{-2}] + c \tag{A.1}$$

where:

[READING] = peak area,
$[SO_4^{-2}]$ = SO_4^{-2} concentration of injected solution, and
b,c = constants.

This equation was rearranged so that the SO_4^{-2} concentration of the 5:50 solution was determined as a function of its peak area. To determine the SO_4^{-2} content of the undiluted solution, the following equation was used:

$$N_{SO4} = \left([SO_4^{-2}]_{5:50}\right)\left(\frac{(Vol_{5:50})\ (Vol_{orig})}{(Vol_{added})\ \ 1000}\right) \tag{A.2}$$

where:

N_{SO4} = number mmoles SO_4^{-2} in undiluted solution,
$([SO_4^{-2}]_{5:50})$ = concentration SO_4^{-2} in analyzed solution; (mmol/l),
$(Vol_{5:50})$ = total volume of analyzed solution; (ml),
(Vol_{added}) = volume original solution used in analyzed solution; (ml), and
(Vol_{orig}) = total volume undiluted solution (ml).

A.2 Sorbent Ca Content

A Varian Atomic Absorption Spectrophotometer was used to quantify the Ca content of the sorbents studied. The sorbents were dissolved into acidic, oxidizing solutions, which were diluted and then combusted in the AA for analysis. In the AA, a beam of light at a specific wavelength passed through the flame in which the Ca-containing solution was combusted, and the amount of light which was absorbed in the flame varied with the Ca content of the combusted solution. The AA output was a numerical value corresponding to the magnitude of the change in the amount of light transmitted. This value, in units of parts per million Ca (ppm), was output to a digital display located on the control panel of the instrument. The ppm Ca in the analyzed sample was determined by calibrating the apparatus with standards of known Ca content and comparing the absorbance of the unknown samples with the absorbance of the standards.

As stated previously, the sorbents were dissolved in 100 ml of an acid solution containing H_2O_2. Typically, 5 ml of this solution were added to 5 ml of 1.0 M NaCl and 40 ml H_2O. The resulting 5:50 solution was analyzed for Ca.

To determine the Ca content of the analyzed solution, it was first necessary to construct a calibration equation based on the peak areas of the standards in the form:

$$[\mathrm{READING}] = b(\mathrm{Ca}) + c \qquad \text{(A.3)}$$

where:

[READING] = machine output; (ppm),
(Ca) = Ca content of analyzed solution; (ppm), and
b,c = constants.

This equation was rearranged so that the Ca content of the 5:50 solution was determined as a function of its machine output.

To determine the Ca content of the undiluted solution, the following equation was used:

$$N_{Ca} = (Ca_{5:50})\left(\frac{Vol_{5:50}\ \ (Vol_{orig})}{Vol_{added}(40)(1000)}\right) \qquad \text{(A.4)}$$

where:

N_{Ca} = number mmoles Ca in original solution,
($Ca_{5:50}$) = Ca content of analyzed solution; (ppm),
($Vol_{5:50}$) = total volume of analyzed solution; (ml),
(Vol_{added}) = volume original solution used in analyzed solution; (ml), and
(Vol_{orig}) = total volume original solution (ml).

The factor of 40 was required to convert from ppm to mM Ca, according to the following expressions:

$$1\ \mathrm{ppm\ Ca} = \frac{1\ \mathrm{g\ Ca}}{1\times10^6\ \mathrm{g\ H_2O}} \qquad \text{(A.5)}$$

$$\mathrm{mM\ Ca} = \frac{(1\ \mathrm{g\ Ca})\qquad(1\ \mathrm{g\ H_2O})\ (1\ \mathrm{mol\ Ca})}{(1\times10^6\ \mathrm{g\ H_2O})\ (1\ \mathrm{ml\ H_2O})\,(40\ \mathrm{g\ Ca})}. \qquad \text{(A.6)}$$

With the calculations presented in Sections A.2 and A.3, it was possible to determine the conversion, as S/Ca, attained in a solid sample.

A.3 Total Carbon Content of Sorbent

As indicated in the Experimental Apparatus Section, an Oceanographic Total Carbon Analyzer measured the number of carbon atoms present as inorganic carbon in an injected liquid sample. The TCA output a numerical value corresponding to this quantity on a digital display located on the control panel of the instrument itself.

The TCA measured the quantity of infrared light which passed through a carrier gas stream containing carbon as CO_2. When the CO_2 passed through the light, the quantity of light transmitted through the gas stream decreased until it reached a minimum value, returning to its background level after the CO_2 had passed. A peak reflecting the change in the quantity of light transmitted was recorded and integrated and the area of the absorbance peak was reported as an integer value.

As stated previously, the sorbent to be analyzed was dissolved in 100 ml of an acidic, oxidizing solution in a sealed flask. This solution was subsequently filtered, and aliquots were removed and diluted for SO_4^{-2} and Ca analysis. The solution was analyzed for inorganic carbon content (as CO_2) prior to the filtration step by removing a known volume of undiluted, unfiltered solution from the sealed sample bottle with a gas-tight syringe and injecting this sample into the TCA. To determine the total carbon content of the analyzed solution, a calibration equation based on the peak areas of standard solutions containing dissolved CO_2 (as carbonate) was constructed in the form:

$$[\mathrm{READING}] = b(CO_2) + c \tag{A.7}$$

where:

[READING] = machine output,
(CO_2) = inorganic C content of analyzed solution, and
b,c = constants.

This equation was rearranged so that the inorganic carbon content of the 5:50 solution was determined as a function of its machine output. The peak outputs of the analyzed samples were compared to this equation to determine their carbon content.

To determine the inorganic carbon content of the unfiltered, undiluted solution, the following equation was used:

$$N_C = \frac{(C_{inj})\left(\frac{Vol_{orig}}{Vol_{injected}}\right) + x_{CO2}H_{CO2}\left(\frac{Vol_{vap}}{RT}\right)}{1000000} \qquad \text{(A.8)}$$

where:

N_C = number mmoles inorganic C in original solution,
(C_{inj}) = inorganic C content of analyzed solution; (μmole),
x_{CO2} = mole fraction CO_2 in liquid phase,
H_{CO2} = Henry's law constant for CO_2 (mole fraction basis),
Vol_{vap} = vapor volume in flask above original solution; (ml),
R = gas constant; ((cm^3-atm)/(μmole°K),
T = system temperature; (°K),
(($Vol_{injected}$) = volume original solution injected; (ml), and
(Vol_{orig}) = total volume original solution (ml).

With this third set of calculations, it was possible to report the carbonate conversion (CO_2/Ca) attained in a solid sample.

A.4 Theoretical Prediction of Sorbent Utilization

The theory derived earlier which predicts SO_2 capture as a function of H_2O evaporation from the solid surface was given as:

$$\Delta SO_2 = \Delta H_2O\sqrt{\frac{\mathcal{D}_{KH2O}}{\mathcal{D}_{SO2}}}\left(\frac{P_{SO2}}{P_{H2O}^{*} - P_{H2O}}\right) \qquad \text{(A.9)}$$

where:

ΔSO_2 = moles SO_2 captured per gram solid; (mol/g),
ΔH_2O = moles H_2O evaporated per gram solid; (mol/g),
$\mathcal{D}_{KH2O}$ = Knudsen diffusion coefficient H_2O; (l^2/ time),
$\mathcal{D}_{KSO2}$ = Knudsen diffusion coefficient SO_2; (l^2/ time),
P_{SO2} = bulk partial pressure SO_2,
P_{H2O}^{*} = interfacial partial pressure H_2O, and
P_{H2O} = bulk partial pressure H_2O.

If the value of ΔSO_2/g solids was multiplied by the Ca content of the solids, as mol-Ca/g-solid, it was possible to predict a conversion based on the reaction occurring in the presence of liquid water, as shown in Chapter 2: Theory. The predictive expression (Equation 2.7) is reproduced here:

$$\frac{\Delta SO_2}{Ca} = \frac{\mathcal{D}_{SO_2} K (P_{SO_2})}{\mathcal{D}_{H_2O} K (P^*_{H_2O} - P_{H_2O})} \left(\frac{\Delta H_2O}{Ca}\right) \tag{A.10}$$

where:

Ca = Ca content of the sorbent; [moles/gram sorbent].

A.5 Example Calculation

The following is a sample calculation of sorbent utilization by SO_2 and CO_2. The first section (A.5.1) details the calculation of the SO_2 captured on the sorbent, while A.5.2 details the calculation of the CO_2 captured on the sorbent, and A.5.3 details the calculation of the Ca present in the sorbent.

A.5.1 Calculation of SO_2 Capture

After reactive sorbent was exposed to flue gas, the entire contents of the reactor, including both the sorbent and the reactor packing, were dissolved in approximately 50 ml of an oxidizing acid solution. After digestion, the solution was filtered and makeup water was added to create a 100 ml mother liquor. This liquor was diluted and a portion of the diluted solution was injected into the IC to determine the total SO_4^{-2} content of the solution.

Given IC outputs of:

1] 0.001 M Na_2SO_4 [=] 422660, @ 5.65 min
2] 0.05 M Na_2SO_4 [=] 1.2919×10^7, @ 5.63 min, and
3] unknown "A" [=] 4540900, @ 5.69 min,

and assuming that the analyzed sample was made by withdrawing a 5 ml aliquot from the 100 ml mother liquor and adding this to 45 ml of H_2O, the following calculations give the sulfate content of the undiluted stock solution.

1] Least squares fit to the standards outputs gives:

$$\text{machine output} = 2.5618 \times 10^8 \text{ (mM (sulfate) inj.)} + 1.07 \times 10^5. \tag{A.11}$$

2] Insert "A" output into (A.10) to obtain:

mM sulfate in analyzed solution = 1.73×10^{-2}.

3] Use (A.2) to obtain:

$$N_{SO4} = \left([SO_4^{-2}]_{5:50}\right)\left(\frac{(Vol_{5:50})\ (Vol_{orig})}{(Vol_{added})\ \ 1000}\right), \text{ or} \tag{A.12}$$

$$N_{SO4} = \left(1.73 \times 10^{-2}\right)\left(\frac{50\ (100)}{5\ (1000)}\right). \tag{A.13}$$

The final result is that there were 1.73×10^{-2} mmoles of sulfate ($= N_{SO4}$) in the mother liquor.

A.5.2 Calculation of CO_2 Capture

To determine the CO_2 capture attained when the reactive sorbent was exposed to flue gas, the practice for digesting the reactive sorbent was different from that employed when CO_2 capture was not studied. When CO_2 capture was to be studied, the sorbent and reactor packing were dissolved in exactly 100 ml of acidic, oxidizing solution. During the digestion, this solution was sealed with a rubber septum. A 1.0 ml aliquot of this solution was withdrawn from the sealed flask with a syringe and injected into the TCA to determine the CO_2 content of the solution.

Given TCA outputs of:

1] 0.5 μmoles $NaHCO_3$ [=] 11911,
2] 0.1 μmoles $NaHCO_3$ [=] 2096, and
3] 1 ml of unknown "A" [=] 3214,

and measuring the vapor volume above the liquid in the 100 ml unfiltered, undiluted mother liquor, the following calculations give the total CO_2 content of the undiluted stock solution.

1] Least squares fit to the standards outputs gives:

$$\text{machine output} = 2.403 \times 10^{4}\ (\mu\text{moles } (CO_2) \text{ inj.}) - 136.29. \tag{A.14}$$

2] Insert "A" output into (A.14) to obtain:

μmoles CO_2 in analyzed solution = 0.14.

3] Measure vapor volume above unfiltered solution to obtain:

$Vol_{vap} = 5$ ml.

4] Insert Henry's constant (mol fraction basis):

$H_{CO2} = 1583$ [=] Partial pres./mole frac. in liquid (Austgen, 1989).

5] Use (A.8) to obtain:

$$N_C = \frac{(0.14)\left(\frac{100}{1}\right)+\left(\frac{0.14}{5.56\text{x}10^6}\right)\left(\frac{1583}{1}\right)\left(\frac{5}{82.56 * 298}\right)}{1000000}. \qquad (A.15)$$

The final result is that there were 1.48x10^{-5} mmoles CO_2 (=N_C) captured on the sorbent.

A.5.3 Calculation of Ca Content

After the reactive sorbent was dissolved and filtered, and after SO_4^{-2} and CO_2 analysis had been performed, it was necessary to determine the Ca content of the dissolved sorbent. To perform this analysis, an aliquot of the undiluted stock solution was diluted and combusted in the AA. During the dilution, NaCl was added to the aliquot to suppress ionization of Ca in the flame. The specifications of the solution to be analyzed are as follows:

1] ml filtered stock solution = 5,
2] ml 1.0 M NaCl = 5, and
3] ml dilution H_20 = 40.

The solution to be analyzed was 0.1 M NaCl, which is the same as the standard Ca solutions, and the stock solution was diluted 5:50. A solution of pure water and two standard Ca solutions, containing 2 and 4 ppm Ca, were used to calibrate the AA. After calibration, these standards were re-analyzed with the AA, the solution of unknown Ca content was analyzed, and the standards were re-analyzed.

Given AA outputs were of:

1] pure water outputs: 0.00, 0.01,
2] 2 ppm standard: 1.97, 1.94,

3] 4 ppm standard: 4.02, 3.99, and

4] unknown: 2.02,

the following calculations allow the Ca content of the sorbent to be determined.

1] Least squares fit to the standards outputs gives:

$$\text{machine output} = 1.00\ (\text{ppm Ca}) - 1.33\times10^{-2}. \tag{A.16}$$

2] Insert output for the unknown into (A.16) to obtain:

Ca content of unknown = 2.03 ppm.

3] Use equation (A.4) to obtain

$$N_{Ca} = (2.03)\left(\frac{(50)\quad(100)}{(5)\ (40)(1000)}\right). \tag{A.17}$$

The mmoles Ca in the undiluted solution (= N_{Ca}) is 5.08×10^{-2}. Based upon the calculations performed in sections A.5.3, A.5.2, and A.5.1, the S/Ca ratio obtained in the sorbent was 0.34, and the CO_2/Ca ratio obtained in the sorbent was 0.00029.

Appendix B

Error Analysis

B.1 General Practices for Data Reporting

In computing a numerical value based on the combination, not necessarily linear, of several experimentally observed values, it is necessary to present an expression of the differences in the observed values with the final result. The mathematical relationships which allowed this type of presentation are found in many standard texts on the statistical analysis and design of experiments. The text used for the formulas presented here was: Himmelblau, D. M., Process Analysis by Statistical Methods.

For a numerical value X_i, such that $X_i = f(x_1, x_2, \ldots, x_n)$, the following relationships were considered:

$$\text{Variance}(X_i) = \text{Var}(f(x_1, x_2, \ldots, x_n)), \tag{B.1}$$

$$\text{Var}(X_i) \approx \sum_{i=1}^{n} \frac{\partial f(x_1, x_2, \ldots, x_n)^2}{(\partial x_i)^2} \cdot \text{Var}(x_i), \text{ and} \tag{B.2}$$

$$\text{Var}(x_i) = (\sigma_x)^2 = \left(x_i - \overline{x_i}\right)^2 \tag{B.3}$$

where:

X_i = a calculated value,

x_i = a measured value used in the calculation of X_i,

$\overline{x_i}$ = the mean value of the measured x_i, and

$\sigma_x{}^2$ = the variance between the measured values of x_i.

Knowing the variance of a calculated value as a function of the differences between the observed values from which it was calculated, it is possible to determine the standard deviation of the calculated value. The determination of the standard deviation is as follows:

$$\text{Standard Deviation} = \sigma_x = \sqrt{\text{Var}(x)} \tag{B.4}$$

Data points which were average values from several repeat experiments are presented in this work as calculated values ± their standard deviation.

B.2 Analysis of Analytical Equipment

Error analysis of the AA and the IC were performed to determine the typical variations in their outputs over their typical operating ranges. Each analytical apparatus was used to perform repeat analyses on the same standard solutions, and the spread in the outputs was noted. The data presented in Table B.1, below, show the results of this study for the AA.

Table B.2 presents the statistical analysis of the data presented in Table B.1. It can be seen that the standard deviation is 92% of the mean value at the low end of the analytical regime, while it is approximately 3% of the mean at both the 2 and 4 ppm regimes. Based on these results, analysis of experimental solutions was performed above the 2 ppm range whenever possible.

Table B.1 Reproducibility of Atomic Absorption Unit

ppm Ca	Reading	ppm Ca	Reading	ppm Ca	Reading
0.00	0.00	2.00	1.99	4.00	3.81
0.00	-0.01	2.00	2.01	4.00	4.05
0.00	-0.05	2.00	2.06	4.00	4.08
0.00	-0.04	2.00	2.03	4.00	3.98
0.00	-0.08	2.00	1.97	4.00	3.92
0.00	-0.01	2.00	1.97	4.00	3.89
0.00	-0.02	2.00	1.94	4.00	3.82
0.00	-0.05	2.00	1.87	4.00	3.81
0.00	-0.02	2.00	1.86	4.00	3.71
0.00	0.00	2.00	2.00	4.00	4.00

Table B.2 Statistical Analysis of Atomic Absorption Unit

ppm Ca	mean output	variance	standard deviation
0.00	-0.03	0.001	0.026
2.00	1.97	0.004	0.065
4.00	3.91	0.015	0.122

Procedures similar to those performed on the AA were performed on the IC. These are presented in Table B.3, and Table B.4 presents the statistical analysis of the data presented in Table B.3. It can be seen that the standard deviation is 15% of the mean value at the low end of the analytical regime, while it is approximately 3% of the mean at the high end. Based on these results, analysis of experimental solutions was performed above the 0.01 mM SO_4^{-2} range whenever possible.

Table B.3 Reproducibility of Ion Chromatograph

mM SO_4	Reading	mM SO_4	Reading
0.001	692420	0.05	1.2187×10^7
0.001	622520	0.05	1.2250×10^7
0.001	952330	0.05	1.1563×10^7
0.001	627130	0.05	1.2110×10^7
0.001	529250	0.05	1.1820×10^7
0.001	475110	0.05	1.2065×10^7
0.001	438920	0.05	1.1484×10^7
0.001	521310	0.05	1.2377×10^7
0.001	478450	0.05	1.1781×10^7
0.001	624310	0.05	1.2566×10^7

Table B.4 Statistical Analysis of Ion Chromatograph

mM SO_4	mean output	variance	standard deviation
.001	556602	7.618E9	87279
.05	12029400	1.260E11	354955

The material presented up to this point defined the errors introduced by the inaccuracies of the analytical equipment. To determine the extent to which these errors affected the reported experimental values of S/Ca, equations B.2, B.3, and B.4 were used to determine the following relationship:

$$\left(\frac{S}{Ca}\right)_t = \left(\frac{\overline{S}}{\overline{Ca}}\right) \pm \sqrt{\frac{1}{\overline{Ca}}\left(\mathrm{Var}\,\overline{S}\right) - \left(\frac{\overline{S}}{(\overline{Ca})^2}\right)\left(\mathrm{Var}\,\overline{Ca}\right)} \qquad \text{(B.5)}$$

where:

$\left(\frac{S}{Ca}\right)_t$ = expected S/Ca ratio for a solution of known S and Ca content,
$\overline{S}$ = mean output of repeat SO_4^{-2} analysis of known solution, and
$\overline{Ca}$ = mean output of repeat Ca analysis of known solution.

Four test cases were run with this formula to determine the range of errors produced as a result of the analytical equipment error. The test cases used involved simulated outputs in:

1] the low output range for both the IC and the AA, which was expected to provide the largest error range about the predicted mean value;
2] the high output range for the AA and the low output range for the IC, which was expected to provide an average error range about the theoretical mean;
3] the high output range for both the AA and the IC, which was expected to provide the smallest error range about the calculated mean output; and
4] the low output range for the AA and the high output range for the IC, which was expected to provide a median error range about the mean output.

The results of this test series are presented in Table B.5, below.

Table B.5 Statistical Analysis of Machine Error in S/Ca Ratio

Simulated I.C. Output	Simulated A.A. Output	SO_4 in stock (mmol)	Ca in stock (mmol)	st. dev./mean (%)
556602	4.00	9.74×10^{-3}	0.5	20.0
556602	1.6	9.74×10^{-3}	0.2	19.9
12029400	4.00	2.13×10^{-2}	0.5	2.58
12029400	1.6	2.13×10^{-2}	0.2	3.19

These data provide information on the expected spread in typical final S/Ca ratios as a result of the inaccuracies of the analytical equipment. The results reinforce the importance of running the IC towards the upper end of its sensitivity scale and shows that running the AA above 1 ppm is adequate to minimize the error introduced in the Ca analysis.

B.3 Analysis of Experimental Method-Background Ratios

The S/Ca and CO_2/Ca ratios inherent in the lime/fly ash material, prior to any additional reaction with SO_2 or CO_2, are referred to as background ratios. The values of these ratios were required in order to determine the incremental conversion of the sorbent achieved during the gas-sorbent reactions. The background ratios were not evaluated in the hydrated lime sorbents, as these sorbents had not been exposed to reactive S materials or fly ash prior to their testing, and the CO_2 capture studies were not performed on the hydrated lime sorbents.

There was considerable spread in the values of the S/Ca and CO_2/Ca ratios obtained from multiple analyses of lime/fly ash aliquots extracted from the same batch of prepared sorbent, as shown in Table B.6. The spread detected in the background S/Ca and CO_2/Ca ratios, coupled with the information in Section B.2 above, indicate that inaccuracies in reported data were not the result of the analytical equipment, but of a combined effect of heterogeneous sorbents and experimental error.

The wet chemical steps required to prepare a sorbent sample for analysis afforded many opportunities to lose sample material by adhesion of the mother liquor to glassware and filter paper, and through spillage. Due to these factors, it was not possible to separate the effects of sorbent heterogeneity from the inherent losses in the experimental procedure.

Table B.6 Statistical Analysis of Background S/Ca Ratio

Run Number	S/Ca Ratio	CO_2/Ca Ratio
1	0.061	2.23E-4
2	0.053	2.40E-4
3	0.066	2.34E-4
4	0.13	1.60E-4
5	0.096	2.71E-4
6	0.082	1.71E-4
	mean ± st. dev.	mean ± st. dev.
Summary	0.084 ± 0.041	$2.17 \times 10^{-4} \pm 4.27 \times 10^{-5}$

The data for the experimentally observed CO_2/Ca ratio are not compared to any error statistics associated with the TCA, as the experimental work associated with the CO_2/Ca reaction was not the prime focus of this study, and a reproducibility study on the error involved with the TCA was not conducted.

B.4 Analysis of Experimental Method-Reaction System

The experimental data presented in the Results and Conclusions section of this work occasionally contains more scatter than is warranted considering the errors in the analytical apparatus, wet chemistry, and background SO_4^{-2} and CO_2 contents of the lime/fly ash sorbent. It is appropriate to address these discrepancies here.

B.4.1 Agglomeration of Sorbents

The reaction system was prepared by loading a potentially highly-agglomerated sorbent containing up to 50% initial moisture (by mass) into a small, gas-tight chamber, equilibrating the sorbent to the reaction temperature, and then exposing the sorbent to flue gas. Prior to loading the reactor, the reactive sorbent was mixed with sand in a ratio of 1:300 (g sorbent:g sand) and agitated in a closed flask containing several glass beads. The beads served to break agglomerates of sorbent while the sand supported the sorbent and separated the individual sorbent particles from each other.

It was difficult to determine whether the agglomerates had been broken adequately in the agitation process. In most cases, it was necessary to quickly transfer the sorbent/sand mixture from the mixing flask to the reactor to avoid evaporating the water from the sorbent, and this minimized the time available to verify the homogeneity of the dispersion. The extent to which the sorbents were agglomerated influenced their conversion as it influenced their drying time, the amount of reaction which occurred by the gas-phase limited reaction mechanism, and the surface area available for reaction.

B.4.2 Ca Content of Lime/Fly Ash Sorbent

The Ca content of the lime/fly ash sorbent was determined when the background ratio of S/Ca and CO_2/Ca in the sorbent was being determined. The Ca content, as mmol-Ca/g-sorbent, was also evaluated for this lime/fly ash sorbent by White (1987), and Borgwardt and Rochelle (1987). The results of these evaluations are presented in Table B.7, below.

Table B.7 Ca Content of Lime/Fly Ash Sorbent

Study	mmol Ca/g solid
Borgwardt and Rochelle, 1989	3.25
White, 1989	2.75 to 3.75
Beaudoin, present	3.68

The value of 3.68 mmol/g is the result of multiple analyses of different aliquots of the lime/fly ash sorbent used in this study. The standard deviation is 16% of the mean value, indicating that the analyses are only in fair agreement. The Ca-content of the lime/fly ash sorbent presented in this work was determined for oven-dried sorbent, which contained no ambient moisture upon analysis. In the work performed by Borgwardt and Rochelle and the work performed by White, it was not clear if the sorbent was dried or if it contained ambient moisture, which may have been up to 5% of the total mass, upon analysis.

As stated previously, the total mass of sorbent applied in an experimental run, as well as the water content of this sorbent, was measured prior to the start of the run. By correcting for the mass of water present in the sorbent, the mass of dry sorbent applied was determined, and based on the mean Ca content per gram of sorbent, the quantity of Ca available for reaction was determined. If the quantity of Ca determined per gram of sorbent differed significantly from that found in Table B.7, the results of the particular run were discarded.

B.4.3 Water Content of Sorbents

It was difficult to determine sorbent water content. The procedure used involved extracting two aliquots of wet sorbent from the preparation vial, weighing one aliquot, drying it, and reweighing it to determine the water loss. The water content of the first sample portion was assumed to be equal to that of the second sample, which was loaded into the reactor unit and reacted immediately after being extracted from the preparation vial. The solids which were reacted were handled considerably after their water content was determined, and they may have lost significant quantities of this initial water prior to reaction.

When preparing a sample for reaction, a portion of wet solids was weighed into a sample vial containing sand and glass beads. After the weight of the wet sorbent was determined, the vial was sealed and rapidly agitated to break any sorbent agglomerates. During this mixing process, there was considerable opportunity for evaporation of water from the sorbent to saturate the vapor space in the vial. The possibility that water was transferred by conduction from the surface of the sorbent to the surface of the sand also was considered.

The surface area of the lime/fly ash sorbent was approximately 16 m^2/g, and the surface areas of the promoted lime sorbents used were 17, 51, and 74 m^2/g, while the surface area of the sand was less than 1 m^2/g. In light of this difference, when 10 mg of sorbent were dispersed in 3 g of sand, there would be a factor of, in the worst case, 6 times more surface area on the sand than on the sorbent. If the sorbents and the sand had the same affinity for water and the water present on the sorbents was not present in the pores of the sorbents, it is very likely that the water would deposit on the sand when the lime/fly ash was used and slightly less likely that the water would deposit on the sand when the other sorbents were used.

If it is true that water present on the sorbents is located within the pores of the sorbent, as is assumed in the models presented in Chapter 2:Theory, no water would be lost to the sand during the mixing process. If this assumption is not totally correct, the theories would overpredict the system performance in all cases.

The possibility that water evaporated to saturate the interior vapor space of the mixing vial and of the reactor was considered. The average interior volume of the different reactor units and mixing vials was determined and the quantity of water required to saturate this vapor space was calculated. This quantity was subtracted from the weighed water content of the wet sorbent.

It was assumed that the most significant error in determining the water content of the solids involved the weighing of the wet solids, drying, and reweighing step, and it is estimated that the actual water contents of the solids used in this work are within ± 5% of the reported values.

Appendix C

Data

C.1 Preliminary Data: SO_2-Capture Studies

Table C.1 presents the six experiments performed to determine the S/Ca and CO_2/Ca ratio present in the unreacted lime/fly ash sorbent used in this work. To determine the SO_2 captured during an experiment, the initial S/Ca ratio shown below was subtracted from the S/Ca ratio present in the sorbent after reaction. Tables C.2 to C.8 present the results of experiments which addressed the SO_2 capture attained by the four sorbents studied (lime/fly ash sorbent and three hydrated lime sorbents).

In Tables C.2 and C.3, a range of relative humidities is presented with several results. In these experiments, the pressure gauge which ordinarily measured the pressure of the flue gas during reaction was not functioning properly. The relative humidity in the flue gas was determined as a function of the pressure of the flue gas during each experiment, and without the pressure measurement, the relative humidity cannot be accurately calculated. The relative humidity range presented for these results is typical of that encountered during the majority of the other experiments conducted at similar conditions to those used in the experiments in question.

Table C.1 Statistical Analysis of Background S/Ca Ratio: Lime/Fly Ash Sorbent

Run Number	S/Ca Ratio	CO_2/Ca Ratio
1	0.061	2.23E-4
2	0.053	2.40E-4
3	0.066	2.34E-4
4	0.13	1.60E-4
5	0.096	2.71E-4
6	0.082	1.71E-4
	mean ± st. dev.	mean ± st. dev.
Summary	0.084 ± 0.041	$2.17 \times 10^{-4} \pm 4.27 \times 10^{-5}$

Table C.2 **Ca-Utilization of Lime/Fly Ash Sorbent:** (10, 60, 120 s reaction times, 0-90% relative humidity, 1000-5000 ppm SO_2)

Run Number	S/Ca	Reaction Time (s)	RH (%)	% H_2O (mass)	ppm SO_2
7	0.00	10	0	3.5	1000
8	0.00	10	0	3.5	1000
9	0.05	10	55-65	3.5	1000
10	0.04	10	55-65	3.5	1000
11	0.08	10	55-65	3.5	1000
12	0.09	10	55-65	3.5	1000
13	0.21	10	80-90	3.5	1000
14	0.13	10	80-90	3.5	1000
15	0.22	10	61	3.5	5000
16	0.27	10	63	3.5	5000
17	0.16	10	60	3.5	5000
18	0.05	60	0	3.5	1000
19	0.05	60	0	3.5	1000
20	0.10	60	55-65	3.5	1000
21	0.18	60	55-65	3.5	1000
22	0.12	60	55-65	3.5	1000
23	0.12	60	55-65	3.5	1000
24	0.33	60	80-90	3.5	1000
25	0.26	60	80-90	3.5	1000
26	0.24	60	65	3.5	5000
27	0.25	60	68	3.5	5000
28	0.21	60	66	3.5	5000

Table C.2 Ca-Utilization of Lime/Fly Ash Sorbent, cont'd:
(10, 60, 120 s reaction times, 0-90% relative humidity, 1000-5000 ppm SO_2)

Run Number	S/Ca	RH (%)	% H_2O (mass)	ppm SO_2
29	0.04	0	3.5	1000
30	0.05	0	3.5	1000
31	0.28	64	3.5	1000
32	0.35	64	3.5	1000
33	0.31	61	3.5	1000
34	0.46	90	3.5	1000
35	0.50	84	3.5	1000
36	0.18	62	3.5	5000
37	0.36	61	3.5	5000
38	0.24	67	3.5	5000

Table C.3 Ca-Utilization of Hydrated Lime Sorbents: (10, 60, 120 s reaction times, 56-69% relative humidity, 5000 ppm SO_2)

Run Number	S/Ca	Reaction Time (s)	RH (%)	% H_2O (mass)	ppm SO_2	Sorbent Type*
39	0.12	10	63	1	5000	MH
40	0.08	10	61	1	5000	MH
41	0.23	10	61	1	5000	A
42	0.24	10	60	1	5000	A
43	0.13	10	58	1	5000	B
44	0.14	10	60	1	5000	B
45	0.12	60	67	1	5000	MH
46	0.15	60	66	1	5000	MH
47	0.22	60	64	1	5000	A
48	0.30	60	62	1	5000	A
49	0.19	60	69	1	5000	B
50	0.23	60	63	1	5000	B
51	0.16	120	62	1	5000	MH
52	0.14	120	63	1	5000	MH
53	0.30	120	62	1	5000	A
54	0.35	120	60	1	5000	A
55	0.29	120	58	1	5000	B
56	0.24	120	60	1	5000	B

*("MH": Mississippi Hydrated Lime (17 m^2/g), "A": Mississippi Hydrated Lime (74 m^2/g),"B":Mississippi Hydrated Lime (51 m^2/g)

Table C.4 Ca-Utilization of Damp Hydrated Lime Sorbent:
(10, 60, 120 s reaction times, 56-69% relative humidity, 5000 ppm SO_2)

Run Number	S/Ca	Reaction Time (s)	RH (%)	% H_2O (mass)	ppm SO_2	Sorbent Type*
57	0.15	10	58	15	5000	MH
58	0.24	10	56	9	5000	MH
59	0.20	10	66	15	5000	A
60	0.20	10	58	14	5000	A
61	0.15	10	58	16	5000	B
62	0.08	10	58	13	5000	B
63	0.21	60	63	11	5000	MH
64	0.23	60	60	13	5000	MH
65	0.24	60	67	15	5000	A
66	0.29	60	62	10	5000	A
67	0.18	60	58	16	5000	B
68	0.19	60	58	13	5000	B
69	0.26	120	58	13	5000	MH
70	0.23	120	58	17	5000	MH
71	0.26	120	64	10	5000	A
72	0.32	120	58	14	5000	A
73	0.20	120	58	17	5000	B
74	0.15	120	58	17	5000	B

*("MH": Mississippi Hydrated Lime (17 m^2/g), "A": Mississippi Hydrated Lime (74 m^2/g),"B":Mississippi Hydrated Lime (51 m^2/g)

Table C.5 Relationship Between Sorbent Conversion and Ca-Dispersion for All Sorbents: (Average conversion values presented, ambient moisture content, 5000 ppm SO_2)

Sorbent Name	m^2/g $Ca(OH)_2$	avg. 10 s conv.	avg. 60 s conv.	avg. 120 s conv.
Lime/Fly Ash	64	0.22	0.23	0.26
Miss. Hydrate	17	0.10	0.14	0.15
Hydrated Lime "A"	74	0.24	0.26	0.33
Hydrated Lime "B"	51	0.12	0.21	0.27

Table C.6 Ca-Utilization of Damp Lime/Fly Ash Sorbent: (10 s reaction time, 1000 ppm SO_2, 0-85% relative humidity)

Run Number	S/Ca	RH (%)	% H_2O (mass)	ppm SO_2
75	0.12	0	14	1000
76	0.07	0	17	1000
77	0.15	0	29	1000
78	0.16	0	29	1000
79	0.47	58	49	1000
80	0.21	57	50	1000
81	0.12	57	29	1000
82	0.13	62	16	1000
83	0.34	57	16	1000
84	0.29	85	28	1000
85	0.38	83	31	1000
86	0.39	83	31	1000

Table C.7 Ca-Utilization of Damp Lime/Fly Ash Sorbent:
(60 s reaction time, 1000 ppm SO_2, 0-91% relative humidity)

Run Number	S/Ca	RH (%)	% H_2O (mass)	ppm SO_2
87	0.11	0	31	1000
88	0.12	0	30	1000
89	0.09	0	16	1000
90	0.13	0	12	1000
91	0.28	61	18	1000
92	0.37	60	7	1000
93	0.33	56	50	1000
94	0.27	61	49	1000
95	0.33	61	32	1000
96	0.56	84	27	1000
97	0.36	91	17	1000
98	0.55	87	31	1000
99	0.72	86	27	1000

Table C.8 Ca-Utilization of Damp Lime/Fly Ash Sorbent:
(120 s reaction time, 1000 ppm SO_2, 0-86% relative humidity)

Run Number	S/Ca	RH (%)	% H_2O (mass)	ppm SO_2
100	0.15	0	28	1000
101	0.15	0	31	1000
102	0.06	0	16	1000
103	0.14	0	17	1000
104	0.37	57	15	1000
105	0.29	59	17	1000
106	0.40	55	46	1000
107	0.40	57	49	1000
108	0.33	58	28	1000
109	0.35	57	30	1000
110	0.35	83	21	1000
111	0.46	86	13	1000
112	0.85	83	31	1000
113	0.71	83	30	1000

Table C.9 Ca-Utilization of Damp Lime/Fly Ash Sorbent:
(10, 60, 120 s reaction time, high SO_2 concentration, 57-66% relative humidity)

Run Number	S/Ca	Reaction Time (s)	RH (%)	% H_2O (mass)	ppm SO_2
114	0.33	10	61	9	5000
115	0.24	10	59	10	5000
116	0.24	10	62	19	5000
117	0.26	10	62	20	5000
118	0.16	10	57	25	5000
119	0.14	10	59	28	5000
120	0.15	10	58	17	5000
121	0.23	10	58	19	5000
122	0.27	60	62	9	5000
123	0.36	60	62	7	5000
124	0.34	60	65	19	5000
125	0.28	60	66	14	5000
126	0.25	60	63	26	5000
127	0.17	60	63	21	5000
128	0.18	60	58	24	5000
129	0.22	60	58	23	5000

Table C.9 Ca-Utilization of Damp Lime/Fly Ash Sorbent, cont'd: (10, 60, 120 s reaction time, high SO_2 concentration, 57-66% relative humidity)

130	0.30	120	62	3.5	5000
131	0.36	120	62	6	5000
132	0.35	120	62	22	5000
133	0.33	120	62	19	5000
134	0.22	120	61	24	5000
135	0.20	120	58	26	5000
136	0.17	120	58	17	5000
137	0.19	120	58	25	5000

C.2 Preliminary Data: CO_2-Capture Studies

Table C.9 presents work done to determine the effect of Ca-conversion by CO_2 in the presence of SO_2. The results presented in this table are derived from experimental work which was not adequately reproducible to be presented in the SO_2-capture study. The study of sorbent reactivity towards SO_2 was the primary focus of the work presented here, while the study of sorbent reactivity to CO_2 was of secondary importance. In Table C.9, the results presented for the initial water content of the sorbent do not take into account the evaporative losses which occurred during the preparation and loading of the sorbents into the reactors. It is estimated that these water contents were up to 10% lower than is stated in Table C.9.

Table C.10 Ca-Utilization of Damp Lime/Fly Ash Sorbent by CO_2: (10, 60, 120 s reaction times,1000 ppm SO_2, 0-90% relative humidity)

Run Number	CO_2/Ca	Reaction Time (s)	RH (%)	% H_2O (mass)	ppm SO_2
138	$-1.82x10^{-4}$	10	57	35	1000
139	$-1.68x10^{-4}$	10	57	27	1000
140	$-1.68x10^{-4}$	10	59	27	1000
141	$9.39x10^{-6}$	10	57	36	1000
142	$4.10x10^{-4}$	10	57	41	1000
143	$5.20x10^{-4}$	10	54	38	1000
144	$6.92x10^{-5}$	10	0	3.5	1000
145	$-1.12x10^{-5}$	10	55-65	3.5	1000
146	$-1.43x10^{-5}$	10	55-65	3.5	1000
147	$3.69x10^{-5}$	10	55-65	3.5	1000
148	$1.67x10^{-4}$	10	80-90	3.5	1000
149	$3.35x10^{-5}$	10	80-90	3.5	1000
150	$-1.10x10^{-4}$	60	62	35	1000
151	$-1.03x10^{-4}$	60	63	27	1000
152	$-1.49x10^{-4}$	60	60	27	1000
153	$-9.92x10^{-5}$	60	57	36	1000
154	$1.51x10^{-4}$	60	59	41	1000
155	$8.12x10^{-5}$	60	0	3.5	1000
156	$1.42x10^{-5}$	60	55-65	3.5	1000
157	$-6.85x10^{-5}$	60	55-65	3.5	1000
158	$-1.06x10^{-5}$	60	55-65	3.5	1000
159	$1.22x10^{-5}$	60	80-90	3.5	1000
160	$4.48x10^{-6}$	60	80-90	3.5	1000

Table C.10 Ca-Utilization of Damp Lime/Fly Ash Sorbent by CO_2, cont'd: (10, 60, 120 s reaction times, 1000 ppm SO_2, 0-90% relative humidity)

Run Number	CO_2/Ca	Reaction Time (s)	RH (%)	% H_2O (mass)	ppm SO_2
161	-1.40×10^{-4}	120	60	27	1000
162	3.52×10^{-4}	120	55	38	1000
163	1.49×10^{-4}	120	61	51	1000
164	7.67×10^{-5}	120	63	51	1000
165	1.13×10^{-4}	120	57	51	1000

C.3 Experimental Conditions

Table C.11 is a reproduction of Table 3.1, from the Apparatus and Procedures Section. It presents the flue gas flowrates and compositions used during the experiments presented in Tables C.2 to C.10. The SO_2 concentrations in the flue gas deviate slightly from the values presented. It is expected that the actual SO_2 concentration was 1000 ± 100 ppm during the experiments presented as 1000 ppm and 5000 ± 200 ppm during the experiments presented as 5000 ppm.

The basis for these estimations is presented in the Apparatus and Procedures Section of this work.

Table C.11 Flue Gas Flowrates and Composition

SO_2 content (ppm)	flue gas RH (%)	total gas flow (slpm)	CO_2 content (vol %)	O_2 content (vol %)
1000	55-65	4.1	10	12
1000	55-65	4.6	9	10
2000	80-90	2.5	10	11
2000	80-90	2.8	9	10
5000	55-65	4.1	10	12
1000, 2000, or 5000	0	4.1	10	12

Table C.12 presents the results used to determine the mean Ca content (mmoles Ca/g dry sorbent) of the lime/fly ash sorbent. The mean value of this number is 3.68 mmoles Ca/g dry sorbent, and the standard deviation is 0.58, which is 16% of the mean value.

Table C.12 Lime/Fly Ash Ca Content

mm Ca/g	run number	mm Ca/g	run number	mm Ca/g	run number
3.04	86	3.20	109	3.97	122
3.42	99	4.85	81	5.27	130
3.27	113	5.18	95	3.68	115
3.18	85	3.73	108	3.65	123
3.81	98	4.52	80	3.99	131
3.14	112	4.25	94	3.79	116
3.41	97	4.17	107	3.80	124
3.12	111	4.06	79	3.20	132
3.81	84	4.11	93	3.73	117
3.62	96	3.88	106	4.33	125
3.50	110	3.87	78	3.70	133
3.01	83	4.55	88	4.73	120
3.39	92	4.01	101	3.95	128
3.82	105	4.44	77	4.38	136
3.77	82	4.26	87	4.15	121
3.49	91	4.54	100	3.89	129
3.38	104	3.49	22	3.65	137
3.79	76	3.55	32	3.01	13
2.83	90	3.48	42	3.04	24
2.60	103	2.81	21	3.22	35
3.43	75	2.99	33	2.84	14
3.58	89	3.30	43	3.24	25
3.20	102	3.39	114	2.49	36

Bibliography

Acurex Corp., "Theoretical Approach for Enhanced Mass Transfer Effects In-Duct Flue Gas Desulfurization Processes:Quarterly Progress Report nos. 3 and 4, U.S. DOE Document, Contract No. DE-AC22-88PC8874, Research Triangle Park, NC, July,1989a.

Acurex Corp., "Theoretical Approach for Enhanced Mass Transfer Effects In-Duct Flue Gas Desulfurization Processes: Topical Report for Task 2. Mass Transfer Investigation; Vol. 1. Short Time Differential Reactor," DOE Document, Contract No. DE-AC22-88PC88874, October,1989b.

Austgen, D.M., "A Model of Vapor-Liquid Equilibria for Acid-Gas-Alkanolamine-Water Systems,", PhD Dissertation, The University of Texas at Austin, 1989.

Babu, M., College, J., Forsythe, R., and Kanary, D., "1.0 Million BTU Combustor Testing: Test Results Part II," Report to DOE, Contract No. DE-AC22-85PC81012, December, 1988.

Blythe, G., Lepovitz, L., and Rhudy, R., "Results from EPRI HSTC High Sulfur Spray Dryer Pilot Tests," presented at EPA and EPRI Cosponsored First Combined FGD and Dry SO$_2$ Control Symposium, St. Louis, MO, 1988.

Chu, P., "Removal of SO$_2$ and NO$_x$ from Stack Gas by Reaction with Ca(OH)$_2$ Solids," M.S. Thesis, The University of Texas at Austin, 1986.

Drummond, C.J., ed., "Duct Injection Technologies for SO$_2$ Control," Presented at First Combined FGD and Dry SO$_2$ Control Symposium, St. Louis, MO, 1988.

Gooch, J.P., et al., "Scaleup Tests and Supporting Research for the Development of Duct Injection Technology," Report to Dept. of Energy, Pittsburgh Energy Technology Center, 1989.

Henzel, D.S., Laseke, B.A., Smith, E.O., and Swenson, D.O., *Limestone FGD Scrubbers: Users Handbook*, U.S. E.P.A. Document, Contract No. 68-02-3173, Task No. 13, April, 1981.

Himmelblau, D. M., *Process Analysis by Statistical Methods*, Alphagraphics, Austin, TX, 1980.

Hines, A.L., and Maddox, R.N., *Mass Transfer Fundamentals and Applications*, Prentice-Hall, Englewood Cliffs, NJ, 1985.

Jorgensen, C., Chang, J.C.S., Brna, T.G., and Sedman, C.B., "Small-Scale Pilot Evaluation of Calcium- and Sodium-Based Sorbents for Dry SO$_2$ Removal," presented at AIChE National Meeting, Houston, TX, April, 1987.

Jozewicz, W., and Rochelle, G.T., "Modeling of SO$_2$ Removal by Spray Dryers," Presented at Pittsburgh Coal Technology Conference, 1984.

Jozewicz, W., and Chang, J.C.S., "Development of High-Reactivity Sorbents," U.S. E.P.A. document, 1986.

Jozewicz, W., and Chang, J.C.S., "Characterization of Advanced Sorbents or Dry SO$_2$ Control," Presented at AIChE Spring National Meeting, Houston, TX, 1987.

Klingspor, J., "An Experimental Study on Spray Dry Scrubbing," Doctorate Thesis, Department of Chemical Engineering, Lund Institute of Technology, Sweden, 1986.

Peterson, J.R., Rochelle, G.T., and Chu, P., "SO_2 and NO_x Removal from Flue Gas by Reaction with Solids Prepared by Slurrying Fly Ash and $Ca(OH)_2$," Report to DOE, Grant No. DE-FG22-85PC81006, October, 1987.

Trempel, D.P., and Rochelle, G.T., "Reaction of SO_2 with $Ca(OH)_2$ and CaO at 100 to 800 °C," Presented at Philadelphia AIChE Meeting on SO_x Emission Control and Strategies, Philadelphia, PA, 1989.

Seinfeld, J.H., *Atmospheric Chemistry and Physics of Air Pollution*, John Wiley and Sons, New York, 1986.

Stumm, W., and Morgan, J.J., *Aquatic Chemistry, An Introduction Emphasizing Chemical Equilibria in Natural Waters,* 2nd Ed., John Wiley and Sons, New York, 1981.

White, W.G., "Differential Reaction of SO_2 in Flue Gas with Lime-Based Sorbents at 66°C for 10 to 7200 Seconds," M.S. Thesis, The University of Texas at Austin, 1989.

Yoon, H., Stouffer, M.R., Rosenhoover, W.A., Withum, J.A., and Burke, F.P., "Pilot Process Variable Study of Coolside Desulfurization," Environmental Progress, Vol. 7, No. 2, 1988.