MODELING OF LIMESTONE SLURRY SCRUBBING IN SPRAY TOWERS WITH FORCED OXIDATION

by

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This work is dedicated to my parents, Joseph and Peggy DeVincentis without whose help and encouragement I could never have made it this far.

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The FGDTX model of the limestone slurry scrubber simulates a staged or spray scrubber with a hold tank. The spray scrubber model can simulate multiple levels of spray headers, and works with natural or forced oxidation specifications.

This work focuses on forced oxidation calculations in a spray scrubber. FGDTX has been run over a wide range of conditions which represents the typical range of forced-oxidation spray scrubber operation. Some simple approximate models are proposed to summarize the calculations of FGDTX and to provide understanding of the chemistry involved. The effects seen in FGDTX of inlet SO_2 concentration, limestone utilization, liquid-to-gas ratio, the number of gas-phase transfer units, and dibasic acid concentration are compared to literature data.

Three fundamental effects determine the performance of forced oxidation spray scrubbers: the total enhancement factor for SO_2 removal, the gas-film mass transfer limit, and the liquid phase equilibrium resistance to SO_2 absorption. Spray scrubbers differ from turbulent contact absorbers by the importance of the equilibrium effect.

TABLE OF CONTENTS

List of Tables

List of Figures

CHAPTER 1: INTRODUCTION

1.1 IMPORTANCE OF LIMESTONE SLURRY SCRUBBING

Sulfur dioxide represents a serious air pollution hazard, one which is being addressed by ever-stricter laws in countries around the world. Limestone slurry scrubbing is one of the primary technologies in use today for removing sulfur dioxide from the flue gas produced by coal-burning electric power plants.

1.2 THE USE OF MODELS FOR LIMESTONE SLURRY SCRUBBING

Models for limestone slurry scrubbing have many uses in optimizing the design of new scrubbers, troubleshooting problems in existing scrubbers, and redesign or optimization of existing scrubbers. Optimization is possible to a significant degree for scrubbers in the United States because the current system of SO_2 emission regulations uses a system of tradable allowances distributed to electric utilities each year. Each allowance permits the emission of one ton of SO_2. This allows the SO_2 penetration of a scrubber to be a variable that may be manipulated in order to optimize costs. Currently, the market price for an allowance is below the cost of removing that ton of SO_2 by limestone slurry scrubbing, but in time the price of allowances is expected to rise, as fewer of them are made available. In other countries the regulations may be different, and if there is simply a fixed threshold for SO_2 removal for a given scrubber, that important variable is fixed, and less optimization is possible.

Other variables that may be considered for optimization include limestone utilization, and the amount of additives such as organic acid buffers. In the case of a new scrubber, the liquid rate (typically considered as L/G, the ratio of liquid to gas rate), the number of spray headers installed, and the limestone grind may also be variables able to be optimized. In the case of optimizing an existing scrubber, the number and choice of spray headers in service may be a variable to be optimized. It may be more efficient to shut down the pump for a spray header and save that energy cost, if the difference in the amount of SO_2 removed is small.

The other most common application is troubleshooting. When the performance of a scrubber degrades, it is necessary to determine which of many possible disturbances are actually the cause of the performance change in order to fix the problem. Fixing the wrong problem can be costly. Models can be used to eliminate some possible causes before any actual process changes are implemented.

1.3 DESCRIPTION OF THE FORCED OXIDATION SPRAY TOWER SYSTEM

The limestone slurry scrubber system under study uses a spray tower as an absorber and forced oxidation in the hold tank. See Figure 1-1. Other systems may instead use tray absorbers of various types, or inhibited oxidation.

Slurry produced in the hold tank is pumped to typically 2 to 4 levels of spray nozzles, typically with 4 to 6 foot spacing between spray levels, with many nozzles on each level with 2 to 6 feet between adjacent nozzles. Spray levels are staggered so that the nozzles of one level are not directly above those on the next level, in order to prevent channeling of gas. The other reason multiple spray levels are used is that in order to spray the necessary amount of liquid on one level, the nozzles would be too close to each other, causing too much interference between adjacent sprays. Typically, the slurry has a total residence time of about 1 second in the absorber.

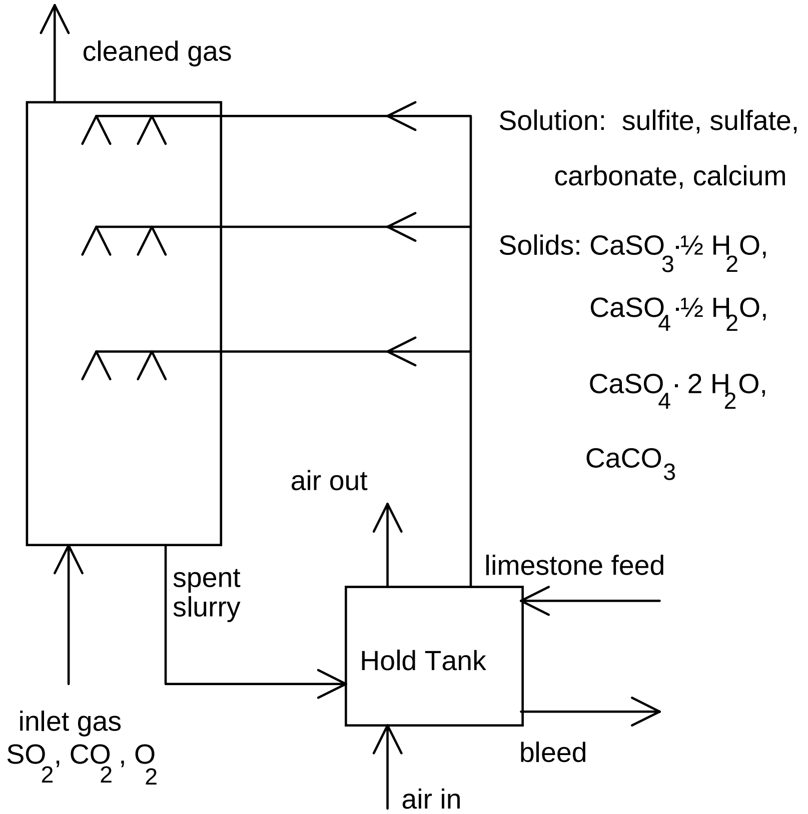

Figure 1-1: The limestone slurry scrubber system

This slurry spray is contacted countercurrently with the flue gas which enters the bottom of the absorber and flows upwards at speeds typically of up to 15 ft/s. Cleaned gas leaves the top of the absorber and used slurry leaves the bottom of the absorber and enters the hold tank, which in practice is often simply the bottom part of the spray tower.

In the hold tank, the slurry has a much longer residence time, on the order of a few minutes. Fresh air is bubbled into the hold tank to oxidize the sulfite to sulfate, typically in about 2 to 3 times the amount stoichiometrically needed to oxidize all the sulfite, in order to force nearly complete oxidation. The sulfate in solution also crystallizes in the hold tank, and a bleed stream is taken off to remove this product. Fresh limestone is also fed into the hold tank, along with water to make up what was drawn off in the bleed stream. The product stream of this tank forms the slurry which is pumped to the spray headers in the absorber.

1.3.1 Rationale

A hold tank is used to provide some residence time for the slurry so that sulfate solids may crystallize somewhere other than in the absorber. It also provides a convenient place to replenish the slurry with limestone, and in the forced oxidation system, it provides a place to oxidize sulfite.

Gypsum scaling occurs when the concentration of sulfate in the slurry builds up enough within the absorber to precipitate it. Gypsum scaling is avoided by operating the system with excess gypsum solids (10-15%) and a large residence time in the hold tank. These conditions allow desupersaturation of the solution in the hold tank and provide seed crystals for tolerable crystallization in the absorber.

A high liquid-to-gas ratio (L/G) is used for two reasons. A high L/G provides for a large surface area of the liquid drops, and in addition reduces the effect of a build-up of sulfate and sulfite in the solution. Both effects suggest that a higher L/G improves scrubber performance.

1.4 OTHER WORK ON MODELING LIMESTONE SLURRY SCRUBBING

1.4.1 Past Development of the Slurry Scrubber Model FGDTX

The limestone slurry scrubber model FGDTX has been developed over many years at the University of Texas at Austin.

Mehta integrated $CaCO_3$ dissolution and SO_2 gas/liquid mass transfer with changing gas and solution composition, producing the first version of the slurry scrubber model (Mehta and Rochelle, 1983; Mehta, 1982). This model included both gas and liquid phase resistance to SO_2 mass transfer, and used approximate surface renewal theory to simulate liquid phase mass transfer (Chang and Rochelle, 1982; Weems, 1981). The Bechtel-Modified Radian Equilibrium Program (BMREP) (Epstein, 1975) was incorporated to calculate solution equilibria.

Chan and Rochelle (1983) added gas/liquid mass transfer of CO_2 and O_2, $CaSO_3$ dissolution enhanced by mass transfer with equilibrium reactions, and parameters to allow the model to account for the effects of chloride on SO_2 removal. Chan also added the hold tank submodel to predict the scrubber inlet slurry composition, forming the closed loop of scrubber and hold tank calculations that remains the basis of the slurry scrubber model to the present day.

Gage (1989, 1990, 1992) studied the inhibition of limestone dissolution by sulfite species and added models for these effects to the limestone slurry scrubber model. Her work quantified the effects of limestone type and grind on scrubber performance.

Agarwal (1993, 1995) made the solids calculations more robust under high organic acid conditions, and developed a parameter estimation procedure using the model and GREG parameter estimation software. Agarwal also added two new routines, GRG2 and LSODE, as alternatives to IMSL routines ZSPOW and DGEAR, to make the model independent of IMSL. He estimated parameters values for turbulent contact absorbers from available data.

Pepe (Lancia et al, 1994) rewrote the gas-liquid mass-transfer modules to decrease convergence time, added an optimization routine based on Newton's method to replace GRG2, and improved solids convergence routines to speed convergence in forced oxidation simulations.

VandeKemp (1993) began the work to expand the model to simulate spray contactors. Previously the model simulated only staged contactors. She made the initial simulations of the spray scrubber and observed that the model predicted observed trends relative to inlet SO_2 concentration, organic acid concentration, and limestone utilization. In addition, VandeKemp made calculations of enhancement factors for SO_2 removal due to reactions, and observed that under most conditions the hydrolysis reaction was the primary enhancement method.

1.4.2 Other Models

Bechtel (Epstein, 1975) produced a model of the solution equilibria present in limestone slurry scrubbing solutions, modifying an earlier Radian model. This model, the Bechtel-Modified Radian Equilibrium Program (BMREP), uses a modified Davies approach for calculating activity coefficients, and a database from Radian (Lowell et al., 1970) for equilibrium constants and parameters. The model is extremely detailed, representing the solution in terms of over 40 species including a number of ion pairs, and over 40 reactions involving these species. BMREP was integrated to some degree into some later models, including FGDTX. In FGDTX, a few minor changes were made to BMREP. Chan (Chan and Rochelle, 1983) adjusted some of the constants for ion pairs involving bisulfite. Gage (1989) modified the solubility parameter for limestone. Tseng (Tseng and Rochelle, 1986) modified the solubility parameter for calcium sulfite.

Noblett et al. (1991, 1993, 1995) produced the FGDPRISM model of the limestone slurry scrubber at Radian under contracts from the Electric Power Research Institute. FGDPRISM allows simulation of a variety of different limestone scrubber configurations. As with FGDTX, FGDPRISM has parameters that must be adjusted to match any given system to be simulated. FGDPRISM is slower than FGDTX because it has not undergone the optimization for speed of calculation and speed of convergence which FGDTX has had. FGDPRISM also includes more features for ease of use and overall system calculations. FGDPRISM uses very simplistic models for sulfite oxidation and has no model for CO_2 stripping. FGDPRISM uses a different method for handling limestone dissolution than what FGDTX uses, and it has a spray trajectory model which provides estimates for mass transfer coefficients and area, where FGDTX has no such model.

Brogren and Karlsson (1997) produced a model of the absorption rate of SO_2 into a droplet of limestone slurry which includes equilibrium and finite-rate reactions, limestone dissolution, sulfite oxidation, and gypsum crystallization. The model represents the variation in conditions between the regions near and far from the nozzles by varying the mass transfer coefficients.

Gerbec et al. (1995) produced an unsteady-state model based primarily on slurry pH. The chemistry models it uses seem simplistic, and perhaps needed to be in order to perform the unsteady-state calculations in a stable and efficient manner.

1.5 SCOPE OF RESEARCH

The primary purpose of this work is to extend FGDTX to fully model the forced-oxidation spray tower system, and to then use the results of FGDTX to help provide a better understanding of the chemistry involved in this system, in part by creating simpler approximate models to represent the results of FGDTX.

It has been observed that both the gas phase mass transfer and the liquid phase resistance can influence the performance of spray scrubber systems as concentrations of sulfite species build up. FGDTX attempts to model these effects based on the best sub-models available. Simple models designed to fit the predictions of FGDTX and actual scrubber data are used to give meaning to some of the many trends that may be observed between the many variables in the system.

CHAPTER 2: DESCRIPTION OF MODEL

2.1 SUMMARY OF MODEL

2.1.1 Model Convergence

When FGDTX simulates a counter-current spray scrubber, it begins in the absorber, where the inlet liquid and solid slurry composition is guessed (the liquid composition is guessed only in terms of some lumped parameters, shown in Table 2-1), and the outlet gas SO_2 composition is guessed in terms of a fractional penetration relative to the specified inlet gas composition. The outlet CO_2 and O_2 composition are specified. The "lumped parameters" model for liquid composition is used by the convergence routine instead of the full speciation, in order to make the slurry feed convergence calculation manageable. The species represented by each liquid variable are in equilibrium with each other and hydrogen ion, and for a given pH, the concentrations of the individual species can be determined.

Table 2-1: Variables used to represent streams in FGDTX

Phase	Variables
Solid	$CaSO_3 \cdot ½H_2O$ $CaSO_4 \cdot ½H_2O$ (hemihydrate) $CaSO_4 \cdot 2H_2O$ (gypsum) $CaCO_3$
Liquid	S(IV): Total sulfite: SO_2, HSO_3^-, $SO_3^=$ S(VI): Total sulfate: HSO_4^-, $SO_4^=$ Total carbonate: CO_2, HCO_3^-, $CO_3^=$ Ca^{++}
Gas	SO_2 CO_2

$\Big| O_2$

The gas composition is integrated down the length of the absorber, and the liquid and solid compositions are integrated (in a spray scrubber) or calculated on each stage (in a tray scrubber), and the fresh slurry is added at the appropriate points. In reality, there is a small amount of contact between the fresh slurry and the gas before it mixes completely with the old slurry from earlier sections, but FGDTX treats the slurry as mixing instantaneously. At the bottom of the absorber, the resulting gas composition is compared with the specified inlet gas and a new penetration guess is made, and this process is repeated until converged. At this point, the outlet slurry composition is fed into the hold tank model, where the hold tank is modeled as a CSTR, oxidation is simulated according to the specified hold tank air rate, and the resulting composition of the slurry feed for the absorber is calculated. This is compared with the last guess for slurry feed composition, and a new guess is made, and this overall loop is then repeated until converged.

FGDTX is also capable of simulating co-current absorbers, but they will not be studied in this work.

2.1.2 Simple Chemistry

The overall reaction for SO_2 removal in the limestone slurry scrubber can be written as:

$$SO_2 + CaCO_3 \rightarrow CaSO_3 + CO_2 \tag{2-1}$$

When oxidation is included the reaction becomes:

$$SO_2 + \tfrac{1}{2} O_2 + CaCO_3 \rightarrow CaSO_4 + CO_2 \tag{2-2}$$

However, there are many steps in the above reactions, which can be summarized as dissolution of limestone, absorption of SO_2 into the solution, oxidation of sulfite to sulfate, crystallization of sulfite/sulfate solids, and CO_2 stripping.

2.1.2.1 Limestone Dissolution

This reaction occurs at the solid-liquid interface of the limestone:

$$CaCO_3(s) \rightarrow Ca^{++} + CO_3^{=} + 2H^+ \Leftrightarrow HCO_3^- + H^+ \Leftrightarrow H_2CO_3 \qquad (2\text{-}3)$$

The extent of this reaction is limited by the solubility of limestone in the slurry solution.

2.1.2.2 SO_2 Absorption

This reaction occurs at the gas-liquid interface as SO_2 is absorbed:

$$SO_2 + H_2O \rightarrow H_2SO_3 \Leftrightarrow H^+ + HSO_3^- \Leftrightarrow 2H^+ + SO_3^{=} \qquad (2\text{-}4)$$

The excess hydrogen ions produced may be absorbed to some extent by buffers in the solution.

2.1.2.3 Sulfite Oxidation

Oxidation occurs to a small extent in the absorber and to a greater extent in the hold tank.

$$HSO_3^- + \tfrac{1}{2}O_2 \rightarrow HSO_4^- \qquad (2\text{-}5)$$

Under forced oxidation operation, sufficient air is fed to the hold tank to achieve essentially complete oxidation.

2.1.3 Limits of Simulation in FGDTX

The fluid dynamics of the spray are not currently modeled by FGDTX. The number of gas-phase transfer units (N_g), the liquid residence time in the absorber, and the ratio of mass transfer coefficients (k_l^o/k_g) are input parameters to the model.

The mixing of the fresh slurry with spent slurry from higher slurry feeds is modeled as instantaneous mixing. Though this is misleading for calculating the rate of SO_2 absorption at points very near the spray headers, experience has shown that the ultimate result of the integration at the end of a spray section is a reasonable representation of the effects of the interference of above sprays.

Currently, the oxidation of sulfite is modeled by calculating the flux of O_2 into the liquid and assuming oxidation occurs instantaneously at the gas-liquid interface; if the flux is higher than the amount of sulfite present, the flux is reduced to match the amount of sulfite. Thus, FGDTX does not track an actual bulk dissolved O_2 concentration. Realistically, FGDTX should track such a concentration, and part of the oxidation should happen in the bulk solution. Specifically, the fraction of oxidation which occurs in the bulk solution should be $1/E^2$, where E is the enhancement factor for oxygen absorption due to the reaction with sulfite.

2.2 CHEMISTRY MODELS

2.2.1 Equilibrium Reactions

The liquid composition is modeled most simply by variables representing the total S(IV), S(VI), carbonate, and calcium ion concentrations. In addition, the concentrations of chloride, sodium, and magnesium ions and the total organic acid concentration are assumed constant over the system, and are specified as input parameters to the model.

The mass transfer calculations require a more complete speciation of the solution. When this is required, the concentrations of the following 17 species are calculated: H^+, OH^-, H_2CO_3, HCO_3^-, $CO_3^=$, H_2SO_3, HSO_3^-, $SO_3^=$, HSO_4^-, $SO_4^=$, H_2Ad, HAd^-, $Ad^=$, Ca^{++}, Cl^-, Na^+, and Mg^{++}. (The symbol Ad stands for Adipic acid, which is used to represent all organic buffer acids.)

A number of reactions of the form $HX \Leftrightarrow H^+ + X^-$ are assumed to reach equilibrium instantaneously, for the following species (in place of HX): H_2O, H_2CO_3, HCO_3^-, H_2SO_3, HSO_3^-, HSO_4^-, H_2Ad, and HAd^-. The equilibrium constants for these reactions give 8 of the relations necessary for the speciation. Five more relations are given by the four lumped liquid variables and total organic acid concentration, which must equal the total concentration of the appropriate species. Three additional relations are given by the specified concentrations for Cl^-, Na^+, and Mg^{++}. These 16 relations are all linear equations in the concentrations to be determined. One additional non-linear equation from the overall charge balance is used to determine the hydrogen ion concentration, from which all the other concentrations may be calculated.

This chemistry model is a simplified version of the model in the Bechtel-Modified Radian Equilibrium Program (BMREP). In BMREP, many ion pairs are also considered in the solution, such as $CaOH^+$, $CaCO_3^o$, and $CaAd^o$. FGDTX simplifies this chemistry by eliminating many of the ion pairs, using the anions to represent a mixture of both the anion and one or more ion pairs, and adjusting the parameters for the anions to account for this effect.

FGDTX's modified version of BMREP is called in the initial part of a simulation, setting up required parameters such as activity coefficients and equilibrium constants. Some of these parameters vary with composition slightly, and FGDTX assumes they change negligibly between the slurry feed and the slurry leaving the bottom of the absorber. This assumption is good as long as there are non-participating ions such as Cl^- present in large concentrations. Though running BMREP once would be sufficient for this, FGDTX runs BMREP once each time a new composition for the slurry feed is guessed, to ensure that the final answer does not depend on the initial guess for the slurry concentration. This is necessary in order to use FGDTX for parameter estimation.

FGDPRISM uses the rigorous BMREP equilibrium model throughout the program, which makes it much slower than FGDTX, but possibly more accurate. The BMREP equilibrium model requires the simultaneous solution of a number of non-linear equations equal to the number of cations involved in ion pairs, plus the number of activity coefficients calculated. FGDTX reduces this to a single non-linear equation by eliminating all ion pairs besides those involving hydrogen as the only cation, and by assuming activity coefficients do not change between the slurry feed and the slurry leaving the absorber.

Brogren's model (Brogren and Karlsson, 1997) uses a version of the BMREP equilibrium model which is reduced, perhaps in the same way as FGDTX, but not quite as much reduced; it retains nine ion pairs involving calcium or magnesium. The details of the equilibrium model used in Gerbec's model (Gerbec et al., 1995) are not known, but it appears to use something entirely different from BMREP.

2.2.2 Mass Transfer

2.2.2.1 Gas-Liquid Mass Transfer

Gas-liquid mass transfer is modeled by two film theory. An approximation to surface renewal theory is used to account for the enhancement of liquid phase diffusion by equilibrium reactions with unequal diffusivities (Chang and Rochelle, 1982; Mehta and Rochelle, 1983). The total flux of a component in the liquid film is approximated by:

$$\text{Flux} = \frac{k_l^o}{\sqrt{D_{SO_2}}} \sum \sqrt{D_j}\,\Delta[C_j] \qquad (2\text{-}6)$$

where j varies over all relevant solution components and $\Delta[C_j]$ represents the difference between the interface and bulk concentrations of component j.

If oxidation to sulfite occurs only at the gas/liquid interface, the gas flux of SO_2 must equal the flux of sulfite and sulfate through the liquid film. This flux balance gives:

$$k_g\left(P_{SO_2} - P_{SO_2,i}\right) = \frac{k_l^o}{\sqrt{D_{SO_2}}}\left[\sum_j \sqrt{D_j}\,\Delta[S(IV)_j] + \sum_k \sqrt{D_k}\,\Delta[S(VI)_k]\right] \qquad (2\text{-}7)$$

where j varies over the S(IV) species SO_2, HSO_3^-, $SO_3^=$, and k varies over the S(VI) species HSO_4^- and $SO_4^=$.

For SO_2 absorption, the liquid and gas phase resistances are both considered, with the interface concentrations given by the Henry's constant.

For CO_2, gas phase resistance is neglected and the liquid flux is calculated using equation 2-6 for H_2CO_3, HCO_3^-, and $CO_3^=$.

Absorption of O_2 is enhanced over physical absorption by the oxidation of sulfite in the gas-liquid interface. This enhancement is a specified factor E, so the flux balance for O_2 is:

$$2E\frac{k_l^o}{\sqrt{D_{SO_2}}}\sqrt{D_{O_2}}H_{O_2}P_{O_2}=\frac{k_l^o}{\sqrt{D_{SO_2}}}\sum_{j=SO_4^=,HSO_4^-}\sqrt{D_j}\Delta[C_j] \qquad (2\text{-}8)$$

Other species are treated as non-volatile and their fluxes are set to 0. By equation 2-6, the gas-liquid interface concentration of these components equals the bulk concentration.

In solving the equations for the equilibrium reactions at the interface, in addition, the charge flux is set to zero, rather than the charge balance. Setting the charge balance to zero overspecifies the system when combined with the diffusivity data; the diffusivity of the ion adjusted to meet the charge balance will not enter into the solution of the system. Setting the charge flux equal to zero neglects the effect of potential gradients on ion diffusion. As long as the diffusing species are present in small concentrations compared to the total electrolytes, this is a good approximation, and in limestone slurry scrubbers, this is almost always the case.

FGDPRISM uses a model similar to FGDTX's which accounts for unequal diffusivities and, in its current version, sets the charge flux equal to zero as described above. The Brogren model also does this. Gerbec's model does something entirely different here, as it attempts to model the unsteady-state behavior of the system.

The gas-liquid mass transfer model uses diffusion coefficients for ions based upon literature data, as developed by Mehta (Mehta and Rochelle, 1983).

Weems (1981) added a correction for the diffusivities of ion pairs. FGDTX does not attempt to model k_l^o, but instead uses a specified value for k_l^o/k_g where such data is required.

FGDTX models multiple spray levels by assuming that the liquid from the level above mixes instantaneously with the fresh spray, so at any given height in the absorber there is a single liquid composition. In reality, the fresh spray absorbs SO_2 for some short time before mixing with the liquid from above. Adding a split-liquid model which simulates two different liquid compositions gradually mixing as the liquid progresses down the section was considered, but the inaccuracy of the current approach was considered small enough as to not justify the considerable complication in the model.

2.2.2.2 Solid-Liquid Mass Transfer

The solid-liquid mass transfer models calculate the rates of crystallization and dissolution based on experimental work and transport theory.

In the presence of sulfate, calcium sulfite crystallizes as a mixed sulfate/sulfite hemihydrate solid containing up to 17% sulfate (Jones et al., 1976). The crystallization rate for calcium sulfite is calculated based on the correlation of Tseng (1984):

$$\frac{d[CaSO_3]}{dt} = \Gamma_{CaSO_3}[CaSO_3]\frac{(RS_{CaSO_3}-1)^2}{RS_{CaSO_4}} \tag{2-9}$$

Γ is a crystallization constant, and RS represents relative saturation. The crystallization rate for calcium sulfate hemihydrate is given by:

$$\frac{d[CaSO_4]}{dt} = \frac{X_{CaSO_4}}{1-X_{CaSO_4}}\frac{d[CaSO_3]}{dt} \tag{2-10}$$

where X_{CaSO_4} is given by:

$$X_{CaSO_4} = \begin{cases} (0.413 - 0.251RS_{CaSO_4})RS_{CaSO_4} & \text{for } RS_{CaSO_4} \le 0.823 \\ 0.170 & \text{for } RS_{CaSO_4} > 0.823 \end{cases} \quad (2\text{-}11)$$

For calcium sulfate dihydrate (gypsum), the crystallization rate is given by:

$$\frac{d[\text{gypsum}]}{dt} = \Gamma_{CaSO_4} C_{CaSO_4} (RS_{CaSO_4} - 1) \quad (2\text{-}12)$$

Limestone is not allowed to crystallize.

When the relative saturation of $CaSO_3$ or $CaSO_4$ is less than 1, dissolution rates are calculated as:

$$\frac{d[X]}{dt} = -\gamma_X [X] \left(\frac{k_l^o}{H_{SO_2}} \sum D_j \Delta C_j \right) \quad (2\text{-}13)$$

where γ is a dissolution parameter analogous to the Γ for crystallization, the term in parentheses is the solid-liquid flux calculated from film theory, where D represents diffusivity and ΔC is the difference in concentration between the solid surface and the bulk liquid, and the sum is over the ions in the solid (Ca^{++} and $SO_3^{=}$ or $SO_4^{=}$).

The limestone dissolution rate is calculated as:

$$\frac{d[CaCO_3]}{dt} = K[CaCO_3(s)] D_{Ca^{++}} \Delta C_{Ca^{++}} \quad (2\text{-}14)$$

where K represents a limestone reactivity parameter.

The limestone reactivity parameter depends on the limestone type and particle size distribution, limestone utilization, concentration of sulfite (which inhibits limestone dissolution), and other parameters. This parameter is calculated by the methods of Gage (1989).

Given the limestone reactivity parameter calculated as above, FGDTX allows the limestone reactivity parameter as calculated above to be modified by a factor which represents effects which are not yet modeled. Effects based on the particle size distribution, the slope of the particle size distribution, solution composition effects, and the effects of utilization are modeled. This model is simple enough to be calculated quickly, but it is not able to model hydroclones.

FGDPRISM uses a more rigorous limestone dissolution model, which keeps track of limestone particle size distributions throughout the system. This allows it to model hydroclones, but makes it much slower.

Other models use very simplistic limestone dissolution models, such as a correlation of limestone dissolution with pH.

The solid-liquid mass transfer model uses kinetic constants developed by Gage (1989). The source of FGDPRISM's kinetic data is not known. The effects of sulfite on limestone dissolution and the effects of dibasic acid buffers are accounted for. FGDPRISM also accounts for these effects, and in addition accounts for some effects of fluoride and magnesium on limestone dissolution. FGDTX does not attempt to model those effects.

2.3 NEW FEATURES OF THE FGDTX MODEL

My work with FGDTX consisted primarily of fixing bugs and expanding the capability of the model by replacing assumptions which are not always true at some of the conditions at which the model is now being applied. When I started, the model had the framework for spray calculations in place, but a number of bugs prevented the model from being able to simulate more than a few specific spray cases. In addition, there were problems which made convergence at forced oxidation difficult; this was fixed by changing the next guess for slurry composition to something more appropriate under forced oxidation conditions. Also, in certain extreme conditions the dissolution and crystallization models gave invalid results, for instance, allowing a concentration to become negative. These models were modified to prevent such problems.

CHAPTER 3: RESULTS

The results for this system use some specialized terminology, which is defined and explained in section 3.1. Following that is a long set of results from FGDTX, and then simpler models are developed to explain the complex effects which occur in this system. The approach model ties together the three fundamental parameters affecting performance of spray scrubbers: the gas-film mass transfer limit, the overall enhancement factor, and liquid phase resistance to SO_2 absorption. The series resistances model gives some representation of the magnitude of the effects of various parameters on performance. Finally, the results from FGDTX are compared to literature data.

3.1 MODEL PARAMETERS

The FGDTX model uses a number of parameters to describe the conditions of the system. Some of these are standard mass-transfer terminology, while others are specific to this system.

Fractional removal of SO_2 is the primary parameter describing the performance of limestone slurry scrubbers. Often, fractional removal occurs in models in the form (1 - removal), or the logarithm of such an expression. Penetration is a name for 1 - fractional removal, or $y_{SO_2,out}/y_{SO_2,in}$. Most of the expressions of system performance in this work will be given in terms of penetration.

The number of gas phase mass transfer units, N_g, is the parameter which represents the ability of the system to cause the gas to come into contact with liquid. The theoretical limit of the penetration of the system is e^{-N_g}, assuming the gas phase mass-transfer is the only limitation. Because of this, the form -ln(penetration) often appears, and -ln(penetration)/N_g is sometimes used as a normalized form of penetration which varies from 0 to 1.

Both N_g and penetration are sometimes written in terms of a single section, usually defined as the space under one spray header and above the next or above the bottom of the tank. In the case of penetration over a section, this is the ratio of the SO_2 leaving the section to that entering it, so the product of all the penetrations of the sections of a system equals the overall penetration.

Scrubber liquid-to-gas ratio, or L/G, is another important parameter. This is the ratio of the liquid and gas feed flow rates. All gas data for FGDTX, such as the gas rate G in L/G, is specified in terms of the wet gas after humidification.

Limestone utilization represents the fraction of the fresh limestone feed that dissolves in the system, and thus is not removed in the hold tank product. The fraction of excess limestone, 1 - utilization, is a convenient form in which this parameter is sometimes written. As a practical matter, the limestone utilization defines the solids composition and is given by the ratio of sulfur and calcium in the solids in the hold tank.

The fraction of limestone dissolved in the absorber is the ratio of the limestone dissolved in the absorber to that dissolved in the absorber and hold tank combined.

3.2 TABULATED DATA FROM FGDTX RUNS

3.2.1 Factorial Run Conditions

A set of factorial runs was made for varying conditions of L/G, N_g, number of spray headers, limestone utilization, inlet SO_2 concentration, and hold tank size. The conditions for these runs are given in tables 3-1 to 3-5. The N_g for the base case is set to 1.9 for the top spray section and decreasing amounts for each following section. The increased liquid rate on the lower levels would initially seem to warrant a higher N_g on those sections, but by the time slurry has fallen from one spray header to the next, it tends to have agglomerated into large drops with poor mass-transfer ability, and the large drops also interfere with the lower sprays, reducing mass-transfer ability further. An additional section below all the spray sections is present for each case; this one has a much smaller value of N_g, as no fresh slurry was added. The distribution of N_g over the headers is arbitrary but appears to match field data. See section 3.5.2.2.

Table 3-1: Factorial conditions for L/G, N_g, and number of spray headers

scrubber L/G (gal/Mcf)	total scrubber N_g	No. spray headers	N_g by section	code
100	6.9	4	1.9, 1.7, 1.5, 1.3, 0.5	A
50	3.45	4	0.95, 0.85, 0.75, 0.65, 0.25	B
150	10.35	4	2.85, 2.55, 2.25, 1.95, 0.75	C
50	6.9	4	1.9, 1.7, 1.5, 1.3, 0.5	D
150	6.9	4	1.9, 1.7, 1.5, 1.3, 0.5	E
50	4.1	2	1.9, 1.7, 0.5	F
150	8.9	6	1.9, 1.7, 1.5, 1.3, 1.1, 0.9, 0.5	G

Table 3-2: Factorial conditions for limestone utilization

Limestone utilization	code
0.8	1
0.9	2
0.95	3
0.97	4
0.99	5

Table 3-3: Factorial conditions for inlet gas SO_2 concentration

Inlet SO_2 concentration, ppm	code
500	1
1800	2
5000	3

Table 3-4: Factorial conditions for hold tank size

Hold tank size, s-Mcf/ppm-gal	code
8.33	1
16.67	2
33.33	3

The hold tank slurry residence time, τ, in seconds, is determined from the hold tank size (in units of s-Mcf/ppm-gal), L/G (gal/Mcf), and inlet SO_2 concentration (ppm) by: τ = (hold tank size)[$SO_{2,in}$]/(L/G). The number of liquid phase transfer units in the hold tank, N_L, is set to $\tau/15$ for all cases. The hold tank size, rather than the residence time, is the parameter with fixed values in order to simulate the same depth of slurry in the hold tank at different liquid rates.

In all cases, the specified number of spray sections were modeled, plus one additional section with no slurry feed; the slurry feed was split evenly over the spray headers. Other constant input parameters are listed in Table 3-5. Temperature, hold tank air stoichiometry, and a few other conditions were held constant because they do not vary much in typical spray scrubber systems. Adipate concentration was varied in a separate set of runs (see section 3.2.3).

Table 3-5: Other common conditions

Parameter	Value
Temperature	60º C
Total solids concentration in slurry	100 g/l
Solution concentrations of Mg^{++}, Na^{+}, K^{+}	all zero
Solution concentration of Cl^{-}	0.1 M
Total adipate concentration	zero
Inlet flue gas CO_2 concentration	10%
Inlet flue gas O_2 concentration	8%
Residence time	0.4 seconds in each section
k_l^o/k_g	200 atm-ml/mol
Hold tank air stoichiometry (O/SO_2 in)	3.0
Limestone dissolution parameter	11.25 (dimensionless)
Dissolution rate parameters for calcium sulfite and gypsum	10^5, 10^{-5} (gmol/cm^2-s)
Crystallization rate parameters for calcium sulfite and gypsum	2x10^{-3}, 2x10^{-3} (gmol/cm^2-s)
Oxidation enhancement factor	1.0 (dimensionless)
Oxidation kinetic constant	10^4 (L^2/cm^8-s)
Limestone grind	Fredonia Feedbelt (see Appendix 2)

In the tabular results which follow, the ID for each run is composed of the codes above for scrubber configuration, limestone utilization, inlet SO_2 concentration, and hold tank size, in that order.

3.2.2 Tabular Results from Factorial Runs

Below are the results for the 301 of the 315 combinations of input cases which converge with no tuning of parameters. The other 14 cases failed to converge for various reasons; these cases mostly consist of unlikely combinations of extreme values of the input parameters.

Table 3-6: Results of factorial runs

ID	overall	penetration for each section							fract. CaCO$_3$
	penetr.	Top	2	3	4	5	6	7	diss. in abs.
A111	0.00202	0.150	0.183	0.239	0.402	0.764	-	-	0.246
A112	0.00193	0.150	0.183	0.234	0.393	0.762	-	-	0.246
A113	0.00188	0.150	0.183	0.232	0.388	0.761	-	-	0.248
A121	0.05132	0.308	0.485	0.590	0.669	0.870	-	-	0.541
A122	0.05042	0.303	0.484	0.590	0.669	0.870	-	-	0.517
A123	0.05041	0.301	0.485	0.591	0.670	0.871	-	-	0.517
A131	0.24403	0.654	0.704	0.744	0.781	0.913	-	-	0.751
A132	0.24106	0.650	0.702	0.742	0.780	0.913	-	-	0.742
A133	0.24093	0.650	0.702	0.742	0.780	0.913	-	-	0.741
A211	0.00275	0.150	0.184	0.278	0.456	0.788	-	-	0.249
A212	0.00234	0.150	0.183	0.253	0.430	0.782	-	-	0.168
A213	0.00214	0.150	0.183	0.242	0.414	0.777	-	-	0.127
A221	0.09467	0.434	0.560	0.635	0.696	0.881	-	-	0.530
A222	0.08838	0.412	0.553	0.633	0.696	0.881	-	-	0.491
A223	0.08556	0.401	0.550	0.632	0.696	0.882	-	-	0.471
A231	0.30645	0.720	0.747	0.773	0.800	0.921	-	-	0.690
A232	0.30463	0.718	0.746	0.772	0.800	0.921	-	-	0.674
A233	0.30363	0.716	0.746	0.772	0.800	0.921	-	-	0.665
A311	0.00499	0.150	0.213	0.371	0.520	0.811	-	-	0.333
A312	0.00335	0.150	0.187	0.305	0.485	0.805	-	-	0.207
A313	0.00256	0.150	0.183	0.263	0.446	0.794	-	-	0.123
A321	0.15975	0.561	0.637	0.685	0.729	0.895	-	-	0.532
A322	0.14343	0.525	0.622	0.677	0.725	0.895	-	-	0.470
A323	0.13232	0.498	0.611	0.673	0.723	0.895	-	-	0.427
A331	0.37348	0.770	0.788	0.804	0.823	0.931	-	-	0.626
A332	0.36843	0.765	0.785	0.802	0.822	0.931	-	-	0.599
A333	0.36175	0.759	0.781	0.799	0.820	0.931	-	-	0.580
A411	0.01193	0.170	0.319	0.462	0.572	0.831	-	-	0.422
A412	0.00604	0.150	0.226	0.396	0.544	0.826	-	-	0.263
A413	0.00348	0.150	0.188	0.308	0.493	0.815	-	-	0.152
A421	0.21752	0.635	0.690	0.723	0.756	0.907	-	-	0.515
A422	0.19590	0.601	0.672	0.713	0.750	0.906	-	-	0.453
A423	0.17636	0.567	0.655	0.704	0.745	0.906	-	-	0.399
A431	0.41650	0.794	0.811	0.823	0.838	0.938	-	-	0.570
A432	0.40927	0.788	0.807	0.821	0.836	0.938	-	-	0.544
A433	0.40289	0.783	0.804	0.818	0.835	0.938	-	-	0.519
A512	0.08059	0.432	0.539	0.602	0.661	0.871	-	-	0.337
A513	0.02344	0.218	0.389	0.522	0.617	0.858	-	-	0.246
A521	0.35760	0.755	0.783	0.797	0.814	0.932	-	-	0.386
A522	0.31041	0.712	0.756	0.778	0.799	0.928	-	-	0.374
A523	0.28228	0.683	0.737	0.765	0.791	0.926	-	-	0.344
A531	0.50940	0.838	0.852	0.860	0.869	0.953	-	-	0.426
B111	0.12280	0.481	0.592	0.666	0.725	0.894	-	-	0.543
B112	0.11882	0.472	0.586	0.664	0.724	0.894	-	-	0.489
B113	0.11627	0.466	0.583	0.662	0.723	0.894	-	-	0.482

B121	0.38556	0.760	0.790	0.815	0.840	0.938	-	-	0.779
B122	0.38497	0.759	0.790	0.815	0.840	0.938	-	-	0.775
B123	0.38474	0.759	0.790	0.815	0.840	0.938	-	-	0.773
B131	0.55711	0.854	0.867	0.879	0.893	0.958	-	-	0.865
B132	0.55695	0.854	0.867	0.879	0.893	0.958	-	-	0.863
B133	0.56384	0.859	0.870	0.881	0.894	0.958	-	-	0.903
B211	0.17502	0.561	0.651	0.705	0.751	0.904	-	-	0.518
B212	0.16248	0.536	0.640	0.700	0.748	0.905	-	-	0.441
B213	0.15458	0.520	0.632	0.696	0.747	0.905	-	-	0.398
B221	0.44423	0.804	0.821	0.836	0.854	0.943	-	-	0.719
B222	0.44155	0.802	0.819	0.835	0.853	0.943	-	-	0.691
B223	0.43999	0.800	0.818	0.835	0.853	0.943	-	-	0.673
B231	0.60895	0.883	0.888	0.894	0.903	0.962	-	-	0.779
B232	0.60812	0.882	0.887	0.894	0.903	0.962	-	-	0.766
B233	0.60762	0.882	0.887	0.894	0.903	0.962	-	-	0.759
B311	0.24276	0.646	0.709	0.744	0.778	0.915	-	-	0.556
B312	0.21843	0.610	0.691	0.734	0.772	0.914	-	-	0.453
B313	0.19858	0.578	0.675	0.726	0.767	0.914	-	-	0.373
B321	0.50487	0.837	0.849	0.859	0.871	0.950	-	-	0.658
B322	0.49883	0.833	0.847	0.857	0.869	0.950	-	-	0.617
B323	0.49425	0.829	0.845	0.855	0.869	0.950	-	-	0.586
B331	0.65594	0.901	0.905	0.909	0.915	0.967	-	-	0.689
B332	0.65136	0.899	0.904	0.907	0.914	0.967	-	-	0.670
B333	0.64992	0.899	0.903	0.907	0.913	0.967	-	-	0.655
B411	0.30170	0.701	0.750	0.776	0.801	0.924	-	-	0.557
B412	0.27193	0.666	0.731	0.763	0.792	0.923	-	-	0.458
B413	0.24222	0.628	0.710	0.751	0.785	0.922	-	-	0.369
B421	0.54659	0.854	0.867	0.874	0.883	0.956	-	-	0.599
B422	0.53950	0.850	0.864	0.872	0.882	0.956	-	-	0.560
B423	0.53220	0.845	0.861	0.870	0.880	0.956	-	-	0.523
B431	0.68211	0.909	0.914	0.917	0.922	0.971	-	-	0.616
B432	0.67956	0.908	0.913	0.916	0.921	0.971	-	-	0.599
B433	0.67749	0.907	0.912	0.916	0.921	0.971	-	-	0.580
B511	0.43154	0.786	0.820	0.835	0.849	0.945	-	-	0.430
B512	0.39107	0.756	0.800	0.820	0.838	0.942	-	-	0.393
B513	0.36075	0.730	0.784	0.808	0.829	0.940	-	-	0.340
B521	0.61791	0.878	0.893	0.899	0.906	0.967	-	-	0.432
B522	0.60763	0.873	0.889	0.896	0.903	0.966	-	-	0.421
B523	0.59850	0.869	0.886	0.893	0.901	0.966	-	-	0.401
C111	0.00006	0.058	0.078	0.106	0.180	0.635	-	-	0.229
C112	0.00005	0.058	0.078	0.106	0.171	0.626	-	-	0.205
C113	0.00005	0.058	0.078	0.106	0.168	0.621	-	-	0.198
C121	0.00044	0.058	0.083	0.247	0.470	0.790	-	-	0.346
C122	0.00041	0.058	0.081	0.237	0.467	0.790	-	-	0.312
C123	0.00044	0.058	0.082	0.245	0.474	0.793	-	-	0.304
C131	0.05304	0.326	0.486	0.585	0.661	0.865	-	-	0.612
C132	0.05304	0.325	0.487	0.585	0.662	0.865	-	-	0.600
C133	0.05366	0.326	0.488	0.587	0.663	0.866	-	-	0.603
C211	0.00007	0.058	0.078	0.107	0.213	0.661	-	-	0.158

C212	0.00006	0.058	0.078	0.106	0.189	0.646	-	-	0.104
C213	0.00005	0.058	0.078	0.106	0.177	0.635	-	-	0.076
C221	0.00097	0.058	0.114	0.345	0.520	0.809	-	-	0.340
C222	0.00069	0.058	0.095	0.304	0.509	0.808	-	-	0.294
C223	0.00058	0.058	0.088	0.282	0.502	0.807	-	-	0.269
C231	0.09927	0.462	0.562	0.631	0.691	0.877	-	-	0.583
C232	0.09607	0.450	0.559	0.630	0.690	0.877	-	-	0.561
C233	0.09503	0.446	0.558	0.630	0.690	0.877	-	-	0.550
C311	0.00011	0.059	0.078	0.121	0.277	0.699	-	-	0.251
C312	0.00008	0.058	0.078	0.108	0.228	0.675	-	-	0.109
C313	0.00006	0.058	0.078	0.106	0.197	0.654	-	-	0.056
C321	0.00556	0.088	0.284	0.462	0.576	0.833	-	-	0.382
C322	0.00173	0.059	0.157	0.405	0.556	0.829	-	-	0.298
C323	0.00098	0.058	0.109	0.347	0.538	0.826	-	-	0.247
C331	0.16293	0.578	0.638	0.682	0.725	0.892	-	-	0.552
C332	0.15280	0.557	0.629	0.677	0.722	0.892	-	-	0.515
C333	0.14619	0.542	0.622	0.674	0.720	0.892	-	-	0.490
C411	0.00025	0.086	0.078	0.155	0.330	0.721	-	-	0.311
C412	0.00011	0.058	0.078	0.121	0.280	0.708	-	-	0.171
C413	0.00008	0.058	0.078	0.108	0.230	0.680	-	-	0.065
C421	0.03294	0.268	0.435	0.537	0.618	0.851	-	-	0.413
C422	0.00991	0.115	0.338	0.499	0.602	0.848	-	-	0.323
C423	0.00241	0.061	0.186	0.437	0.580	0.843	-	-	0.243
C431	0.20936	0.637	0.682	0.714	0.748	0.903	-	-	0.516
C432	0.19890	0.619	0.673	0.710	0.745	0.903	-	-	0.481
C433	0.18697	0.599	0.663	0.704	0.742	0.902	-	-	0.447
C512	0.00309	0.261	0.138	0.267	0.419	0.765	-	-	0.282
C513	0.00025	0.075	0.078	0.164	0.351	0.743	-	-	0.152
C521	0.21211	0.667	0.690	0.705	0.729	0.897	-	-	0.340
C522	0.12482	0.525	0.601	0.646	0.691	0.885	-	-	0.318
C523	0.07100	0.384	0.525	0.603	0.666	0.877	-	-	0.275
C531	0.35454	0.764	0.781	0.792	0.807	0.929	-	-	0.383
C532	0.30696	0.722	0.753	0.771	0.792	0.924	-	-	0.391
C533	0.27903	0.695	0.734	0.759	0.783	0.921	-	-	0.383
D111	0.00442	0.150	0.196	0.360	0.518	0.807	-	-	0.466
D112	0.00422	0.150	0.192	0.350	0.517	0.807	-	-	0.425
D113	0.00416	0.150	0.191	0.347	0.518	0.808	-	-	0.426
D121	0.17875	0.603	0.646	0.694	0.739	0.895	-	-	0.759
D122	0.17871	0.602	0.646	0.694	0.739	0.895	-	-	0.757
D123	0.17932	0.603	0.647	0.695	0.739	0.895	-	-	0.745
D131	0.39920	0.792	0.799	0.814	0.832	0.932	-	-	0.834
D132	0.39901	0.791	0.799	0.814	0.832	0.932	-	-	0.832
D133	0.40945	0.801	0.805	0.817	0.835	0.932	-	-	0.865
D211	0.00988	0.151	0.290	0.466	0.581	0.834	-	-	0.512
D212	0.00779	0.150	0.246	0.445	0.571	0.832	-	-	0.439
D213	0.00759	0.150	0.237	0.444	0.575	0.834	-	-	0.404
D221	0.27146	0.716	0.722	0.746	0.774	0.909	-	-	0.726
D222	0.26835	0.711	0.720	0.745	0.773	0.910	-	-	0.703
D223	0.26694	0.709	0.719	0.744	0.773	0.910	-	-	0.690

D231	0.48665	0.848	0.841	0.846	0.857	0.942	-	-	0.767
D232	0.48537	0.847	0.840	0.846	0.856	0.942	-	-	0.756
D233	0.48460	0.846	0.840	0.845	0.856	0.942	-	-	0.749
D311	0.03856	0.262	0.465	0.569	0.644	0.861	-	-	0.638
D312	0.02416	0.192	0.419	0.549	0.634	0.860	-	-	0.536
D313	0.01681	0.163	0.363	0.528	0.624	0.859	-	-	0.440
D321	0.37165	0.789	0.786	0.796	0.812	0.927	-	-	0.682
D322	0.35937	0.780	0.779	0.791	0.808	0.926	-	-	0.648
D323	0.35372	0.774	0.775	0.789	0.806	0.926	-	-	0.621
D331	0.56195	0.880	0.872	0.873	0.879	0.953	-	-	0.692
D332	0.55927	0.879	0.871	0.873	0.879	0.953	-	-	0.676
D333	0.55714	0.878	0.870	0.872	0.878	0.953	-	-	0.663
D411	0.10356	0.457	0.577	0.642	0.693	0.883	-	-	0.651
D412	0.07799	0.384	0.543	0.623	0.682	0.881	-	-	0.563
D413	0.05647	0.311	0.507	0.605	0.672	0.881	-	-	0.477
D421	0.43135	0.819	0.816	0.824	0.835	0.938	-	-	0.632
D422	0.42242	0.813	0.812	0.820	0.832	0.938	-	-	0.597
D423	0.41404	0.807	0.807	0.817	0.830	0.938	-	-	0.565
D431	0.60569	0.895	0.888	0.889	0.893	0.961	-	-	0.630
D432	0.60261	0.893	0.887	0.888	0.892	0.961	-	-	0.615
D433	0.59957	0.892	0.885	0.887	0.891	0.961	-	-	0.599
D511	0.28525	0.702	0.737	0.762	0.784	0.924	-	-	0.506
D512	0.23030	0.636	0.698	0.736	0.767	0.919	-	-	0.474
D513	0.18976	0.579	0.665	0.715	0.753	0.916	-	-	0.429
D521	0.53749	0.861	0.861	0.867	0.873	0.959	-	-	0.474
D522	0.52096	0.852	0.854	0.861	0.869	0.957	-	-	0.467
D523	0.51089	0.846	0.849	0.857	0.866	0.957	-	-	0.450
E111	0.00165	0.150	0.183	0.227	0.358	0.740	-	-	0.202
E112	0.00159	0.150	0.183	0.226	0.347	0.736	-	-	0.196
E113	0.00158	0.150	0.183	0.225	0.347	0.737	-	-	0.221
E121	0.01823	0.176	0.363	0.528	0.632	0.857	-	-	0.366
E122	0.01690	0.170	0.351	0.524	0.631	0.857	-	-	0.360
E123	0.01614	0.167	0.344	0.521	0.630	0.856	-	-	0.356
E131	0.17418	0.562	0.647	0.704	0.753	0.903	-	-	0.675
E132	0.17378	0.561	0.647	0.704	0.753	0.903	-	-	0.658
E133	0.17371	0.560	0.647	0.704	0.753	0.903	-	-	0.657
E211	0.00211	0.150	0.183	0.247	0.407	0.762	-	-	0.176
E212	0.00186	0.150	0.183	0.234	0.384	0.755	-	-	0.123
E213	0.00172	0.150	0.183	0.228	0.367	0.749	-	-	0.101
E221	0.03625	0.245	0.452	0.574	0.658	0.867	-	-	0.370
E222	0.02922	0.212	0.426	0.567	0.656	0.867	-	-	0.314
E223	0.02498	0.195	0.405	0.559	0.653	0.867	-	-	0.285
E231	0.21651	0.622	0.685	0.728	0.768	0.909	-	-	0.620
E232	0.21379	0.616	0.683	0.727	0.768	0.909	-	-	0.596
E233	0.21269	0.614	0.683	0.727	0.768	0.909	-	-	0.583
E311	0.00343	0.151	0.195	0.314	0.470	0.789	-	-	0.245
E312	0.00241	0.150	0.184	0.263	0.428	0.774	-	-	0.110
E313	0.00196	0.150	0.183	0.238	0.394	0.760	-	-	0.069
E321	0.07698	0.383	0.537	0.621	0.686	0.878	-	-	0.414

E322	0.05712	0.310	0.505	0.609	0.681	0.878	-	-	0.327
E323	0.03835	0.241	0.460	0.589	0.671	0.876	-	-	0.262
E331	0.27356	0.681	0.730	0.759	0.790	0.918	-	-	0.573
E332	0.26356	0.668	0.723	0.755	0.787	0.918	-	-	0.534
E333	0.25656	0.659	0.718	0.753	0.785	0.917	-	-	0.508
E411	0.00706	0.168	0.256	0.391	0.519	0.807	-	-	0.322
E412	0.00348	0.150	0.195	0.315	0.474	0.795	-	-	0.172
E413	0.00236	0.150	0.184	0.260	0.425	0.775	-	-	0.072
E421	0.12108	0.487	0.598	0.658	0.711	0.888	-	-	0.430
E422	0.09342	0.414	0.564	0.642	0.702	0.887	-	-	0.344
E423	0.06734	0.333	0.526	0.625	0.694	0.886	-	-	0.267
E431	0.31298	0.713	0.756	0.780	0.805	0.925	-	-	0.528
E432	0.30165	0.700	0.750	0.776	0.802	0.924	-	-	0.490
E433	0.29210	0.689	0.743	0.772	0.800	0.924	-	-	0.456
E512	0.04215	0.360	0.446	0.521	0.599	0.842	-	-	0.267
E513	0.00846	0.171	0.269	0.411	0.541	0.824	-	-	0.160
E521	0.27602	0.690	0.737	0.758	0.781	0.917	-	-	0.337
E522	0.20518	0.606	0.684	0.721	0.756	0.909	-	-	0.315
E523	0.16410	0.541	0.647	0.699	0.742	0.905	-	-	0.273
E531	0.41656	0.781	0.814	0.827	0.842	0.941	-	-	0.387
E532	0.38018	0.754	0.795	0.813	0.831	0.938	-	-	0.390
E533	0.36506	0.742	0.787	0.807	0.827	0.936	-	-	0.377
F111	0.06640	0.207	0.395	0.810	-	-	-	-	0.379
F112	0.06297	0.199	0.389	0.811	-	-	-	-	0.376
F113	0.06085	0.195	0.385	0.811	-	-	-	-	0.333
F121	0.32400	0.568	0.641	0.890	-	-	-	-	0.563
F122	0.32321	0.566	0.641	0.890	-	-	-	-	0.563
F123	0.32292	0.566	0.641	0.890	-	-	-	-	0.548
F131	0.51093	0.727	0.759	0.926	-	-	-	-	0.616
F132	0.51070	0.726	0.759	0.926	-	-	-	-	0.615
F133	0.51865	0.734	0.763	0.926	-	-	-	-	0.639
F211	0.10861	0.283	0.460	0.836	-	-	-	-	0.393
F212	0.09420	0.252	0.446	0.836	-	-	-	-	0.339
F213	0.08562	0.234	0.437	0.837	-	-	-	-	0.305
F221	0.39907	0.641	0.687	0.906	-	-	-	-	0.523
F222	0.39543	0.636	0.686	0.906	-	-	-	-	0.504
F223	0.39331	0.634	0.685	0.906	-	-	-	-	0.491
F231	0.57970	0.778	0.794	0.938	-	-	-	-	0.559
F232	0.57861	0.777	0.793	0.938	-	-	-	-	0.549
F233	0.57794	0.777	0.793	0.938	-	-	-	-	0.544
F311	0.18360	0.398	0.533	0.865	-	-	-	-	0.410
F312	0.15049	0.342	0.509	0.864	-	-	-	-	0.337
F313	0.12537	0.297	0.489	0.864	-	-	-	-	0.280
F321	0.47208	0.698	0.732	0.925	-	-	-	-	0.470
F322	0.46412	0.690	0.727	0.925	-	-	-	-	0.441
F323	0.45804	0.683	0.724	0.926	-	-	-	-	0.419
F331	0.63319	0.810	0.822	0.951	-	-	-	-	0.486
F332	0.63072	0.808	0.821	0.951	-	-	-	-	0.473
F333	0.62850	0.806	0.820	0.951	-	-	-	-	0.462

F411	0.25373	0.485	0.589	0.887	-	-	-	-	0.397
F412	0.21117	0.426	0.561	0.884	-	-	-	-	0.329
F413	0.17393	0.368	0.535	0.883	-	-	-	-	0.268
F421	0.52088	0.730	0.761	0.939	-	-	-	-	0.417
F422	0.50879	0.719	0.754	0.938	-	-	-	-	0.390
F423	0.49945	0.711	0.749	0.938	-	-	-	-	0.364
F431	0.66645	0.827	0.840	0.960	-	-	-	-	0.425
F432	0.66111	0.824	0.837	0.959	-	-	-	-	0.413
F433	0.65844	0.822	0.835	0.960	-	-	-	-	0.401
F511	0.39842	0.626	0.688	0.925	-	-	-	-	0.277
F512	0.34346	0.570	0.656	0.919	-	-	-	-	0.255
F513	0.30261	0.524	0.631	0.915	-	-	-	-	0.223
F521	0.59029	0.770	0.800	0.958	-	-	-	-	0.281
F522	0.57926	0.762	0.795	0.957	-	-	-	-	0.276
F523	0.56920	0.754	0.789	0.956	-	-	-	-	0.265
G111	0.00023	0.150	0.183	0.224	0.274	0.355	0.517	0.741	0.244
G112	0.00022	0.150	0.183	0.224	0.273	0.349	0.508	0.738	0.233
G113	0.00021	0.150	0.183	0.224	0.273	0.345	0.500	0.734	0.217
G121	0.00233	0.150	0.196	0.363	0.538	0.649	0.730	0.854	0.415
G122	0.00200	0.150	0.189	0.338	0.524	0.642	0.726	0.852	0.390
G123	0.00197	0.150	0.188	0.335	0.524	0.643	0.726	0.852	0.391
G131	0.10487	0.551	0.633	0.691	0.741	0.786	0.826	0.905	0.777
G132	0.10466	0.550	0.633	0.691	0.741	0.786	0.827	0.905	0.762
G133	0.10474	0.549	0.633	0.691	0.741	0.786	0.827	0.905	0.760
G211	0.00029	0.150	0.183	0.224	0.278	0.402	0.558	0.763	0.209
G212	0.00025	0.150	0.183	0.224	0.274	0.372	0.538	0.754	0.148
G213	0.00023	0.150	0.183	0.224	0.274	0.355	0.519	0.746	0.111
G221	0.00560	0.156	0.282	0.479	0.600	0.683	0.751	0.865	0.411
G222	0.00394	0.151	0.233	0.438	0.586	0.677	0.748	0.864	0.352
G223	0.00327	0.150	0.213	0.410	0.574	0.673	0.745	0.863	0.325
G231	0.14854	0.639	0.688	0.727	0.764	0.801	0.836	0.910	0.727
G232	0.14626	0.633	0.685	0.726	0.764	0.800	0.836	0.910	0.702
G233	0.14565	0.630	0.685	0.726	0.764	0.801	0.836	0.910	0.689
G311	0.00045	0.151	0.183	0.226	0.323	0.471	0.605	0.786	0.278
G312	0.00032	0.150	0.183	0.224	0.285	0.420	0.572	0.772	0.131
G313	0.00027	0.150	0.183	0.224	0.275	0.380	0.544	0.759	0.073
G321	0.02841	0.313	0.486	0.583	0.657	0.718	0.773	0.876	0.490
G322	0.01289	0.196	0.395	0.547	0.640	0.709	0.767	0.875	0.380
G323	0.00775	0.160	0.315	0.517	0.630	0.706	0.766	0.875	0.311
G331	0.20771	0.715	0.745	0.768	0.794	0.821	0.850	0.917	0.692
G332	0.19878	0.701	0.737	0.763	0.791	0.819	0.848	0.917	0.648
G333	0.19380	0.693	0.733	0.761	0.789	0.818	0.848	0.917	0.620
G411	0.00078	0.162	0.183	0.255	0.388	0.524	0.635	0.800	0.371
G412	0.00046	0.150	0.183	0.226	0.324	0.474	0.611	0.793	0.200
G413	0.00032	0.150	0.183	0.224	0.283	0.418	0.572	0.774	0.084
G421	0.06813	0.490	0.591	0.647	0.698	0.746	0.791	0.886	0.530
G422	0.04129	0.365	0.530	0.616	0.680	0.735	0.784	0.884	0.427
G423	0.02124	0.241	0.454	0.584	0.665	0.727	0.779	0.883	0.330
G431	0.25228	0.754	0.778	0.795	0.814	0.836	0.861	0.923	0.655

G432	0.24107	0.741	0.770	0.789	0.810	0.834	0.859	0.923	0.610
G433	0.23485	0.732	0.765	0.787	0.809	0.833	0.858	0.923	0.572
G511	0.07620	0.657	0.651	0.632	0.650	0.689	0.738	0.853	0.506
G512	0.00519	0.257	0.285	0.401	0.511	0.606	0.689	0.830	0.376
G513	0.00093	0.158	0.183	0.265	0.410	0.548	0.657	0.817	0.202
G521	0.23259	0.754	0.776	0.786	0.800	0.820	0.844	0.914	0.457
G522	0.15777	0.658	0.712	0.738	0.766	0.795	0.827	0.906	0.428
G523	0.11265	0.570	0.659	0.704	0.742	0.779	0.816	0.902	0.371
G531	0.37456	0.831	0.844	0.852	0.861	0.873	0.889	0.940	0.513
G532	0.33660	0.805	0.825	0.837	0.849	0.864	0.882	0.936	0.517
G533	0.31804	0.791	0.815	0.829	0.843	0.860	0.879	0.935	0.499

3.2.3 Other Runs

In addition to the above, other cases have been performed as necessary to demonstrate the behavior of the model. Table 3-7 summarizes the conditions of these cases, and Table 3-8 lists the results. In the case IDs for these cases, the first letter is always an X, the next digit divides the cases into sets based on where they were used, and the remaining digits are merely assigned in numerical order to distinguish cases. In the descriptions of the conditions, a # is used in place of one of the symbols for the factorial cases when one of these runs uses a value for that condition different from any of the factorial conditions.

Table 3-7: Conditions for other runs

Case ID	Conditions
X101-X105	As in A1#2-A5#2 but at $SO_{2,in}$ = 1200 ppm
X106-X110	As in A1#2-A5#2 but at $SO_{2,in}$ = 2700 ppm
X201-X202	As in A#21, A#23 with utilization varying to keep hold tank pH constant
X203-X204	As in A#21, A#23 with utilization and hold tank pH both varying to keep penetration constant
X301-X302	As in B322 with L/G = 100, 150
X303-X304	As in C322 with L/G = 50, 100
X401-X403	As in A2#2, A3#2, A5#2 but at $SO_{2,in}$ = 1000 ppm
X501-X506	As in A322, with DBA = 0.685 in X501, and 2, 5, 10, 20, and 40 times as much in X502-X506 respectively
X507-X513	As in A322 and X501-X506, but oxidation kinetic constant reduced by half, scrubber residence time increased by a factor of 6, and utilization varied to keep pH constant at 5.5-5.6

Table 3-8: Results of other runs

ID	overall penetration	penetration for each section					fract. of $CaCO_3$ diss. in abs.
		Top	2	3	4	5	
X101	0.01048	0.154	0.281	0.479	0.600	0.843	0.381
X102	0.12114	0.485	0.591	0.661	0.719	0.890	0.644
X103	0.02291	0.194	0.396	0.545	0.637	0.860	0.365
X104	0.17293	0.575	0.647	0.697	0.742	0.899	0.583
X105	0.05778	0.322	0.505	0.602	0.673	0.875	0.384
X106	0.23439	0.650	0.701	0.735	0.768	0.911	0.534
X107	0.10485	0.450	0.579	0.647	0.702	0.888	0.399
X108	0.28615	0.698	0.738	0.764	0.790	0.921	0.497
X109	0.23502	0.646	0.706	0.736	0.765	0.914	0.354
X110	0.38638	0.767	0.797	0.813	0.829	0.939	0.396
X201	0.10790	0.465	0.578	0.646	0.703	0.884	0.531
X202	0.14399	0.535	0.621	0.674	0.722	0.892	0.531
X203	0.14449	0.518	0.624	0.682	0.729	0.898	0.418
X204	0.17636	0.567	0.655	0.704	0.745	0.906	0.399
X301	0.04148	0.287	0.464	0.564	0.640	0.861	0.464
X302	0.35107	0.723	0.776	0.804	0.831	0.936	0.467
X303	0.27806	0.654	0.731	0.774	0.810	0.928	0.338
X304	0.28206	0.740	0.732	0.746	0.767	0.910	0.679
X401	0.00986	0.153	0.270	0.473	0.598	0.844	0.313
X402	0.02910	0.221	0.424	0.557	0.644	0.865	0.336
X403	0.19870	0.608	0.678	0.713	0.746	0.907	0.346

ID	overall penetration
X501	0.09392
X502	0.03248
X503	0.00406
X504	0.00194
X505	0.00151
X506	0.00138
X507	0.14343
X508	0.06869
X509	0.01665
X510	0.00265
X511	0.00138
X512	0.00111
X513	0.00106

3.3 THEORY

3.3.1 Approach Model

It is useful to consider performance at any given point in the absorber by breaking it down in the form of equation 3-1.

$$\text{normalized performance} = \text{relative enhancement} \times \text{equilibrium effect} \quad (3\text{-}1)$$

Normalized performance is the fraction of the gas-film mass transfer capability which is being utilized. Relative enhancement is given by K_G/k_g, which is related to ϕ, the overall enhancement factor, by:

$$\frac{K_G}{k_g} = \frac{1}{1+\dfrac{m}{\phi\, k_l^o \big/ k_g}} \qquad (3\text{-}2)$$

where m is the Henry's constant for SO_2.

The enhancement factor is the ratio of the actual SO_2 absorption to the physical SO_2 absorption. The equilibrium effect is given by the ratio of Δy, the difference between the actual gas concentration of SO_2 and the gas concentration in equilibrium with the solution, to y, the actual gas concentration.

Similarly, over an entire absorber or a section of an absorber, it is possible to represent normalized performance as the product of the enhancement term (approach to the gas film limit) and a term which represents the liquid-phase resistance, as follows:

$$\frac{-\ln(\text{penetration})}{N_g} = \frac{K_G}{k_g} \times (\text{equilibrium term}) \qquad (3\text{-}3)$$

In the above, -ln(penetration) can be written as $\ln(y_1/y_2)$, where y_1 represents inlet gas SO_2 concentration, and y_2 represents outlet gas SO_2 concentration. Also, we know that $K_G/k_g=N_G/N_g$, and

$$N_G = \frac{y_1 - y_2}{\log \text{mean} \Delta y} = \frac{y_1 - y_2}{\left(\dfrac{\Delta y_1 - \Delta y_2}{\ln(\Delta y_1 / \Delta y_2)}\right)} \qquad (3\text{-}4)$$

where Δy represents the driving force, y-y*, where y* is the gas concentration which would be in equilibrium with the liquid. Filling these terms into equation 3-11 provides a value for the equilibrium term:

$$\frac{\ln(y_1 / y_2)}{N_g} = \frac{y_1 - y_2}{N_g \left(\dfrac{\Delta y_1 - \Delta y_2}{\ln(\Delta y_1 / \Delta y_2)}\right)} \times \frac{\left(\dfrac{\Delta y_1 - \Delta y_2}{\ln(\Delta y_1 / \Delta y_2)}\right)}{\left(\dfrac{y_1 - y_2}{\ln(y_1 / y_2)}\right)} \qquad (3\text{-}5)$$

Thus, the equilibrium term is (log mean Δy)/(log mean y), the log mean driving force divided by the log mean concentration. This term is 1 when y* is 0, that is, in the absence of any equilibrium limitation from the liquid. If this term is 0, y = y* and the liquid is completely in equilibrium with the gas. Thus, this term is called the approach to the non-equilibrium limit.

The three terms here represent the three most important effects on penetration. The gas-film mass transfer limit is represented by N_g, used as the normalizing factor in the penetration term. The overall enhancement factor is related to the approach to the gas-film limit. The solution capacity limit is represented by the approach to the non-equilibrium limit.

3.3.2 Enhancement Factors

As an aid in understanding the reactions associated with SO_2 removal and understanding the relative rates of SO_2 removal over the height of a spray tower, enhancement factors are defined as the ratio of the extent of a given reaction to the extent of physical absorption of SO_2 at any given point in the absorber, by the expression (for any species X):

$$\phi_X = r\sqrt{\frac{D_x}{D_{SO_2}}}\left(\frac{[X]_b - [X]_i}{[SO_2]_i - [SO_2]_b}\right) \tag{3-6}$$

Here, r represents a stoichiometric coefficient, and is 1 except for $Ad^=$ where it is 2.

Enhancement factors are calculated by FGDTX for the species H^+, $SO_3^=$, HCO_3^-, $SO_4^=$, $Ad^=$, and HAd^-, and these correspond to the following reactions:

H^+ $$SO_2 + H_2O \Leftrightarrow HSO_3^- + H^+ \tag{3-7}$$

$SO_3^=$ $$SO_3^= + SO_2 + H_2O \Leftrightarrow 2H_2SO_3^- \tag{3-8}$$

HCO_3^- $$HCO_3^- + SO_2 \Leftrightarrow HSO_3^- + CO_2 \tag{3-9}$$

$SO_4^=$ $$\left\langle \begin{array}{l} \frac{1}{2}O_2 + SO_4^= + SO_2 + H_2O \rightarrow 2HSO_4^- \\ SO_4^= + SO_2 + H_2O \Leftrightarrow HSO_3^- + HSO_4^- \end{array} \right. \tag{3-10}$$

$Ad^=$ $$Ad^= + SO_2 + H_2O \Leftrightarrow HSO_3^- + HAd^- \tag{3-11}$$

HAd^- $$HAd^- + SO_2 + H_2O \Leftrightarrow HSO_3^- + H_2Ad \tag{3-12}$$

Total enhancement, or the ratio of the total SO_2 removal to the physical absorption, is then 1 plus the sum of the other enhancement factors.

The $SO_4^=$ enhancement factor is used to represent the oxidation reaction combined with a sulfate/bisulfate equilibrium. The oxidation reaction occurs to the extent that available oxygen allows.

3.3.3 Variation Within a Spray Section and Between Spray Sections

Enhancement factors were calculated at the top (just after fresh spray is added) and bottom of each section for the base case. In addition, the SO_2 concentration and the relative enhancement and equilibrium effect terms from the approach model are given here. Table 3-9 gives data at the top of each section, just below the spray headers, while Table 3-10 gives data at the bottom of each section, just above the spray headers for the next section.

Table 3-9: Enhancement factors at top of each section for case A322

	Top	2	3	4	Bottom
HCO_3^-	54.86	0.52	0.05	0.02	0.01
$SO_3^=$	5.47	0.39	0.04	0.02	0.01
$SO_4^=$	-6.83	0.12	0.27	0.33	0.21
H^+	11.50	6.59	4.51	3.49	2.61
Total	65.99	8.63	5.87	4.86	3.83
SO_2 (ppm)	262	499	803	1190	1640
K_g/k_g	0.841	0.410	0.321	0.281	0.235
$\Delta y/y$	1.000	0.984	0.914	0.892	0.766

Table 3-10: Enhancement factors at bottom of each section for case A322

	Top	2	3	4	Bottom
HCO_3^-	0.01	0.01	0.01	0.01	0.01
$SO_3^=$	0.01	0.01	0.01	0.01	0.01
$SO_4^=$	-2.51	-0.39	0.06	0.21	0.27
H^+	5.58	3.75	3.04	2.61	2.45
Total	4.10	4.38	4.12	3.83	3.74
SO_2 (ppm)	499	803	1190	1640	1830
K_g/k_g	0.248	0.260	0.249	0.235	0.231
$\Delta y/y$	0.353	0.579	0.694	0.766	0.831

Note that the total enhancement factor shown is one plus the sum of all the other enhancement factors. The one represents physical absorption, which all the others are relative to. Also, in some of the cases, the sulfate enhancement factor is negative. The sulfate-bisulfate reaction is a buffer in this system, proceeding in either direction depending on the composition of the solution.

The results generated appear to indicate two trends: (1) the SO_2 removal is enhanced by chemical reactions in the top spray level much more than it is in the ones below it, and (2) by the bottom of each section, including the top section, the effect of the fresh spray is largely lost, leaving a total enhancement of about 4, most of which can be attributed to the hydrolysis reaction. Trend (1) in the top-of-section results is exaggerated in these results by FGDTX's mixing assumption. Consider, though, that half the liquid at level 2 is fresh, and the rest of it was just achieving the enhancement factors shown for the bottom of the first section before new slurry was added. Clearly, there is a real trend here in addition to the one induced by the mixing assumption in FGDTX.

Enhancement from hydrolysis is also greatest at the top of the absorber. The H^+ concentration at the gas/liquid interface is driven by equilibrium. In the absence of accumulated HSO_3^-, the enhancement from the hydrolysis varies inversely as the square root of the SO_2 concentration:

$$\phi = 1 + \frac{k\sqrt{[SO_2]_i}}{[SO_2]_i} \tag{3-13}$$

Therefore, greater enhancement is evident at the top of the absorber and at the top of each section.

At lower sections of the absorber, the HCO_3^- and $SO_3^=$ alkalinity is insignificant. This alkalinity is depleted by rich solution mixed in from above and by pickup of SO_2 at higher SO_2 concentrations typical of the lower sections.

The relative enhancement term is low in these cases, less than 0.3 except at the tops of the first three sections. The equilibrium term $\Delta y/y$ varies from 0.35 to 1, being irrelevant at the top of the first section where the slurry is all fresh, but being very significant at the bottom of that section, and varying less strongly on each lower section. Equilibrium is not a significant factor at any of the points where fresh slurry is fed, with $\Delta y/y$ being 0.892 at the top of the fourth section, but always matters at the bottoms of the sections. The approach to the gas-film limit, K_G/k_g, varies monotonically with the total enhancement factor, as the two terms are related by equation 3-2.

3.3.4 Application of Approach Model to Data from FGDTX

In Figure 3-1, performance is plotted against averaged SO_2 concentration for the four cases from Figure 3-1 along with two additional cases where limestone utilization is varied at 1000 ppm SO_2 (cases X401, X403). The data for the SO_2 concentration is plotted as a weighted geometric mean of the inlet and outlet concentrations, equivalent to $y_{in}\times penetration^{0.2}$. The 0.2 exponent was determined by trial and error; exponents of 0.1 and 0.3 did not fit the data as well. The data for different inlet SO_2 levels at the same utilization collapses to something close to a single curve, but the data for different limestone utilizations deviates from the trend.

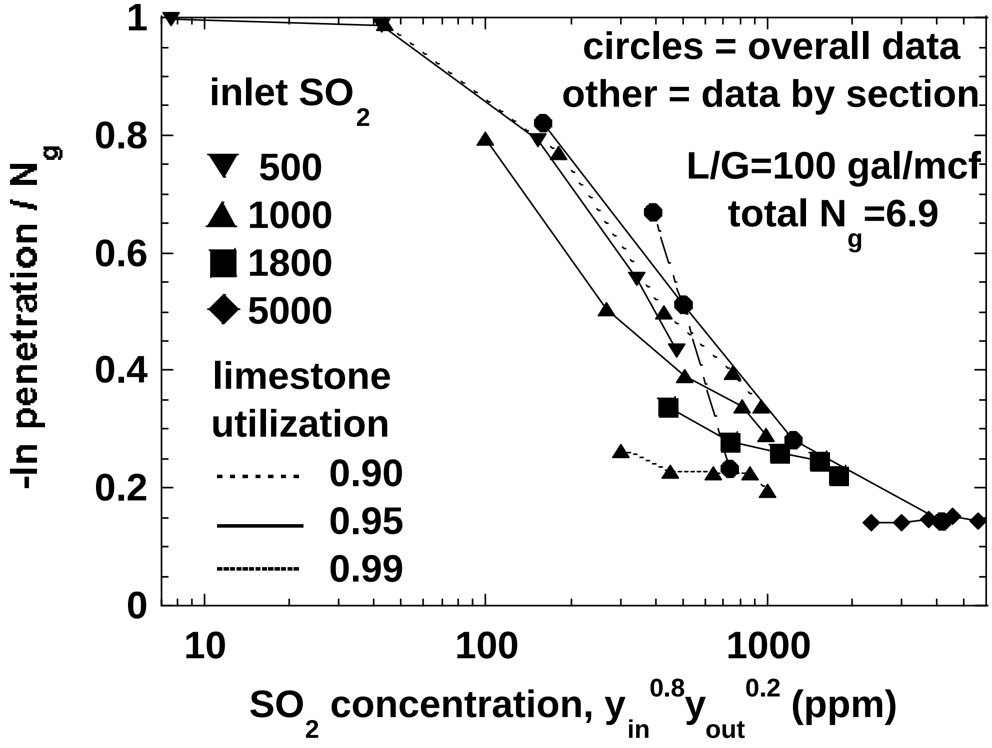

Figure 3-1: The effects of averaged SO_2 concentration and limestone utilization on normalized performance (cases A312-A332 and X401-X403)

In Figure 3-2, the approach to the gas film limit, K_G/k_g, is plotted against the same averaged inlet gas term for the same cases. Here, the data collapses much better.

The overall enhancement factor, ϕ is related to the approach to the gas-film limit by the following expression, where m is the Henry's constant for SO_2, which the models in BMREP calculate at 2.488 l/gmol at the conditions of these cases:

$$\phi = \frac{m}{\left(k_l^o / k_g\right)\left(\frac{1}{K_G / k_g} - 1\right)} \tag{3-14}$$

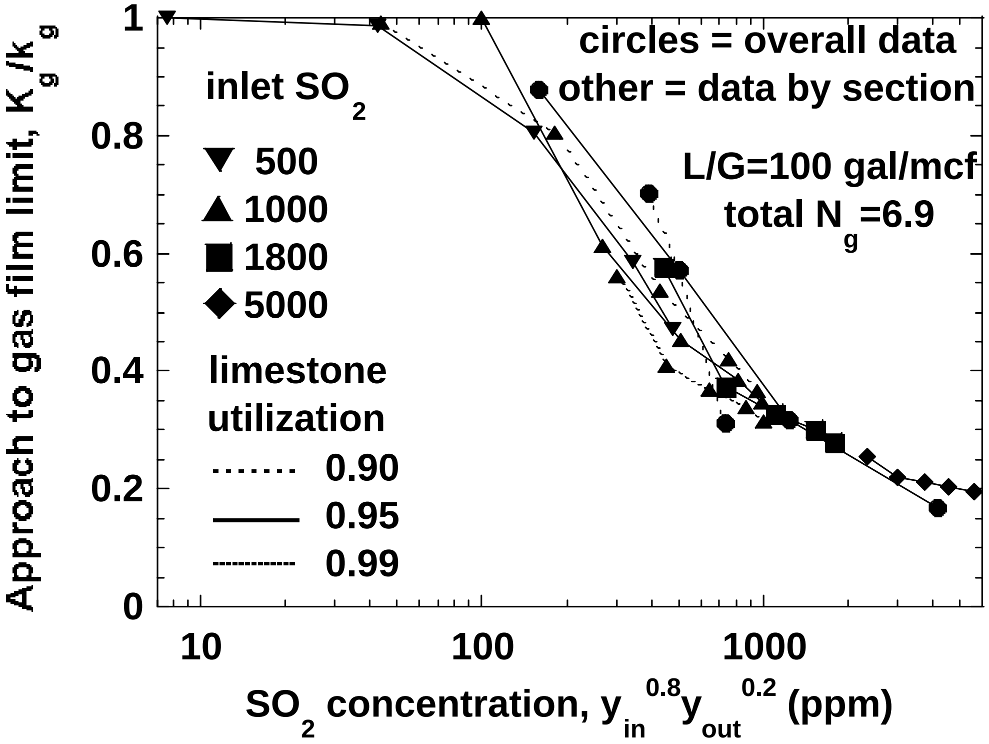

Figure 3-2: The effects of averaged SO_2 concentration and limestone

utilization on the approach to the gas-film limit (cases A312-A332 and X401-X403)

In Figure 3-3 the overall enhancement factor is plotted against averaged SO_2 concentration, with the last four points omitted where K_G/k_g approaches 1 very closely and the enhancement factor becomes very large. In addition, the enhancement factor point data from section 3.3 are plotted as open squares. The point data and section averages are different quantities, so they do not line up perfectly, just as the overall averages do not line up with the section averages, but the data fall more or less along the same trend.

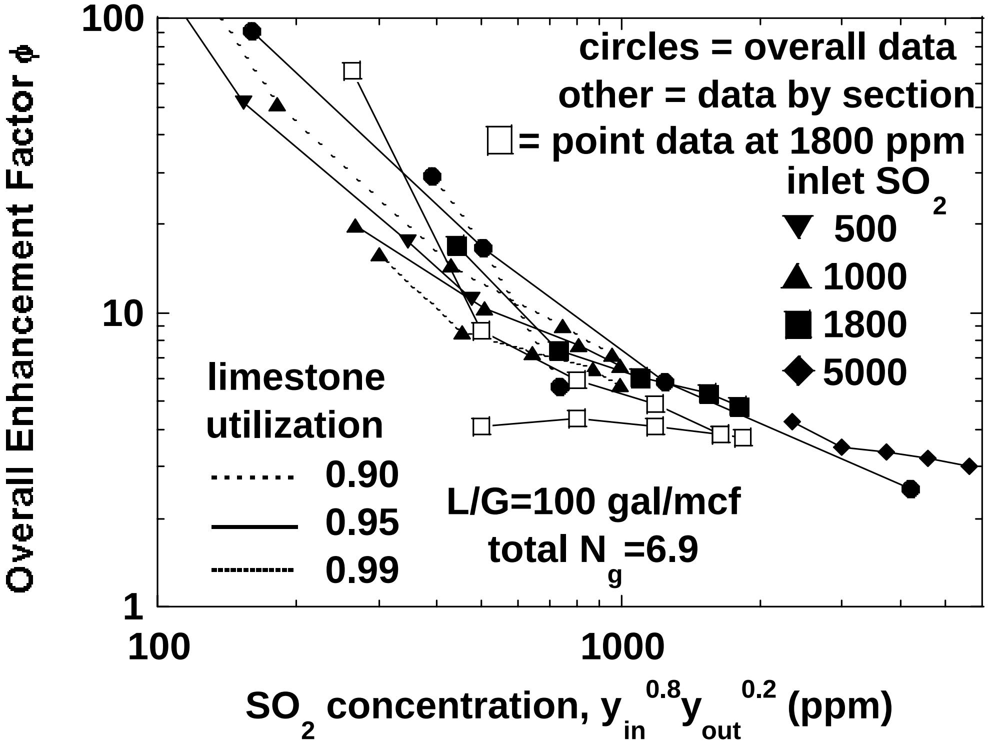

Figure 3-3: The effects of averaged SO_2 concentration and limestone

utilization on the overall enhancement factor ϕ (cases A312-A332 and X401-X403, and the point data from Tables 3-9 and 3-10 for case A322)

In Figure 3-4, the approach to the non-equilibrium limit is shown. This represents the effect of equilibrium limitations on the system, but since the value 1.0 represents no effect of equilibrium, it is called the approach to the non-equilibrium limit. In the data at constant inlet SO_2 rate but variable utilization, as expected, performance improves as utilization is reduced, or, therefore, as more excess limestone is present. The other trends in this data are discussed in section 3.5.1.

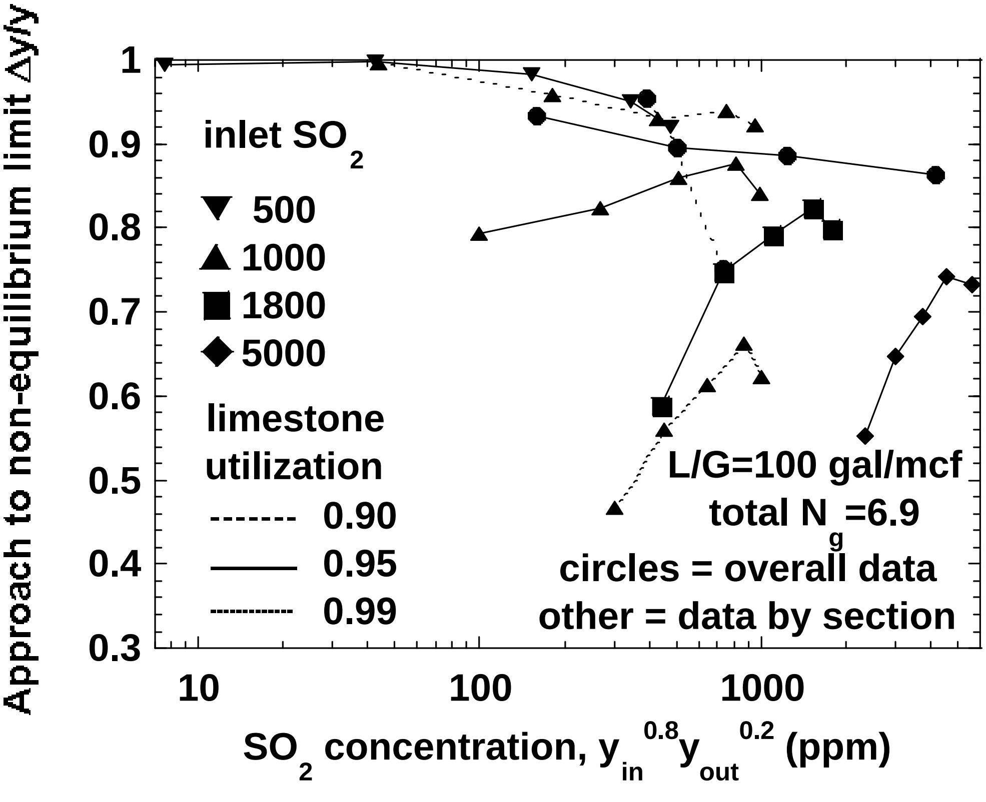

Figure 3-4: The effects of averaged SO_2 concentration and limestone

utilization on the approach to the non-equilibrium limit, Δy/y, the average total driving force over the average gas SO_2 concentration (cases A312-A332 and X401-X403)

The importance of liquid equilibrium effects is one of the differences between spray scrubbers and turbulent contact absorbers. In the TCA, even at 5000 ppm of SO_2, the equilibrium effects are minor. In the 5000 ppm inlet SO_2 case of Agarwal (1995), at the bottom section, the approach to the non-equilibrium limit is 0.84. The top section and other cases with less SO_2 are closer than this to the non-equilibrium limit. The top section does not have the increased equilibrium effect in these systems because all the liquid is fed at the top, so all sections see the full liquid rate. Furthermore, the increased residence time of the slurry in the absorber and the greater excess limestone of those runs raises the absorber pH to over 4 even in the most extreme case, compared with around 3 in the high SO_2 spray scrubber cases.

3.3.5 Series Resistances Model

This model was an attempt to produce a simple approximate model to represent the complex effects seen in limestone slurry scrubbing systems. The idea is to write a model in the "series resistances" form of film theory, which gives us:

$$N_G \approx \frac{y_{in} - y_{out}}{\bar{y}} = -\ln(\text{penetration}) \tag{3-15}$$

Then, N_G is related to the number of transfer units in each phase by:

$$\frac{1}{N_G} = \frac{1}{N_g} + \frac{m}{N_l} \tag{3-16}$$

For this model, the liquid phase term is replaced by some relationship of other scrubber parameters:

$$\frac{1}{N_G} = \frac{1}{N_g} + \frac{1}{f(\text{liquid composition})} \tag{3-17}$$

To determine f, the data from the factorial runs was used, dropping those cases which did not converge, and cases with such low penetration that loss of precision could become important. Also, cases with penetration higher than 0.2 seemed to deviate from the trend observed over the typical range of scrubber operation, so these cases were also dropped. Finally, the remaining data was regressed against a number of parameters, in a number of different forms. The chosen form was:

$$\ln(f) = A + B\ln\beta + C\ln\chi + D\ln\delta + \ldots \tag{3-18}$$

where A is a constant term, and the B, C, D, etc. are coefficients of the β, χ, δ, etc., which are some form of the key variables of the system. This form was chosen because it fit the data best out of forms which were linearizable and thus able to be regressed on a least-squares basis, and because it provides an order of the effect of each variable on performance. Many variables and different forms of some of the variables were tested. Some parameters which had little effect on the correlation, or which were highly interdependent with others were removed. The result was a correlation with five parameters in addition to the constant term, which are given in Table 3-11.

The 1-utilization term represents the amount of excess limestone in the system in a dimensionless form. The L/G term includes the amount of SO_2 removed; this is a form of make per pass. The term with SO_2 concentration alone is a form of averaged SO_2 concentration; exponents from 0.1 to 0.4 were tested for the penetration and 0.25 gave the best fit, on a visual basis. The hold tank size is the parameter defined for the factorial runs.

Table 3-11: Series resistances model parameters

parameter	coefficient
constant term	4.621
1-utilization	0.620
N_g	1.550
$\frac{L / G}{SO_{2,in} - SO_{2,out}}$	1.217
$SO_{2,in} \times penetration^{0.25}$	-0.243
hold tank size	0.163

This model looks superficially good in a parity plot, but the presence of penetration in the make per pass and SO_2 concentration terms makes the model not particularly useful for prediction. It does, however, follow a distinct trend in the data, and is useful for understanding the order of each effect on the system. The N_g would be expected to have only a first-order effect, as it is the limit of -ln(penetration). The higher order is most likely due to lower SO_2 concentration at high N_g, which improves performance further.

3.4 FRACTION OF LIMESTONE DISSOLVED IN ABSORBER

The fraction of limestone dissolved in the absorber indicates how the scrubber is performing. The system runs optimally when this parameter has a value of about 0.5, corresponding to the stoichiometry:

$$CaCO_3 + 2SO_2 + H_2O \rightarrow Ca^{++} + 2HSO_3^- + CO_2 \qquad (3\text{-}19)$$

If less limestone is being dissolved in the absorber, the system is not dissolving as much limestone in the absorber as possible, and thus is removing less SO_2 than it could otherwise. If more limestone is being dissolved in the absorber, crystallization problems are likely. Over the entire set of runs, the fraction of limestone dissolved in the absorber varies from less than 0.1 to more than 0.9.

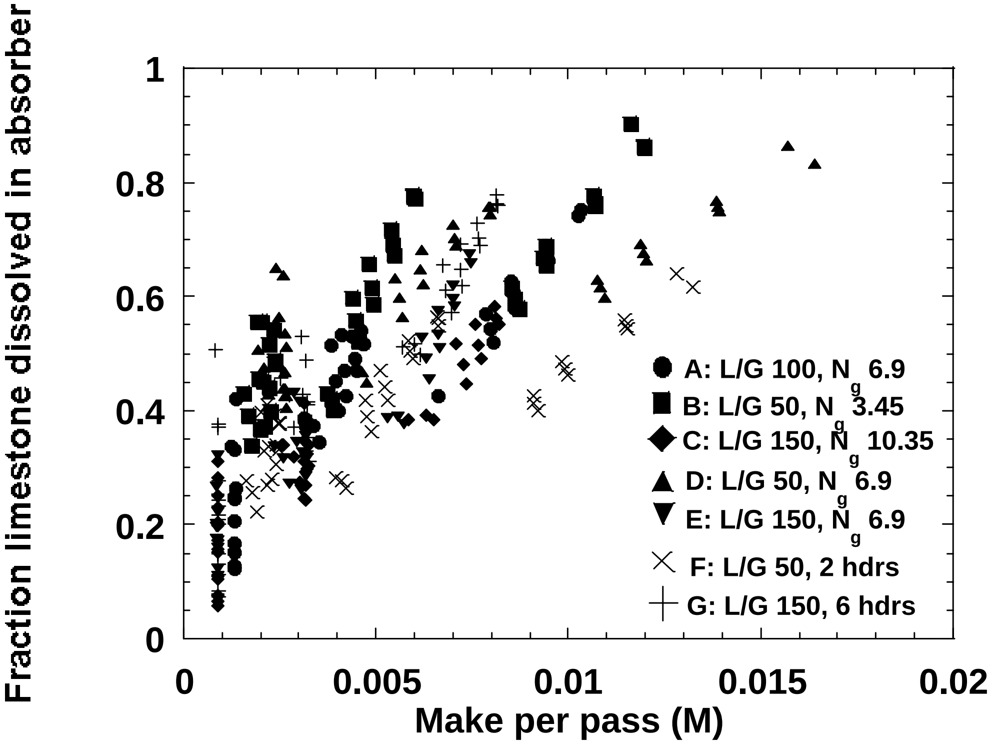

Figure 3-5: The effect of make per pass on the fraction of limestone dissolved in the absorber. All the factorial runs from Table 3-6 are shown here.

The fraction of limestone dissolved in the absorber varies most strongly with a parameter called make per pass, which is a ratio of the amount of SO_2 removed to the liquid-to-gas ratio. The dependence is shown in Figure 3-5, and details for specific cases are in Figure 3-6. Notice the trend with the inlet concentration of SO_2 in the first 9 cases in Table 3-6. Cases A111-A113 all have about 0.25 of the limestone dissolving in the absorber, cases A121-A123 have about 0.52, and cases A131-A133 have about 0.74. The second digit in these case names represents the inlet SO_2 concentration. Also notice that the hold tank size, represented by the final digit, does not matter much in these runs, at the lowest limestone utilization.

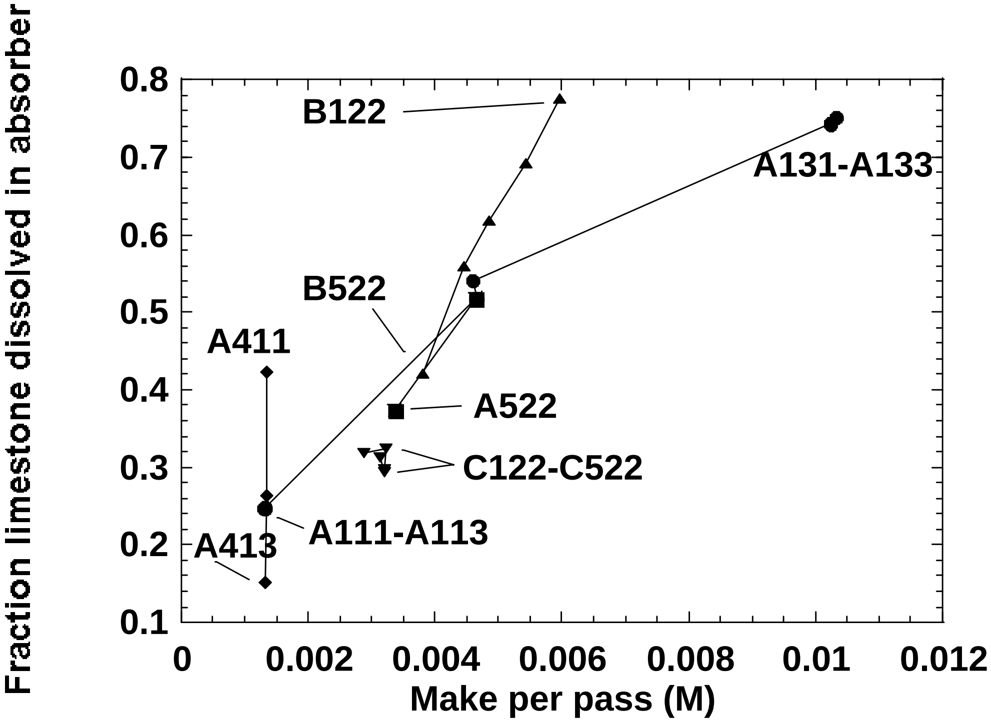

Figure 3-6: Effects of other parameters on the fraction limestone dissolved in absorber. A111-A131: varying inlet SO_2 concentration. B122-B522: varying limestone utilization at high L/G. C122-C522: varying limestone utilization at low L/G. A131-A133: varying hold tank size at low limestone utilization. A411-A413: varying hold tank size at high utilization and low SO_2.

As limestone utilization is increased, the fraction of limestone dissolved in the absorber decreases slightly, from 0.52 at case A122 to 0.37 for case A522. This is due to the change in the amount of SO_2 removed, which drops from 95% to 69% (of 1800 ppm inlet) over this range. In the B cases, where lower L/G results in both less SO_2 removed (62% for case B122) and more change (on a relative basis) in the amount of SO_2 removed as limestone utilization varies (39% for case B522), the change in the fraction of limestone dissolved in the absorber is stronger, from 0.78 to 0.42. In the C cases, where higher L/G results in more SO_2 removed (over 99% at case C122 to 88% at case C522), the fraction of limestone dissolved in the absorber is almost uniform over cases C122-C522, around 0.31.

The B and D runs, with low L/G, have high fractions of limestone dissolved in the absorber, all but a few higher than 0.5, and similarly the high-L/G C and E runs have low fractions of limestone dissolved in the absorber, almost all less than 0.5. The F and G runs, where the number of spray sections was varied in addition to the L/G, do not show this trend. Instead, they look more like the A runs where SO_2 is the dominant factor. The change in liquid holdup in the absorber is responsible for this effect. In the F runs, the reduced liquid holdup allows less time for limestone to dissolve than in the B or D runs, and in the G runs, the extra liquid holdup allows for more limestone to dissolve.

The hold tank size does have an effect in cases where there is high limestone utilization and low SO_2. In cases A411-A413 this is observed, as the fraction of limestone dissolved in the absorber drops from 0.42 in the small hold tank of case A411 to 0.15 in the large hold tank of case A413. This is due to the presence of plenty of removal capacity and not nearly enough SO_2 to remove; the system is capable of running without dissolving much limestone in the absorber, so it dissolves in the hold tank to a degree varying with the size of the hold tank.

3.5 EFFECTS OF PARAMETERS ON SO_2 PENETRATION

3.5.1 Inlet SO_2 Concentration

3.5.1.1 Effects Seen in Other Literature

The effect of SO_2 concentration on the performance of scrubbers, in terms of SO_2 removal, has not been studied in as much depth as might be expected for such a key parameter. Often, a single scrubber does not see enough variation in inlet SO_2 concentration to result in meaningful correlations. Different scrubbers may differ in ways not indicated in the published data, thus making correlations of data from different scrubbers suspect. One such correlation (Head, 1977) gives the following relation for penetration and inlet SO_2 concentration:

$$-\ln(\text{penetration}) = 2.8e^{-1.73\times10^{-4}(SO_{2,in}(\text{ppm}))} \tag{3-20}$$

This correlation is based on data for four inlet SO_2 values for an EPA turbulent contact absorber (Borgwardt, 1973) and three inlet SO_2 values for a TVA spray tower (Potts, et al., 1971). The two sets of data do not agree very well, so this curve is a bit of a compromise between the two. Head later suggests the coefficient 2.8 can be replaced by an adjustable factor to model specific scrubbers.

3.5.1.2 Effects Seen in Our Model

In Figure 3-7, data for normalized penetration from 4 different simulations (cases A312, A322, A332, and X402) are plotted against an averaged SO_2 inlet concentration, of the form $y_{in}^{0.8}y_{out}^{0.2}$. The curves for the individual simulations consist of the data for each of the five sections of the absorber. Data computed for the absorbers as a whole also appear, represented by circles.

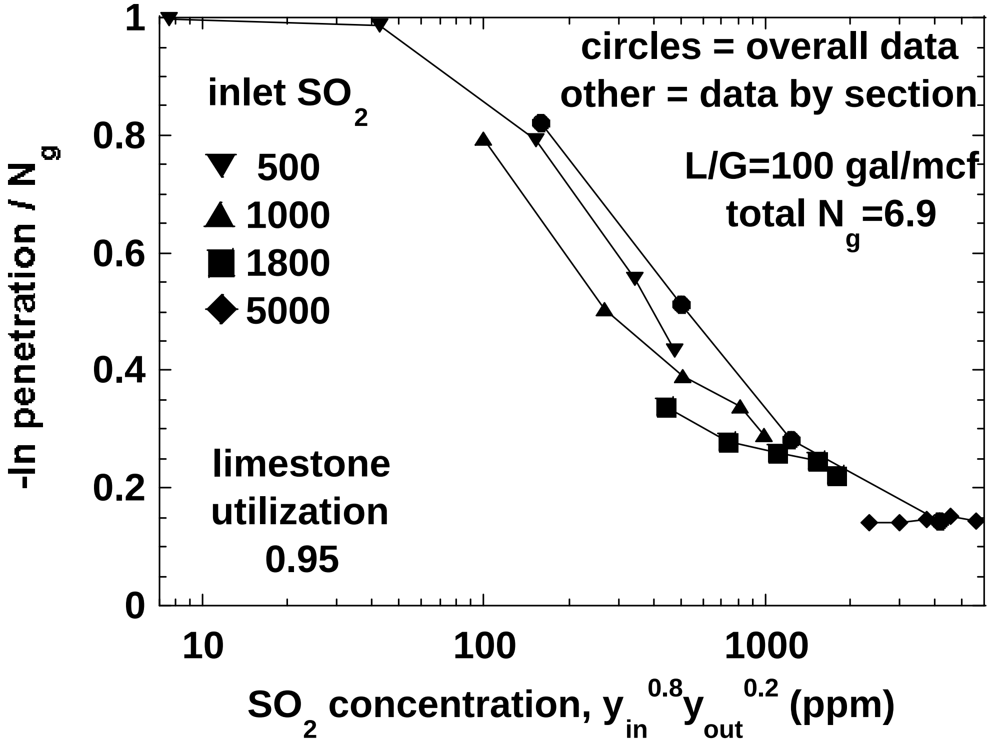

Figure 3-7: The effect of SO_2 concentration on performance, within a scrubber and at different inlet SO_2 conditions (cases A312, A322, A332, and X402)

The quite evident trend here is that performance improves at lower SO_2 concentrations. With all else equal, at a lower inlet SO_2 concentration a greater fraction of the SO_2 will be removed.

3.5.1.3 Previous Interpretations

In Figure 3-8, the 4 overall runs from Figure 3-6 are plotted along with the curve from the EPA/TVA scrubber correlation over the range of the data used to determine it.

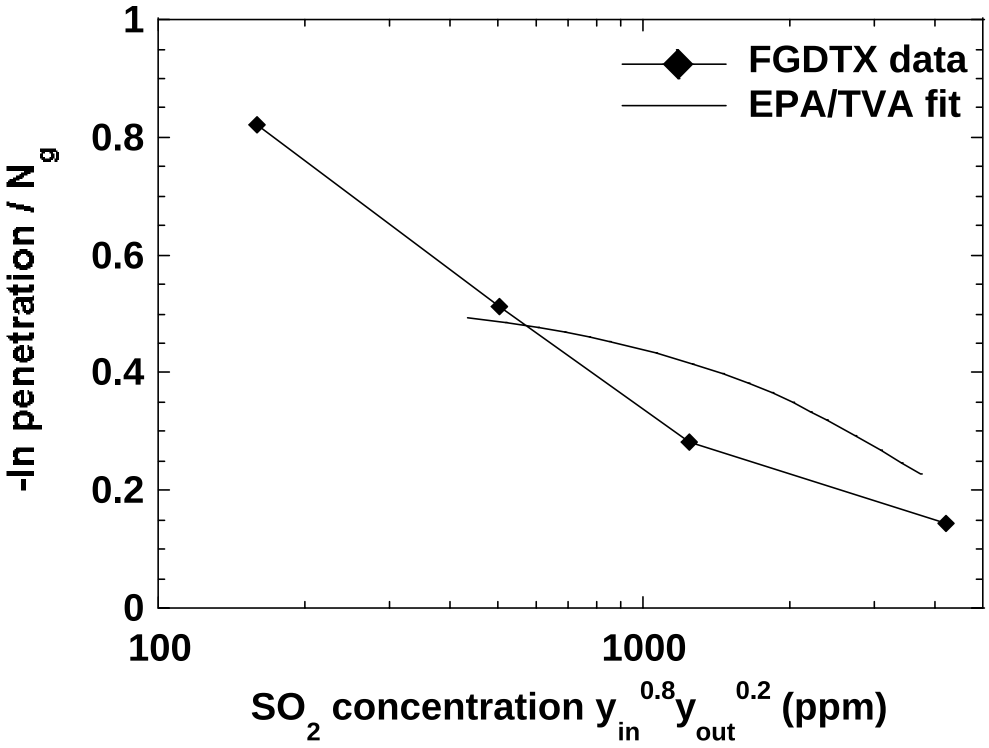

Figure 3-8: Shawnee EPA/TVA correlation compared to FGDTX data (cases A312, A322, A332, and X402)

The N_g for the EPA and TVA scrubbers is unknown, so 5.2 has been assumed to allow the data to be compared; this is equivalent to adjusting the coefficient 2.8 in this correlation. Given the uncertainty in the data used to construct this fit, the FGDTX data is in agreement.

3.5.1.4 Understanding

In the approach model, the performance term -ln(penetration)/N_g is split into two factors, the approach to the gas film limit and the approach to the non-equilibrium limit. The approach to the non-equilibrium limit is the ratio of the log mean (y-y*) to the log mean y, where y is the gas phase concentration of SO_2, and y* is the gas concentration of SO_2 that would be in equilibrium with the actual liquid concentration. The approach to the gas film limit is the primary trend in the data in Figure 3-7, and the approach to the non-equilibrium limit, plotted in Figure 3-9, represents most of the variation in the data.

The overall trend seen here is for equilibrium to become more important when more SO_2 enters, but within each set of data (except the 500 ppm data) the effect of equilibrium becomes more pronounced at the top of the column, where the SO_2 concentration is lowest. This is a result of the reduced liquid rate at the top of the column, where only one-fourth of the total liquid has entered, and thus the capacity of the solution is much less. Much less SO_2 is required to be absorbed for equilibrium effects to become important in the top section. As less SO_2 is fed into the absorber, both the overall magnitude of the equilibrium effect and the change from the bottom to the top of the absorber diminish, as there is simply less SO_2 present to cause the equilibrium effect.

In some of the runs, it is quite evident that the trend within the absorber is reversed for the bottom section. Remember that this section is only a modeling concept; it does not have any fresh spray. Because of this, it has the same liquid rate as the section above it, and, unavoidably, more SO_2 in solution, so the reversal of the trend is expected.

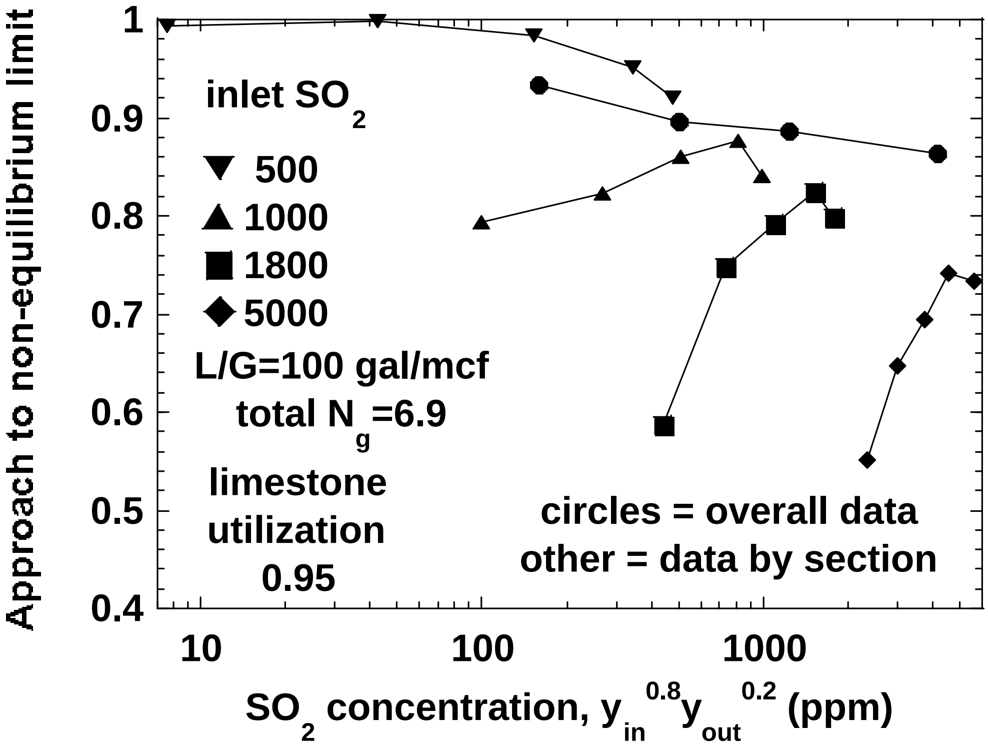

Figure 3-9: Effect of SO_2 concentration on the approach to the non-equilibrium limit (cases A312, A322, A332, and X402)

3.5.2 Liquid-to-Gas Ratio and Number of Transfer Units

3.5.2.1 Effects Seen in Other Literature

Head (1977) summarized the results of running spray tower limestone systems at Shawnee Power Plant by the following expression:

$$
\begin{aligned}
-\ln(\text{penetration}) = 9.8\text{x}10^{-5}\left(\frac{L}{G}\right)^{0.92} v^{0.19} \times \\
\exp(\text{pH}_i + 1.35\text{x}10^{-4}\,\text{Mg}_e - 1.7\text{x}10^{-4}\,\text{SO}_{2,i} + 1.45\text{x}10^{-5}\,\text{Cl})
\end{aligned}
\tag{3-21}
$$

In this expression, L/G is the liquid-to-gas ratio in gal/Mcf, v is the gas velocity in ft/sec, pH_i is the hold tank (or scrubber slurry inlet) pH, Mg_e is the Mg^{++} concentration in ppm, adjusted by a term which accounts for MgCl_2 formation, $\text{SO}_{2,i}$ is the inlet SO_2 gas concentration in ppm, and Cl is the solution Cl^- concentration in ppm. The L/G in the data included in this fit varied only from 25 to 95 gal/Mcf, so any extrapolation to higher L/G may be inaccurate. Table 3-12 compares this model to FGDTX over a range of L/G values at the base case, and Figure 3-9 compares the Head data for the base case to FGDTX data at several conditions.

Table 3-12: Comparison of FGDTX to Head's (1977) model for prediction of SO_2 penetration. In Head's model, L/G of 50-150 gal/Mcf, gas velocity of 10 ft/s, pH of 6.01, zero Mg, and a Cl^- concentration of 3550 ppm were used.

Case	L/G (gal/Mcf)	FGDTX penetration	Head model penetration
B322	50	0.499	0.173
A322	100	0.143	0.0363
C322	150	0.0017	0.0081

3.5.2.2 Effects Seen in Our Model

In practice, N_g varies with L/G, so it is difficult to distinguish the effects of the two parameters. With the FGDTX model, this separation of effects can be performed, by varying the input values of L/G and N_g separately.

In Figure 3-10, penetration is plotted against L/G for 9 cases run in FGDTX, for all combinations of three different values for N_g and three values for L/G, with the runs at the same N_g connected with lines. The values from the Head model do not agree well with the values predicted by FGDTX at the base case N_g or the N_g varying in proportion with L/G. However, ignoring the 150 L/G extrapolation, the Head model somewhat matches the FGDTX data at N_g of 10.35. The Head model does not contain an N_g parameter, since this is not an easily measured parameter, and uses only gas velocity and L/G to correlate with the N_g effect. Furthermore, Head's data do not vary gas velocity too much, and most of his runs (48 of 77) are at the gas velocity of 7.3 ft/s, with 24 at 9.3 ft/s and just 5 at 5.3 ft/s. Most of his variance of L/G is due to changing liquid rate, and most of that is due to shutting off some spray headers.

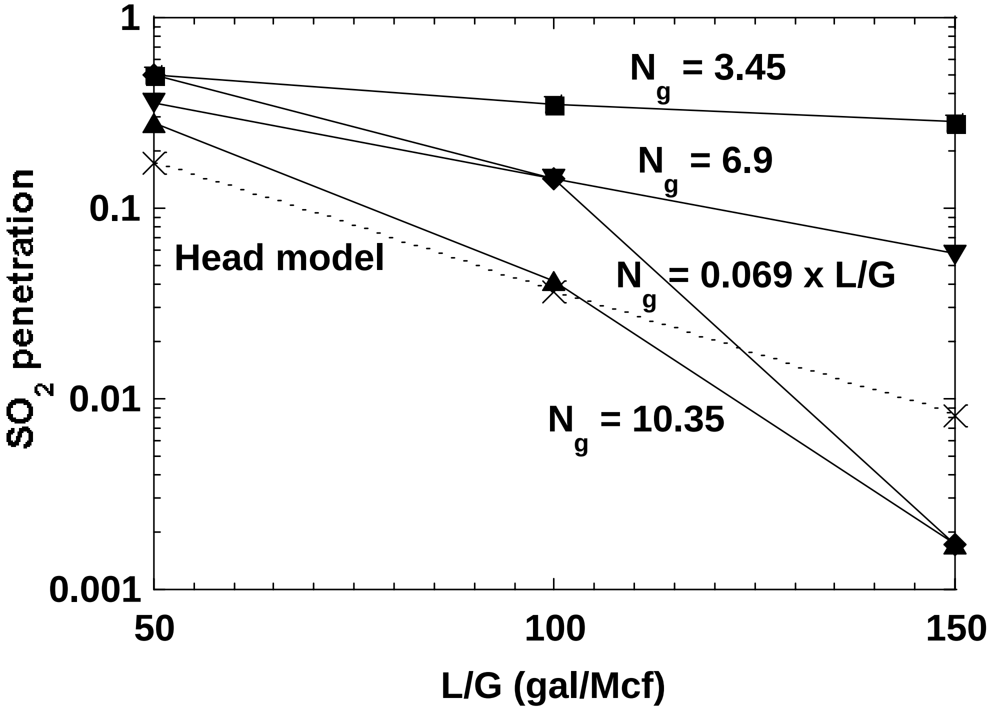

Figure 3-10: Effects of L/G and N_g on performance. Cases A322-E322 and X301-X304, at 0.95 limestone utilization and 1800 ppm SO_2 in, are shown. The predictions of the Head (1977) model are also shown. The Head model is correlated to data only up to L/G of 95 gal/Mcf, so the 150 gal/Mcf extrapolation is not expected to be reliable.

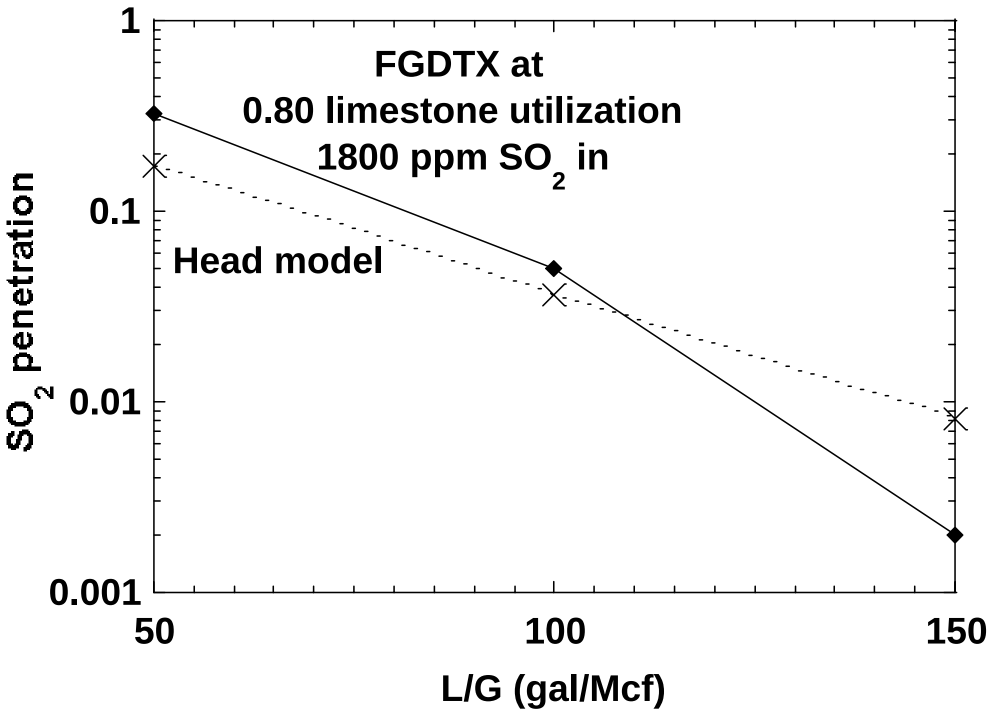

Figure 3-11: Effect of number of spray sections on performance. Cases A122, F122, and G122 from the factorial run of FGDTX are shown against the correlation from Head (1977).

Thus, a better comparison would be to compare Head's data to cases A322, F322, and G322, in which the number of spray headers is varied and the N_g varies less strongly with L/G. To use something which matches Head's level of performance more closely, compare cases A122, F122, and G122 at 80% utilization to Head's data, as in Figure 3-11. Again, Head's model does not predict the increased performance at L/G over 100 gal/Mcf, but the 50-100 gal/Mcf data match well. This also supports the reduction in number of mass transfer units for additional spray sections, as Head's data show the same diminishing efficiency as additional spray headers are added as has been modeled in FGDTX.

3.5.2.3 Understanding

Two trends are evident in the data from FGDTX. Performance improves with increasing N_g, as well as with increasing L/G. The fourth line which crosses the others represents N_g and L/G varying in proportion, and emphasizes the double effect of increasing L/G: an effect on solution capacity, and an effect on N_g, which both serve to improve performance.

3.5.3 Effects of Limestone Utilization on Performance

3.5.3.1 Effects Seen in Other Literature

Data from Bailly Power Station (Manavi et al., 1995), ABB (Klingspor and Bresowar, 1995), and the High Sulfur Test Center (Burke et al., 1990) for performance is plotted against limestone loading on a log-log plot in Figure 3-12. In some of these cases, we do not know the limestone particle size or reactivity, L/G, N_g, SO_2 concentrations, and possibly other relevant variables, so we cannot fit the data exactly.

3.5.3.2 Effects Seen in Our Model

Data from five values of limestone utilization and three inlet SO_2 levels from FGDTX are also shown in Figure 3-12, connected by lines. The same trend is observed.

3.5.3.3 Previous Interpretations

Through the scatter there is a clear trend in the data, which can be fit roughly with a line of the form

$$-\ln \text{penetration} = A(\text{loading})^B \tag{3-21}$$

where B has a value of about 0.3 to 0.4. Thus, limestone dissolution in the absorber is an important effect on scrubber performance.

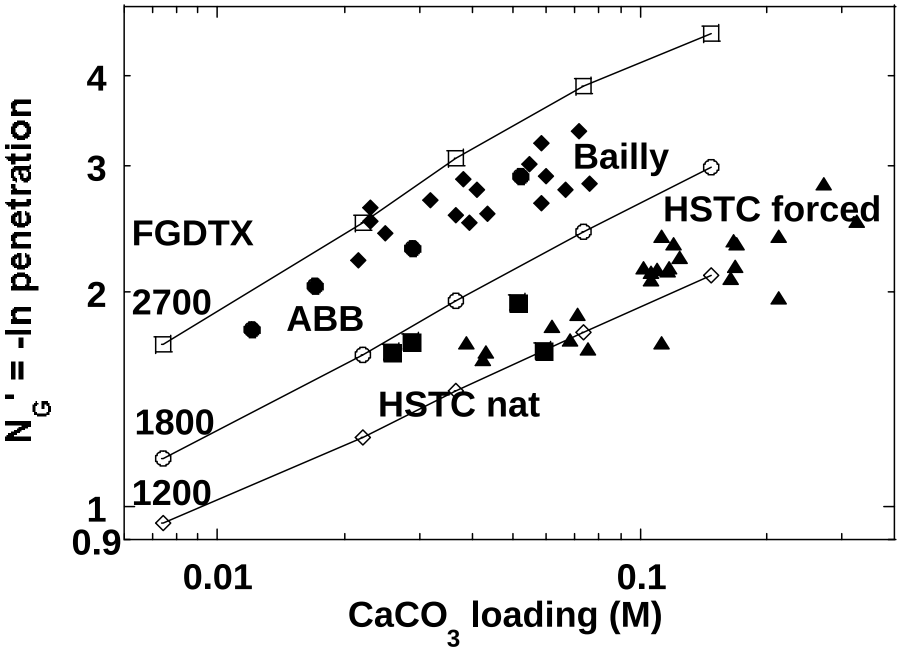

Figure 3-12: The effect of limestone loading on performance. The runs for the 1800 ppm level are factorial cases A122-A522; the other FGDTX runs are cases X101-X110. Other data from Bailly Power Station (Manavi et al., 1995), ABB (Klingspor and Bresowar, 1995), and the High Sulfur Test Center (Burke et al., 1990)

3.5.4 Effects of pH, Limestone Utilization, and Hold Tank Size

3.5.4.1 Effects Seen in Other Literature

The inlet slurry pH has often been used to model limestone slurry scrubbers. For instance, Head (1977) uses pH as a parameter in many correlations of the Shawnee data.

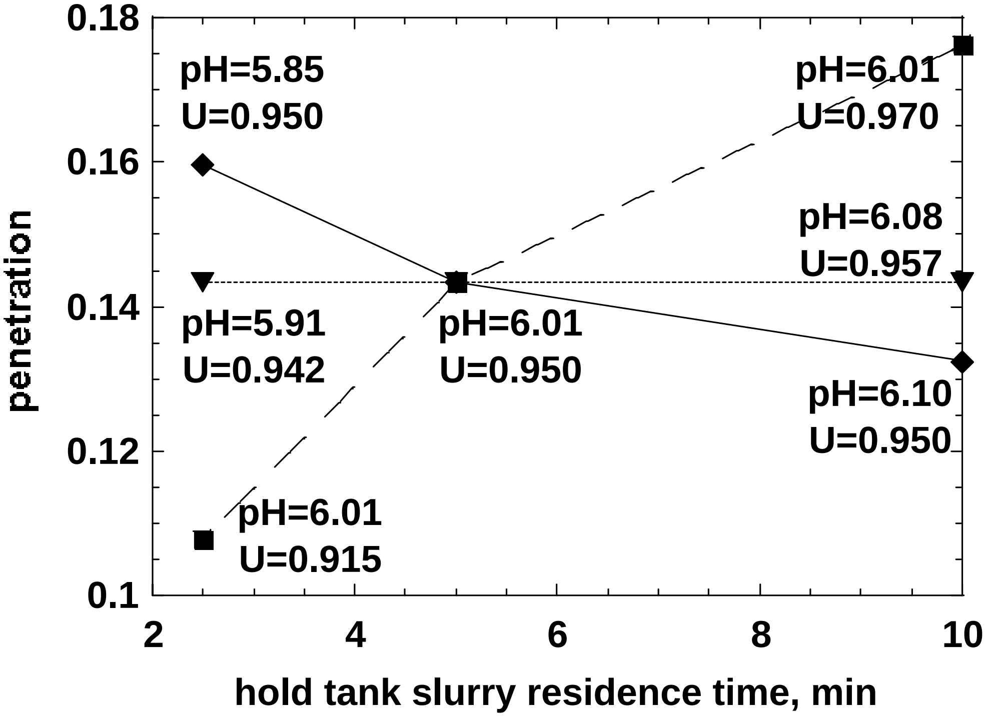

Figure 3-13: Effects of hold tank size and utilization on performance. Cases A321-A323 and X201-X204 are shown. The solid line represents constant utilization, the dashed line constant pH, and the dotted line constant penetration.

3.5.4.2 Effects Seen in Our Model

In Figure 3-13, penetration data from cases A321-A323 and X201-X204 are plotted against hold tank residence time. Limestone utilization and hold tank pH values are also given. This data represents 3 different ways to vary the hold tank size by a factor of 2 from the standard case A322. In one set, limestone utilization is held constant. In another set, pH is held constant. In the third set, penetration is held constant.

In these runs, hold tank N_L varies in proportion with the residence time, representing a constant hold tank diameter. We see that as pH is increased by increasing the size of the hold tank, performance improves, while if we increase limestone utilization so as to keep the same pH as hold tank size increases, performance is severely hindered. Thus the effect of utilization is seen to have much more effect on the scrubber's performance than pH; indeed, pH is merely a result of the limestone utilization and hold tank size. If we then try to maintain the same level of performance as the hold tank size increases, we see that pH increases and limestone utilization also increases, which means we use less limestone. Thus there is a tradeoff here between using a bigger hold tank or more limestone to achieve a desired level of performance.

3.5.4.3 Understanding

From this data, it is clear that pH is a poor predictor of slurry scrubber performance for scrubber design purposes. The pH is affected both by limestone utilization and the size of the hold tank, and these two parameters cause effects in opposite directions in the penetration for the same change in pH. It is also clear that a larger hold tank can give better system performance by enhancing limestone utilization and/or SO_2 penetration.

3.5.5 Slurry Additives (Dibasic Acid)

3.5.5.1 Effects Seen in Other Literature

In runs at the High Sulfur Test Center, Stevens et al. (1991) observed a gradual increase from a -ln(penetration) of 2 to 6 as the dibasic acid (DBA) concentration was increased from 0 to 2500 ppm. Unfortunately, they do not specify which dibasic acid they used, so the ppm data does not give the molar concentration of DBA, but assuming glutaric acid, 2500 ppm equals 18.9 mM; this should be correct within about 10%-20% error at most.

3.5.5.2 Effects Seen in Our Model

FGDTX predicts a different, much stronger effect of DBA, nearing asymptotic behavior due to the gas film mass-transfer limit with less than 10 mM of DBA.

Initially, the effect of DBA was modeled by simply adding DBA in various concentrations to the base case A322. This generated the curve "FGDTX base" in Figure 3-14. This indicates a much stronger effect of DBA than the experimental data suggests.

Attempts to adjust the FGDTX input parameters to produce an effect more like the experimental data failed. The only result seen is a shifting of the curve up, down, left, or right; it still retains essentially the same shape. The pH was adjusted to be constant at a value close to that in the experimental data by varying limestone utilization, the value of k_l^o/k_g was modified, the scrubber liquid residence time was adjusted, and the oxidation kinetic constant was adjusted; one such adjusted series of runs also appears in Figure 3-14.

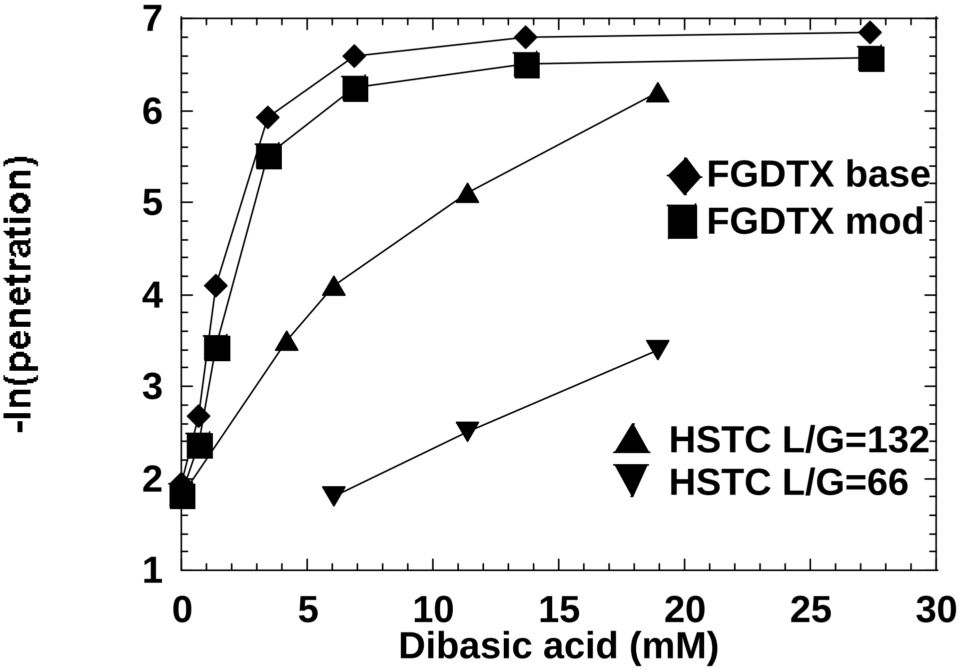

Figure 3-14: Effect of dibasic acid additives on penetration. High Sulfur Test Center data (Stevens et al., 1991) is at constant inlet slurry pH of 5.5. FGDTX base curve represents merely adding DBA to case A322 (other points are cases X501-X506). In the case "FGDTX mod," the oxidation kinetic constant was reduced by a factor of 2, pH was held fixed at 5.5-5.6 by varying limestone utilization, and scrubber liquid residence time was increased by a factor of 6 (cases X507-X513).

The difference between the model and experimental data in the effect of DBA has not been explained. It is possible that there are gas distribution issues which hinder the approach to the gas-film limit because pockets of gas which encounter less liquid require very much DBA in that liquid in order to reach the gas film limit in removal. In enhancement-limited situations, which DBA improves, the small drops, with greater specific surface area, are most important, while in capacity-limited situations, it is the big drops with greater volume that are most important. Unequal distribution of drop sizes in the liquid could be important. Also, analytical uncertainties in the experimental data may be an issue. Degradation of DBA, primarily due to oxidation and related reactions, is known to be a key factor in the depletion of DBA in scrubbers. If the tests used to determine the DBA concentration detect degradation products as DBA, yet these products provide no buffering activity at the range of pH used in these systems, this could result in the over-prediction seen above.

CHAPTER 4: CONCLUSIONS AND RECOMMENDATIONS

4.1 CONCLUSIONS

The normalized performance, -ln(penetration)/N_g, can be represented quite well as the product of the approach to a gas film limit (K_G/k_g) and the approach to the non-equilibrium limit (log mean driving force for SO_2 removal over log mean SO_2 concentration). The three primary factors limiting SO_2 removal in limestone spray scrubbers are the gas-film mass transfer limit, the enhancement factor, and the liquid-phase equilibrium limitations. The equilibrium limitations become important at low L/G, low excess limestone, and other solution-capacity-limited situations.

The overall enhancement factor for SO_2 removal varies from about 2 to 50 or more, and is most strongly related to SO_2 concentration. The enhancement by hydrolysis dominates the enhancement behavior. At the very top of the absorber, enhancement due to bicarbonate and sulfite alkalinity can become important, but this effect fades quickly and is not important at the bottom of sections or below the top section.

The effect of inlet SO_2 concentration is to shift the relative importance of gas and liquid limitations. At low SO_2 conditions, liquid-phase equilibrium effects become unimportant and the gas-phase mass transfer limit controls performance. At high SO_2 conditions, solution capacity becomes very important.

In spray scrubbers with the same design for each header, modeling headers below the top one as achieving less gas-phase mass transfer agrees with published data.

Spray scrubbers differ from turbulent contact absorbers in that liquid equilibrium effects are significant in many cases in spray scrubbers, while they only ever have minor effects in TCAs.

The performance of spray scrubbers, measured as -ln(penetration), varies with the concentration of excess limestone to approximately the 0.3 to 0.4 power.

A bigger hold tank improves performance, either improving SO_2 removal at the same limestone utilization or improving utilization at a constant SO_2 removal. The hold tank pH varies with both limestone utilization and hold tank size, and thus is not a good parameter for scrubber design modeling.

Increasing the liquid-to-gas ratio improves both the solution capacity and the N_g, achieving a dual improvement in performance.

The fraction of limestone dissolved in the hold tank averages around 0.5, and varies most strongly with make per pass.

The SO_2 penetration of spray scrubbers can be modeled by a series resistances model; however, the terms required to get a good fit are awkward and not of much predictive value.

The effects of dibasic acid seem to be over-predicted by FGDTX by a significant degree, and adjusting the model parameters does not seem to change this.

4.2 RECOMMENDATIONS

A model for the mass transfer coefficients of sprays or at least some good experimentally-determined values for the mass-transfer coefficients would allow more confidence in the results of FGDTX.

Further study is warranted to understand why FGDTX overpredicts the effects of DBA.

The sulfite oxidation model should be improved by tracking the bulk dissolved oxygen concentration and predicting the rate of oxidation in the bulk solution as well as at the interface.

APPENDIX 1: STRUCTURE OF THE INPUT FILE

The main input file FGDTX.INP consists of 24 or more lines, structured as follows:

Line 1:

IDENT: Identifier for the run, maximum 80 alphanumeric characters.

Line 2:

TK: Temperature, in Kelvin.

Line 3:

IIPH: Flag indicating whether the supplied pH is a guess (iiph=0) or specification (iiph=1). If iiph=1, limestone reactivity will be varied (from the value derived from utilization) to reach this pH.

PH: Value for pH of scrubber inlet slurry (guessed or specified). See "Running with Specified pH."

Line 4:

U: Fractional limestone utilization specified.

OX: Guess for fractional oxidation.

Line 5:

IFLAGS: Flag indicating units for total solids. 0=g/liter solution, 1=gmole/liter solution.

SOLTOT: Total solids concentration, in the units specified.

Line 6:

K1: Units of input concentrations (1=mg/liter solution, 2=gmole/liter solution)

CCM(1,5,6,7): Guesses for the solution concentrations of total calcium, S(IV), S(VI), and total carbonate, in the units specified by K1.

Line 7:

CCM(2,3,4,8,9): Specified concentrations for Mg^{++}, Na^{+}, K^{+}, Cl^{-}, and adipic acid (buffer acid). Set the buffer acid concentration to 0.0015 ppm or 10^{-8} gmole/liter if buffer acid is not used.

Line 8:

FSP: scrubber inlet partial pressure of SO_2 at saturated conditions (atm)

BPPI(2),BPPI(3): Scrubber (outlet) partial pressures of CO_2 and O_2 (atm).

Line 9:

OVREM: Initial guess for overall fractional removal of SO_2.

RLGMAX: Total scrubber liquid-to-gas ratio, adjusted for pressure ($L/G/P_{tot}$ if all liquid enters at top of scrubber) (liter H_2O/gmole wet flue gas/atm)

Line 10:

KTYPE: Scrubber type. 0 for countercurrent, 1 for cocurrent.

Line 11:

NMIX: Number of scrubber sections. The next five lines have one data entry for each section.

Line 12:

XLOPT: Flag indicating whether liquid is calculated as mixed or plug flow on each section ('mixd' = mixed, 'plug' = plug flow).

Line 13:

XTAUSC: Liquid residence time in each scrubber section, in seconds.

Line 14:

XFRACT: Fraction of slurry input at top of each scrubber section.

Line 15:

XNTUSP: Number of gas-phase mass transfer units in each section.

Line 16:

XRKLKG: Ratio of liquid to gas phase mass transfer coefficients in each section. (atm-ml/gmole)

Line 17:

TAUHT: Hold tank liquid residence time, in seconds.

NL: Number of liquid phase mass transfer units in the hold tank.

STOICH: Ratio of moles oxygen (atoms) in inlet hold tank air to moles SO_2 in inlet scrubber gas.

Line 18:

PIN(1),PIN(2): Mole fractions of CO_2 and O_2 in inlet air to hold tank, usually 0.00033 and 0.21.

Line 19:

RATEK: Limestone-specific rate constant for surface kinetics

RD: Constant to modify reactivity. (normally RD=1, currently unused)

Line 20:

XKDISS(1,1),XKDISS(2,1): Dissolution rate parameters for $CaSO_3$ and gypsum.

Line 21:

XKCRYS(1,1),XKCRYS(2,1): Crystallization rate parameters for $CaSO_3$ and gypsum.

Line 22:

EF: Oxidation enhancement factor for the scrubber.

E: Oxidation enhancement factor for the hold tank.

OKONST: Oxidation kinetic constant.

Line 23:

LA: Flag indicating whether the particle size distribution (PSD) for limestone is specified or to be calculated. (0=PSD calculated from sieve data, 1=PSD specified)

Line 24:

If LA=0, then P1,D1,P2,D2 are required. D1 and D2 are particle diameters, in microns. P1 and P2 are the mass fraction of limestone smaller in diameter than D1 and D2, respectively.

If LA=1, then N is required. N is the number of lines which follow this one, containing PSD data.

Lines 25+ (only if LA=1):

D is a particle diameter, in microns.

PHI is the fraction of particles smaller than D but larger than the D from the previous line.

APPENDIX 2: INPUT AND OUTPUT CASES

A2.1 INPUT AND OUTPUT FILES

FGDTX uses two input files and produces three output files. The main input file is named FGDTX.INP and is structured as specified in Appendix 1. The other input file, P_EST.INP, is used for parameter estimation calculations and is not used in this work. The shortest of the three output files, OUTPUT.OUT (the one which is presented below) contains a summary of the input parameters and the final converged conditions. The output file FGDLONG.OUT contains the same information as OUTPUT.OUT but prints the conditions at each iteration of the convergence procedure. The last output file, DEBUG.OUT, contains values of convergence parameters and other intermediate values not relevant enough for the regular output, and mostly useful for debugging and testing the program.

A2.2 FACTORIAL CASE F322

A2.2.1 Input File for F322

See Appendix 1 for a more detailed description of these parameters.

```
F322 - This line is a name only, and the bits after ! are comments
333.                 !Temperature (K), or long input if inflag=0
0,5.8                !iiph (1=pH specified, 0=pH guessed), pH
0.95,0.99            !limestone utilization, fractional oxidation guess
0,100.0              !unit of solids (0:g/l;1:mol/l), total solids
2,0.01,0.0005,0.013,.001 !K1(1=ppm,2=M),conc guess of Ca,SO3,SO4,CO3
0.,0.,0.,0.1,1.0d-8      !conc spec of Mg,Na,K,Cl,H2Ad in units of K1
1.8d-3,0.10,0.08     !scrubber: pSO2in, pCO2, pO2 (atm)
0.90,0.1875          !overall removal guess, Scrubber L/G (liter/gmole)
0                    !0=countercurrent, 1=cocurrent`
3                    !Number of sections
'plug','plug','plug' !mixed or plug flow for each section
0.4,0.4,0.4          !residence time in each scrubber section in seconds
```

```
0.5,0.5,0.00          !fraction of slurry fed to each scrubber section
1.9,1.7,0.5           !Number of gas phase mass trans. units (each sect.)
200.,200.,200.        !ratio of mass transfer coefficients (atm-ml/gmole)
600.0,40.0,3.0        !Hold Tank slurry res. time, HT NL, HT air rate
0.33d-3,0.21          !pCO2 and pO2 in air to HT (atm)
11.25,1.0             !CaCO3 diss. parameter, RD (reactivity mod. const.)
1.0d+5,1.0d-5         !dissolution rate parameters for CaSO3 and gypsum
2.0d-3,2.0d-3         !crystallization rate params. for CaSO3 and gypsum
1.0,1.0,1.0d+4        !Scrubber & HT O2 enh. factors, oxid. kinetic const
1                     !LA (1=full PSD follows,0=only 2 grids)
24                    !number of lines of PSD data which follow
0.630,0.4             !diameter of particles, fraction smaller than this
0.794,0.7             !diameter, fraction between this size and previous
1.00,1.3              !etc.
1.26,2.4              ! This particular distribution is for Fredonia
1.59,3.9              ! Feedbelt, a finely-ground limestone.
2.0,5.9
2.52,7.9
3.17,8.5
4.0,7.5
5.04,6.6
6.35,5.9
8.0,2.2
10.08,5.2
12.7,4.8
16.0,4.7
20.2,4.7
25.4,4.6
32.0,4.5
40.3,4.5
50.8,3.8
64.0,3.5
80.6,1.7
101.6,1.2
128.0,0.1
```

A2.2.2 Output File for F322

In the following annotated output file, sections written in the fixed-width courier font are the actual output file, and sections written in this font are descriptions of the various sections.

The first section is a repeat of the input parameters, in a more human-readable form:

```
F322 - This line is a name only, and the bits after ! are comments

 Specified Temperature =                  333.00 Kelvin
 Initial guess pH =                         5.800
 Specified Limestone utilization =           .9500
 Guess for fractional oxidation =            .9900
 Total solids guess =                     100.000 g/l

 Guessed Concentrations in mol/liter solution:
Ca  =      .0100     SO3 =      .0005
SO4 =      .0130     CO3 =      .0010

 Specified Concentrations in mol/liter solution:
Mg  =      .0000     Na  =      .0000
K   =      .0000     Cl  =      .1000
H2Ad=      .0000

 Spec. inlet gas SO2 partial pressure=       .1800E-02 atm
 Specified CO2 from scrubber=                .1000 atm
 Specified O2 from scrubber=                 .0800 atm
 Guessed fractional SO2 removal=             .9000
 Spec. scrubber L/G ratio at bottom=         .1875 l/gmol-atm
                             =             51.341  gal/MCF-atm
 Scrubber L/G is adjusted by dividing by the total pressure in
atmospheres.

 3 countercurrent scrubber sections

Scrubber section types:
plug, plug, plug

Scrubber residence times (seconds):
   .40,    .40,    .40

Slurry feed split to scrubber sections:
  .5000,   .5000,   .0000

Mass transfer units in gas in each scrubber section:
 1.900,  1.700,   .500

Ratio of mass transfer coefficients in each scrubber section (atm-
ml/gmole)
 200.00,  200.00,  200.00

 Hold tank residence time=                600.00 seconds
 Hold tank mass transfer units (liquid)=   40.00
```

```
 Hold tank O/SO2 stoichiometry=             3.0000

Hold tank inlet gas concentrations (atm):
 CO2= .330E-03  O2=  .2100

 Oxidation kinetic constant= .100E+05
```

The next section gives a short summary of the convergence procedure. In the first part, FGDTX took several iterations to get a reasonably-close value for the SO_2 removal in the absorber based on the guessed slurry composition.

```
  ENTERING SCRUBBER. LOOP NUMBER  1
 SOLIDIN(3)= 0.327159599534338555E-01
   % REMOVAL        71.71
   SO2 PENETRATION      .282901
 Loop:  1  End of Scrubber loop:  1
 SOLIDIN(3)= 0.327159599534338555E-01
   % REMOVAL        58.10
   SO2 PENETRATION      .418960
 Loop:  1  End of Scrubber loop:  2
 SOLIDIN(3)= 0.327159599534338555E-01
   % REMOVAL        49.63
   SO2 PENETRATION      .503689
 Loop:  1  End of Scrubber loop:  3
 SOLIDIN(3)= 0.327159599534338555E-01
   % REMOVAL        50.64
   SO2 PENETRATION      .493586
 Loop:  1  End of Scrubber loop:  4
```

Having converged the removal, several more iterations are needed to converge the slurry composition, and fewer steps are needed to converge the removal each time because it starts with the last value used, which is already close. The next 5 lines represent the results of the hold tank model; "DELT" is a parameter that measures how far the converged value was to the guess, used in determining the next guess.

```
 PERCENT OXIDATION:      100.0    %
 CaSO3(S)           .37108E-02     DELT       .52282
 Hemihydrate        .63084E-03     DELT       .52282
 CaCO3(S)           .27072E-01     DELT       .89762E-01
```

```
Gypsum             .56075         DELT       .40480E-02
 ENTERING SCRUBBER. LOOP NUMBER  2
SOLIDIN(3)= 0.353589394886968458E-01
  % REMOVAL        53.00
  SO2 PENETRATION      .469963
Loop:  2  End of Scrubber loop:  1
SOLIDIN(3)= 0.353589394886968458E-01
  % REMOVAL        53.68
  SO2 PENETRATION      .463242
Loop:  2  End of Scrubber loop:  2
PERCENT OXIDATION:      100.0    %
CaSO3(S)           .24055E-04     DELT       .54262
Hemihydrate        .40894E-05     DELT       .54262
CaCO3(S)           .29762E-01     DELT       .67584E-03
Gypsum             .56507         DELT       .27027E-04
 ENTERING SCRUBBER. LOOP NUMBER  3
SOLIDIN(3)= 0.353390399351735524E-01
  % REMOVAL        53.59
  SO2 PENETRATION      .464079
Loop:  3  End of Scrubber loop:  1
PERCENT OXIDATION:      100.0    %
CaSO3(S)           .15581E-06     DELT       .54430
Hemihydrate        .26487E-07     DELT       .54430
CaCO3(S)           .29715E-01     DELT       .89023E-03
Gypsum             .56509         DELT       .17558E-06
 ENTERING SCRUBBER. LOOP NUMBER  4
SOLIDIN(3)= 0.353652522507648531E-01
  % REMOVAL        53.59
  SO2 PENETRATION      .464133
Loop:  4  End of Scrubber loop:  1
PERCENT OXIDATION:      100.0    %
CaSO3(S)           .10451E-08     DELT       .54438
Hemihydrate        .17766E-09     DELT       .54438
CaCO3(S)           .29739E-01     DELT       .10765E-03
Gypsum             .56509         DELT       .11779E-08
 ENTERING SCRUBBER. LOOP NUMBER  5
SOLIDIN(3)= 0.353684218873236283E-01
  % REMOVAL        53.59
  SO2 PENETRATION      .464125
Loop:  5  End of Scrubber loop:  1
PERCENT OXIDATION:      100.0    %
CaSO3(S)           .42992E-10     DELT       .54438
Hemihydrate        .73086E-11     DELT       .54438
CaCO3(S)           .29742E-01     DELT       .77353E-05
Gypsum             .56509         DELT       .48456E-10
 ENTERING SCRUBBER. LOOP NUMBER  6
SOLIDIN(3)= 0.353686496486727217E-01
```

```
  % REMOVAL        53.59
  SO2 PENETRATION      .464124
Loop:  6  End of Scrubber loop:  1
PERCENT OXIDATION:     100.00    %
CaSO3(S)           .36503E-10     DELT       .54438
Hemihydrate        .62055E-11     DELT       .54438
CaCO3(S)           .29742E-01     DELT       .66468E-06
Gypsum             .56509         DELT       .41143E-10
```

Below, the final conditions are printed. The "total" concentrations are the lumped liquid concentrations, i.e., SO2T represents the total of the concentrations of $SO_3^{=}$, HSO_3^{-}, and H_2SO_3, which also include the other ion pairs involving these species which are modeled indirectly.

```
 ----- FINAL CONDITIONS -----

  SECTION #              1               2               3
  TOTAL INLET CONCENTRATION, EACH SECTION (GMOL/L)
      SO2T           .8820E-04       .1844E-02       .4049E-02
      CO2T           .1706E-02       .1719E-02       .1887E-02
      SO4T           .1205E-01       .1232E-01       .1256E-01
      CaT            .6256E-01       .6298E-01       .6373E-01
  TOTAL OUTLET CONCENTRATION, EACH SECTION (GMOL/L)
      SO2T           .3599E-02       .4049E-02       .4703E-02
      CO2T           .1732E-02       .1887E-02       .2241E-02
      SO4T           .1259E-01       .1256E-01       .1260E-01
      CaT            .6339E-01       .6373E-01       .6441E-01
```

The next four parts give the bulk liquid and gas-liquid interface compositions at the top (just after the spray header) and bottom (just above the next spray header, or the last bit simulated) of each section. At the end of this, the SO_2 removal/penetration data is given.

```
  BULK COMPOSITION, TOP OF EACH SECTION (GMOL/L)
      H+             .1056E-05       .3547E-03       .9966E-03
      OH             .2239E-06       .6665E-09       .2372E-09
      H2CO3          .8273E-03       .1714E-02       .1885E-02
      HCO3-          .8760E-03       .5401E-05       .2114E-05
      CO3--          .3141E-05       .5763E-10       .8029E-11
      H2SO3          .3089E-08       .5540E-04       .3252E-03
      HSO3-          .3333E-04       .1779E-02       .3717E-02
```

```
    SO3--          .5486E-04       .8716E-05       .6480E-05
    HSO4-          .4083E-06       .1387E-03       .3893E-03
    SO4--          .1205E-01       .1218E-01       .1217E-01
    H2Ad           .1223E-10       .8412E-08       .9384E-08
    HAd-           .7483E-09       .1532E-08       .6082E-09
    Ad--           .9240E-08       .5630E-10       .7953E-11
    Ca++           .6256E-01       .6298E-01       .6373E-01
    Cl-            .1000           .1000           .1000
    pH             6.063           3.536           3.087
BULK COMPOSITION, BOTTOM OF EACH SECTION (GMOL/L)
    H+             .1202E-02       .9974E-03       .6180E-03
    OH             .1966E-09       .2370E-09       .3824E-09
    H2CO3          .1731E-02       .1886E-02       .2243E-02
    HCO3-          .1609E-05       .2113E-05       .4056E-05
    CO3--          .5065E-11       .8018E-11       .2484E-10
    H2SO3          .3433E-03       .3255E-03       .2412E-03
    HSO3-          .3253E-02       .3718E-02       .4446E-02
    SO3--          .4701E-05       .6476E-05       .1250E-04
    HSO4-          .4681E-03       .3896E-03       .2453E-03
    SO4--          .1213E-01       .1217E-01       .1236E-01
    H2Ad           .9485E-08       .9384E-08       .9036E-08
    HAd-           .5096E-09       .6077E-09       .9443E-09
    Ad--           .5525E-11       .7942E-11       .1991E-10
    Ca++           .6339E-01       .6373E-01       .6441E-01
    Cl-            .1000           .1000           .1000
    pH             3.006           3.087           3.295
INTERFACE COMPOSITION, TOP OF EACH SECTION (GMOL/L)
    H+             .6420E-03       .1037E-02       .1394E-02
    OH             .3681E-09       .2279E-09       .1695E-09
    H2CO3          .1461E-02       .1460E-02       .1458E-02
    HCO3-          .2543E-05       .1573E-05       .1169E-05
    CO3--          .1499E-10       .5739E-11       .3174E-11
    H2SO3          .1529E-03       .3350E-03       .5718E-03
    HSO3-          .2713E-02       .3679E-02       .4672E-02
    SO3--          .7340E-05       .6162E-05       .5822E-05
    HSO4-          .2462E-03       .4016E-03       .5452E-03
    SO4--          .1194E-01       .1206E-01       .1218E-01
    H2Ad           .8246E-08       .9393E-08       .9551E-08
    HAd-           .8296E-09       .5848E-09       .4425E-09
    Ad--           .1684E-10       .7348E-11       .4137E-11
INTERFACE COMPOSITION, BOTTOM OF EACH SECTION (GMOL/L)
    H+             .1407E-02       .1395E-02       .1150E-02
    OH             .1680E-09       .1695E-09       .2056E-09
    H2CO3          .1460E-02       .1458E-02       .1457E-02
    HCO3-          .1160E-05       .1169E-05       .1417E-05
    CO3--          .3120E-11       .3172E-11       .4665E-11
    H2SO3          .4412E-03       .5719E-03       .5905E-03
```

```
    HSO3-          .3573E-02       .4672E-02       .5852E-02
    SO3--          .4412E-05       .5820E-05       .8843E-05
    HSO4-          .5526E-03       .5454E-03       .4542E-03
    SO4--          .1223E-01       .1218E-01       .1230E-01
    H2Ad           .9556E-08       .9551E-08       .9457E-08
    HAd-           .4388E-09       .4424E-09       .5313E-09
    Ad--           .4065E-11       .4135E-11       .6024E-11
SO2 bulk / SO2 interface for each section
    top            .2020E-04       .1654           .5688
    bottom         .7779           .5692           .4085
% REMOVAL        31.04           27.26           7.473
OVERALL % REMOVAL        53.588
OVERALL SO2 PENETRATION      .464124
```

The next section contains the gas concentrations and various parameters useful for modeling, including the enhancement factors, and finally the solids data for each section and the percent oxidation achieved.

```
GAS INLET CONCENTRATION (ATM.)
    pSO2           .1227E-02       .1686E-02       .1823E-02
    pCO2           .9992E-01       .9981E-01       .9975E-01
    pO2            .8003E-01       .8005E-01       .8006E-01
DEL.FLUXCaCO3      .2325E-06       .1920E-06       .1188E-06
DEL.FLUXCaSO3      .2573E-06       .2150E-06       .1366E-06
FLUXSO2            .1251E-03       .1510E-03       .4474E-04
DDELC(2)          -.2495E-04      -.3676E-04      -.2142E-04
DDELC(3)           .8478E-05       .7588E-05       .2232E-05
DIFFERENCE BETWEEN OUTLET AND INLET TOTAL CONC. (GMOL/L)
    SO2T           .3511E-02       .4501E-03       .6540E-03
    CO2T           .2528E-04       .1557E-03       .3536E-03
    SO4T           .5469E-03      -.3895E-04       .4878E-04
    CaT            .8317E-03       .3375E-03       .6776E-03
MAKE PER PASS      .4062E-02       .2452E-02       .7265E-03
SCRUBBER CASO3     .4157E-12       .3899E-12       .3678E-12
SCRUBBER CACO3     .8355E-03       .7652E-03       .7013E-03
CACO3 BOUNDARY CONDITION
                   .2325E-06       .1920E-06       .1188E-06
    Ca++           .7747E-01       .7536E-01       .7161E-01
    CO3--          .3501E-06       .3283E-06       .3018E-06
    SO3--          .5202E-04       .6744E-04       .1193E-03
    pH            4.053           4.108           4.280
ENHANCEMENT FACTORS AT BOTTOM OF SECTIONS
    CO3--          .0000           .0000           .0000
    HCO3-          .0039           .0033           .0065
    H2Ad           .0000           .0000           .0000
```

```
       SO3--          .0021           .0019           .0076
       SO4--         -.8646          -.0457           .1247
       H+            3.0684          2.3676          2.2353
       Total         3.2099          3.3272          3.3741
   ENHANCEMENT FACTORS AT TOP OF SECTIONS
       CO3--          .0297           .0000           .0000
       HCO3-         4.8860           .0117           .0033
       H2Ad           .0001           .0000           .0000
       SO3--          .2252           .0066           .0019
       SO4--          .5349           .3551          -.0451
       H+            6.1578          3.5859          2.3679
       Total        12.8337          4.9594          3.3279

   SOLID CONCENTRATION(GMOL/L.SOLN)
      CaSO3(S)         .5596E-10       .5557E-10       .5520E-10
      Hemihydrate      .9513E-11       .9447E-11       .9384E-11
      CaCO3(S)         .3453E-01       .3377E-01       .3307E-01
      Gypsum           .5651           .5651           .5651

   RELATIVE SATURATION
       RSCASO3         .4901E-02       .6788E-02       .1324E-01
       RSCASO4         1.028           1.037           1.064
 PERCENT OXIDATION:     100.00    %
 RUN CONCLUDED, CONVERGENCE SUCCESSFUL.
```

A2.3 Factorial Base Case A322

A2.3.1 Input File for A322

```
Fredonia Feedbelt - new base
333.                !Temperature (K), or long input if inflag=0
0,5.8               !iiph (1=pH specified, 0=pH guessed), pH
0.95,0.99           !limestone utilization, fractional oxidation guess
0,100.0             !unit of solids (0:g/l;1:mol/l), total solids
2,0.01,0.0005,0.013,.001 !K1(1=ppm,2=M),conc guess of Ca,SO3,SO4,CO3
0.,0.,0.,0.1,1.0d-8 !conc spec of Mg,Na,K,Cl,H2Ad in the units of K1
1.8d-3,0.10,0.08    !scrubber: pSO2in, pCO2, pO2 (atm)
0.90,0.375          !overall removal guess, Scrubber L/G (liter/gmole)
0                   !0=countercurrent, 1=cocurrent`
5                   !# of sections
'plug','plug','plug','plug','plug'   !mixed/plug flow sections
0.4,0.4,0.4,0.4,0.4 !residence time in each scrubber section in seconds
0.25,0.25,0.25,0.25,0.00 !fraction of slurry fed to each scrubber sect.
1.9,1.7,1.5,1.3,0.5 !# of gas phase mass transfer units (each section)
200.,200.,200.,200.,200. !ratio of mass transfer coeffs (atm-ml/gmole)
300.0,20.0,3.0      !HT res. time, HT NL, HT air rate
0.33d-3,0.21        !pCO2 and pO2 in air to HT (atm)
11.25,1.0           !CaCO3 diss. parameter, RD
```

```
1.0d+5,1.0d-5       !dissolution rate parameters for CaSO3 and gypsum
2.0d-3,2.0d-3       !crystallization rate params. for CaSO3 and gypsum
1.0,1.0,1.0d+4      !Scrubber and HT O2 enh factors, oxid kinetic const
1                   !LA (1=full PSD follows,0=only 2 grids)
24                  !number of lines of PSD data which follow
0.630,0.4           !diameter of particles, fraction smaller than this
0.794,0.7           !diameter, fraction between this size and previous
1.00,1.3            !etc.
1.26,2.4
1.59,3.9
2.0,5.9
2.52,7.9
3.17,8.5
4.0,7.5
5.04,6.6
6.35,5.9
8.0,2.2
10.08,5.2
12.7,4.8
16.0,4.7
20.2,4.7
25.4,4.6
32.0,4.5
40.3,4.5
50.8,3.8
64.0,3.5
80.6,1.7
101.6,1.2
128.0,0.1
```

A2.3.2 Output File for A322

In this output file, the spaces between the columns in the per-section data have been reduced in order to fit the data into this format.

```
Fredonia Feedbelt - new base

 Specified Temperature =                 333.00 Kelvin
 Initial guess pH =                        5.800
 Specified Limestone utilization =          .9500
 Guess for fractional oxidation =           .9900
 Total solids guess =                    100.000 g/l

 Guessed Concentrations in mol/liter solution:
Ca  =      .0100     SO3 =      .0005
SO4 =      .0130     CO3 =      .0010
```

```
 Specified Concentrations in mol/liter solution:
Mg  =      .0000     Na  =      .0000
K   =      .0000     Cl  =      .1000
H2Ad=      .0000

 Spec. inlet gas SO2 partial pressure=       .1800E-02 atm
 Specified CO2 from scrubber=                .1000 atm
 Specified O2 from scrubber=                 .0800 atm
 Guessed fractional SO2 removal=             .9000
 Spec. scrubber L/G ratio at bottom=         .3750 l/gmol-atm
                             =            102.683  gal/MCF-atm
 Scrubber L/G is adjusted by dividing by the total pressure in
atmospheres.

 5 countercurrent scrubber sections

Scrubber section types:
plug, plug, plug, plug, plug

Scrubber residence times (seconds):
   .40,    .40,    .40,    .40,    .40

Slurry feed split to scrubber sections:
  .2500,   .2500,   .2500,   .2500,   .0000

Mass transfer units in gas in each scrubber section:
 1.900,  1.700,  1.500,  1.300,   .500

Ratio of mass transfer coefficients in each scrubber section (atm-
ml/gmole)
 200.00,  200.00,  200.00,  200.00,  200.00

 Hold tank residence time=                300.00 seconds
 Hold tank mass transfer units (liquid)=   20.00
 Hold tank O/SO2 stoichiometry=             3.0000

Hold tank inlet gas concentrations (atm):
 CO2= .330E-03  O2=  .2100

 Oxidation kinetic constant= .100E+05
```

```
 ENTERING SCRUBBER. LOOP NUMBER  1
SOLIDIN(3)= 0.327159599534338555E-01
  % REMOVAL        86.91
  SO2 PENETRATION      .130874
Loop:  1  End of Scrubber loop:  1
SOLIDIN(3)= 0.327159599534338555E-01
  % REMOVAL        84.68
  SO2 PENETRATION      .153163
Loop:  1  End of Scrubber loop:  2
SOLIDIN(3)= 0.327159599534338555E-01
  % REMOVAL        81.15
  SO2 PENETRATION      .188512
Loop:  1  End of Scrubber loop:  3
PERCENT OXIDATION:      100.0    %
CaSO3(S)           .45167E-02     DELT        .25111
Hemihydrate        .76784E-03     DELT        .25111
CaCO3(S)           .27654E-01     DELT        .70213E-01
Gypsum             .55981         DELT        .23705E-02
 ENTERING SCRUBBER. LOOP NUMBER  2
SOLIDIN(3)= 0.347833494056916173E-01
  % REMOVAL        82.90
  SO2 PENETRATION      .170986
Loop:  2  End of Scrubber loop:  1
SOLIDIN(3)= 0.347833494056916173E-01
  % REMOVAL        83.99
  SO2 PENETRATION      .160102
Loop:  2  End of Scrubber loop:  2
SOLIDIN(3)= 0.347833494056916173E-01
  % REMOVAL        85.49
  SO2 PENETRATION      .145091
Loop:  2  End of Scrubber loop:  3
PERCENT OXIDATION:      100.0    %
CaSO3(S)           .35103E-04     DELT        .28669
Hemihydrate        .59676E-05     DELT        .28669
CaCO3(S)           .30123E-01     DELT        .12812E-01
Gypsum             .56505         DELT        .20838E-04
 ENTERING SCRUBBER. LOOP NUMBER  3
SOLIDIN(3)= 0.344060953974283795E-01
  % REMOVAL        85.66
  SO2 PENETRATION      .143429
Loop:  3  End of Scrubber loop:  1
PERCENT OXIDATION:      100.0    %
CaSO3(S)           .27126E-06     DELT        .29428
Hemihydrate        .46115E-07     DELT        .29428
CaCO3(S)           .29686E-01     DELT        .18672E-02
Gypsum             .56509         DELT        .16528E-06
```

```
 ENTERING SCRUBBER. LOOP NUMBER  4
SOLIDIN(3)= 0.344610728065488786E-01
  % REMOVAL        85.65
  SO2 PENETRATION      .143450
Loop:  4  End of Scrubber loop:  1
PERCENT OXIDATION:      100.0    %
CaSO3(S)           .21370E-08     DELT       .29556
Hemihydrate        .36329E-09     DELT       .29556
CaCO3(S)           .29725E-01     DELT       .55446E-03
Gypsum             .56509         DELT       .13077E-08
 ENTERING SCRUBBER. LOOP NUMBER  5
SOLIDIN(3)= 0.344773984417358903E-01
  % REMOVAL        85.66
  SO2 PENETRATION      .143431
Loop:  5  End of Scrubber loop:  1
PERCENT OXIDATION:      100.0    %
CaSO3(S)           .59668E-10     DELT       .29574
Hemihydrate        .10144E-10     DELT       .29574
CaCO3(S)           .29739E-01     DELT       .10758E-03
Gypsum             .56509         DELT       .36536E-10
 ENTERING SCRUBBER. LOOP NUMBER  6
SOLIDIN(3)= 0.344805661629782323E-01
  % REMOVAL        85.66
  SO2 PENETRATION      .143426
Loop:  6  End of Scrubber loop:  1
PERCENT OXIDATION:      100.0    %
CaSO3(S)           .43635E-10     DELT       .29577
Hemihydrate        .74180E-11     DELT       .29577
CaCO3(S)           .29741E-01     DELT       .16626E-04
Gypsum             .56509         DELT       .26721E-10
 ----- FINAL CONDITIONS -----

  SECTION #         1          2          3          4          5
  TOTAL INLET CONCENTRATION, EACH SECTION (GMOL/L)
      SO2T      .2493E-03  .1240E-02  .1826E-02  .2342E-02  .3446E-02
      CO2T      .2283E-02  .1952E-02  .1934E-02  .1989E-02  .2020E-02
      SO4T      .1205E-01  .1232E-01  .1239E-01  .1240E-01  .1247E-01
      CaT       .6281E-01  .6298E-01  .6318E-01  .6338E-01  .6375E-01
  TOTAL OUTLET CONCENTRATION, EACH SECTION (GMOL/L)
      SO2T      .2230E-02  .2614E-02  .3040E-02  .3446E-02  .3921E-02
      CO2T      .1620E-02  .1759E-02  .1890E-02  .2020E-02  .2237E-02
      SO4T      .1259E-01  .1255E-01  .1251E-01  .1247E-01  .1249E-01
      CaT       .6316E-01  .6336E-01  .6356E-01  .6375E-01  .6413E-01
  BULK COMPOSITION, TOP OF EACH SECTION (GMOL/L)
      H+        .1180E-05  .3242E-04  .1766E-03  .2581E-03  .5347E-03
      OH        .2002E-06  .7290E-08  .1339E-08  .9156E-09  .4420E-09
      H2CO3     .1171E-02  .1887E-02  .1921E-02  .1980E-02  .2015E-02
```

```
    HCO3-     .1109E-02  .6504E-04  .1216E-04  .8573E-05  .4213E-05
    CO3--     .3555E-05  .7591E-08  .2607E-09  .1257E-09  .2982E-10
    H2SO3     .1045E-07  .3340E-05  .2760E-04  .5157E-04  .1540E-03
    HSO3-     .1008E-03  .1174E-02  .1781E-02  .2276E-02  .3281E-02
    SO3--     .1484E-03  .6288E-04  .1752E-04  .1531E-04  .1066E-04
    HSO4-     .4568E-06  .1282E-04  .6983E-04  .1019E-03  .2105E-03
    SO4--     .1205E-01  .1231E-01  .1232E-01  .1230E-01  .1226E-01
    H2Ad      .1515E-10  .2637E-08  .7180E-08  .7919E-08  .8899E-08
    HAd-      .8292E-09  .5252E-08  .2626E-08  .1981E-08  .1075E-08
    Ad--      .9156E-08  .2111E-08  .1939E-09  .1000E-09  .2620E-10
    Ca++      .6281E-01  .6298E-01  .6318E-01  .6338E-01  .6375E-01
    Cl-       .1000      .1000      .1000      .1000      .1000
    pH       6.014      4.575      3.839      3.674      3.358
BULK COMPOSITION, BOTTOM OF EACH SECTION (GMOL/L)
    H+        .7052E-03  .6260E-03  .5773E-03  .5351E-03  .3751E-03
    OH        .3352E-09  .3776E-09  .4095E-09  .4417E-09  .6301E-09
    H2CO3     .1618E-02  .1755E-02  .1886E-02  .2015E-02  .2233E-02
    HCO3-     .2564E-05  .3134E-05  .3653E-05  .4209E-05  .6654E-05
    CO3--     .1376E-10  .1895E-10  .2395E-10  .2976E-10  .6713E-10
    H2SO3     .1298E-03  .1358E-03  .1462E-03  .1541E-03  .1244E-03
    HSO3-     .2097E-02  .2472E-02  .2885E-02  .3281E-02  .3778E-02
    SO3--     .5165E-05  .6859E-05  .8683E-05  .1065E-04  .1750E-04
    HSO4-     .2788E-03  .2473E-03  .2277E-03  .2107E-03  .1486E-03
    SO4--     .1231E-01  .1231E-01  .1229E-01  .1226E-01  .1234E-01
    H2Ad      .9147E-08  .9047E-08  .8973E-08  .8900E-08  .8488E-08
    HAd-      .8377E-09  .9335E-09  .1004E-08  .1074E-08  .1461E-08
    Ad--      .1548E-10  .1944E-10  .2267E-10  .2616E-10  .5078E-10
    Ca++      .6316E-01  .6336E-01  .6356E-01  .6375E-01  .6413E-01
    Cl-       .1000      .1000      .1000      .1000      .1000
    pH       3.238      3.289      3.325      3.358      3.512
INTERFACE COMPOSITION, TOP OF EACH SECTION (GMOL/L)
    H+        .1358E-03  .4849E-03  .7187E-03  .9080E-03  .1151E-02
    OH        .1741E-08  .4874E-09  .3289E-09  .2603E-09  .2054E-09
    H2CO3     .1461E-02  .1460E-02  .1458E-02  .1456E-02  .1454E-02
    HCO3-     .1203E-04  .3364E-05  .2268E-05  .1792E-05  .1412E-05
    CO3--     .3353E-09  .2625E-10  .1194E-10  .7471E-11  .4643E-11
    H2SO3     .1720E-04  .1041E-03  .2042E-03  .3252E-03  .5015E-03
    HSO3-     .1444E-02  .2447E-02  .3236E-02  .4080E-02  .4963E-02
    SO3--     .1847E-04  .8764E-05  .7823E-05  .7806E-05  .7491E-05
    HSO4-     .5319E-04  .1914E-03  .2828E-03  .3552E-03  .4497E-03
    SO4--     .1220E-01  .1229E-01  .1226E-01  .1218E-01  .1217E-01
    H2Ad      .6012E-08  .8577E-08  .9127E-08  .9305E-08  .9455E-08
    HAd-      .2861E-08  .1142E-08  .8203E-09  .6619E-09  .5306E-09
    Ad--      .2746E-09  .3070E-10  .1488E-10  .9501E-11  .6009E-11
INTERFACE COMPOSITION, BOTTOM OF EACH SECTION (GMOL/L)
    H+        .8628E-03  .9308E-03  .1034E-02  .1151E-02  .1086E-02
    OH        .2740E-09  .2539E-09  .2285E-09  .2053E-09  .2177E-09
```

```
     H2CO3     .1460E-02  .1458E-02  .1456E-02  .1454E-02  .1453E-02
     HCO3-     .1891E-05  .1751E-05  .1574E-05  .1412E-05  .1496E-05
     CO3--     .8294E-11  .7119E-11  .5757E-11  .4641E-11  .5213E-11
     H2SO3     .1713E-03  .2552E-03  .3669E-03  .5015E-03  .5512E-03
     HSO3-     .2261E-02  .3123E-02  .4041E-02  .4962E-02  .5783E-02
     SO3--     .4553E-05  .5830E-05  .6787E-05  .7488E-05  .9251E-05
     HSO4-     .3448E-03  .3695E-03  .4075E-03  .4498E-03  .4252E-03
     SO4--     .1245E-01  .1236E-01  .1227E-01  .1217E-01  .1219E-01
     H2Ad      .9292E-08  .9339E-08  .9400E-08  .9456E-08  .9419E-08
     HAd-      .6956E-09  .6481E-09  .5869E-09  .5305E-09  .5602E-09
     Ad--      .1051E-10  .9075E-11  .7396E-11  .6006E-11  .6724E-11
 SO2 bulk / SO2 interface for each section
     top       .6074E-03  .3207E-01  .1352      .1586      .3071
     bottom    .7579      .5322      .3985      .3073      .2257
 % REMOVAL   47.53      37.83      32.25      27.47      10.51
 OVERALL % REMOVAL        85.657
 OVERALL SO2 PENETRATION      .143426

 GAS INLET CONCENTRATION (ATM.)
     pSO2      .4993E-03  .8032E-03  .1186E-02  .1635E-02  .1827E-02
     pCO2      .9990E-01  .9979E-01  .9967E-01  .9953E-01  .9946E-01
     pO2       .8003E-01  .8005E-01  .8007E-01  .8009E-01  .8009E-01
 DEL.FLUXCaCO3 .1394E-06  .1232E-06  .1131E-06  .1045E-06  .7376E-07
 DEL.FLUXCaSO3 .1559E-06  .1394E-06  .1291E-06  .1202E-06  .8687E-07
 FLUXSO2       .7795E-04  .9979E-04  .1256E-03  .1475E-03  .6302E-04
 DDELC(2)     -.3143E-04 -.3621E-04 -.4144E-04 -.4516E-04 -.2267E-04
 DDELC(3)      .8478E-05  .7588E-05  .6697E-05  .5805E-05  .2233E-05
 DIFFERENCE BETWEEN OUTLET AND INLET TOTAL CONC. (GMOL/L)
     SO2T      .1981E-02  .3836E-03  .4263E-03  .4057E-03  .4754E-03
     CO2T     -.6632E-03  .1384E-03  .1317E-03  .1293E-03  .2178E-03
     SO4T      .5395E-03 -.3973E-04 -.3975E-04 -.3988E-04  .1259E-04
     CaT       .3465E-03  .2052E-03  .2034E-03  .1897E-03  .3782E-03
 MAKE PER PASS .2532E-02  .1621E-02  .1360E-02  .1198E-02  .5117E-03
SCRUBBER CASO3 .1897E-12  .2107E-12  .2185E-12  .2168E-12  .2214E-12
SCRUBBER CACO3 .3577E-03  .3949E-03  .4055E-03  .3977E-03  .4019E-03
 CACO3 BOUNDARY CONDITION
               .1394E-06  .1232E-06  .1131E-06  .1045E-06  .7376E-07
     Ca++      .7160E-01  .7082E-01  .7042E-01  .7008E-01  .6860E-01
     CO3--     .4380E-06  .4042E-06  .3747E-06  .3518E-06  .3293E-06
     SO3--     .6943E-04  .8539E-04  .1006E-03  .1162E-03  .1766E-03
     pH       4.372      4.391      4.395      4.402      4.524
 ENHANCEMENT FACTORS AT BOTTOM OF SECTIONS
     CO3--     .0000      .0000      .0000      .0000      .0000
     HCO3-     .0139      .0099      .0081      .0069      .0103
     H2Ad      .0000      .0000      .0000      .0000      .0000
     SO3--     .0107      .0062      .0062      .0066      .0140
     SO4--   -2.5070     -.3849      .0609      .2149      .2655
```

```
      H+       5.5821     3.7501     3.0420     2.6052     2.4460
      Total    4.0997     4.3813     4.1172     3.8336     3.7358
  ENHANCEMENT FACTORS AT TOP OF SECTIONS
      CO3--     .2991      .0001      .0000      .0000      .0000
      HCO3-   54.5574      .5232      .0479      .0212      .0069
      H2Ad      .0007      .0001      .0000      .0000      .0000
      SO3--    5.4748      .3889      .0398      .0199      .0066
      SO4--   -6.8342      .1227      .2707      .3265      .2150
      H+      11.4970     6.5934     4.5094     3.4883     2.6053
      Total   65.9947     8.6284     5.8678     4.8559     3.8338

  SOLID CONCENTRATION(GMOL/L.SOLN)
    CaSO3(S)    .5635E-10  .5614E-10  .5592E-10  .5571E-10  .5548E-10
    Hemihydrate .9580E-11  .9544E-11  .9507E-11  .9470E-11  .9432E-11
    CaCO3(S)    .3412E-01  .3373E-01  .3332E-01  .3292E-01  .3252E-01
    Gypsum      .5651      .5651      .5651      .5652      .5652

  RELATIVE SATURATION
    RSCASO3     .5365E-02  .7148E-02  .9078E-02  .1117E-01  .1846E-01
    RSCASO4    1.040      1.042      1.044      1.045      1.058
PERCENT OXIDATION:     100.00    %
RUN CONCLUDED, CONVERGENCE SUCCESSFUL.
```

APPENDIX 3: SUMMARY OF MODEL DOCUMENTATION

A3.1 SUBROUTINE DESCRIPTIONS

The FGDTX code is composed of over 40 Fortran subroutines and a few functions, totaling about 6000 lines of code. Below is a short description of each of these, and in the next section the flow of the program is presented.

Beq	Beq, Tcon, Kcalc, CaSO3, CaSO4, CaSOx, and Beqprt make up the Bechtel-Modified Radian Equilibrium Program, or BMREP. The version used here has had some minor changes made. All through the program, floating-point calculations were converted to double precision; for other changes, see section 1.4.2. Beq is the driver routine which calls the other routines, and determines all the solution equilibrium parameters needed for the limestone slurry system.
Beqprt	This routine is used to print out data from BMREP. Beqprt is not normally used by FGDTX but is retained for convenience in testing.
Bis	A bisection routine used by Gvar to find the random variable, y, of the log-gamma function which satisfies a specified weight fraction.
Calcsol	This routine calculates the initial guesses for solids concentrations.
CaSO3, CaSO4, CaSOx	These three routines, part of BMREP, are used to calculate parameters relevant to the sulfite and sulfate species. See Beq.
CaSO3di	This routine calculates the calcium sulfite dissolution rate.
Charbl	This routine iterates on the concentration of [Ca^{++}] to force a zero charge balance in BMREP.
Conopt	This is the driver subroutine for predicting multi-section scrubber performance.
Conv99	This routine iterates on the guessed concentration of H^+ at the gas-liquid interface until a zero charge flux is reached.

Deadend	This routine is used to exit from the program nicely when an error in input or convergence prevents FGDTX from continuing.
Delin	A function whose zero is found by a secant method in Gcomp. Delin calculates the difference between the O_2 absorbed based on the log-mean driving force expression and the O_2 absorbed based on a material balance for $SO_4^{=}$.
Dist	This routine calculates a complete particle size distribution using a log-gamma distribution when only two sieve measurements are specified.
Eulers	This routine simultaneously integrates the gas, liquid and solid phases in the scrubber to simulate spray scrubber performance.
Equil	This routine calculates the slurry liquor composition given total $[SO_4^{=}]$, $[CO_3^{=}]$, $[SO_3^{=}]$, and $[Ca^{++}]$.
Equilholdt	This routine calculates $[Ca^{++}]$ at a particular pH, for use with the pH-specified mode of operations.
Fgdtx	This is the driver routine which reads input from files and calls all of the other main subroutines.
Fgktau	This routine makes a first guess for KTAU in the prediction of limestone reactivity.
Film	This routine calculates the average film thickness around the limestone particles which are dissolving in a CSTR system.
Fint	This routine calculates the dissolution rate and the integrand which must be evaluated to calculate utilization.
Fmint	This routine calculates the value of the integrand needed to determine the average film thickness.
Funct	A function whose zero is found by a secant method in Equil. Funct calculates the deviation from charge balance.
Gcomp	This routine calculates the objective function for the optimization routine.

Gktau	This routine estimates the values of KTAU once a first guess has been made.
Gvar	This routine calculates the log-gamma parameters, β and d_{100}, from two sieve measurements.
Hcomp	This routine is an alternate interface to Gcomp used in the hold tank calculations.
Holdt	This is the driver subroutine for the hold tank calculations.
Houtput	This routine prints output from Holdt about hold tank conditions to the output files.
Intgr	This routine determines the changes in gas concentrations of SO_2, CO_2, and O_2 across a plug-flow section.
Inv	This routine inverts a 4x4 or 5x5 Jacobian matrix for Newt1 or Newt2.
Kcalc	This routine, part of BMREP, determines activity coefficients and equilibrium constants. See Beq.
Limreac	This routine calculates the limestone reactivity parameter.
Listone	This routine calculates the flux of dissolving calcium carbonate.
Lubksb, Ludcmp	These two routines perform L-U decomposition and back-substitution for Inv.
Newt1	This routine uses Newton's method to determine 4 variables describing the outlet liquid concentrations on a section or in the hold tank.
Newt2	A routine very similar to Newt1, but for use in certain calculation modes where a 5-variable convergence must be performed, always in the scrubber.
Poutput	This routine prints output from Conopt about the scrubber conditions to the output files.
Pseudo	This routine calculates the pseudo-concentrations of $[Ca^{++}]$, $[HCO_3^-]$, $[CO_3^=]$, $[SO_4^=]$, $[SO_3^=]$, $[Ad^=]$, and $[OH^-]$, and calculates

	diffusivities and pseudo-equilibrium constants with the pseudo-concentrations.
React	This is the driver routine for the prediction of limestone reactivity from utilization and a particle size distribution.
Scrint	This is the driver subroutine for convergence of the overall scrubber/hold tank loop of the slurry scrubber model.
Simp	This routine applies Simpson's rule as the integration technique when calculating utilization.
Soldbal	This routine calculates the dissolution and/or crystallization rates of $CaSO_3$, $CaSO_4$ hemihydrate, $CaCO_3$, and gypsum.
Solguess	A short routine called by Scrint which determines the next guess for solids compositions.
Spray	This routine determines the changes in gas concentrations of SO_2, CO_2, and O_2 across a section.
Surcone	This routine calculates species concentrations at the surface of the limestone and determines the boundary condition to be satisfied.
Surface	This routine calculates species concentrations at the surface of calcium sulfite/sulfate hemihydrate particles.
Szn	A function called by Conv99 to determine the charge flux.
Tcon	This routine, part of BMREP, calculates "constants" that vary only with temperature. See Beq.

A3.2 FLOWSHEET FOR FGDTX

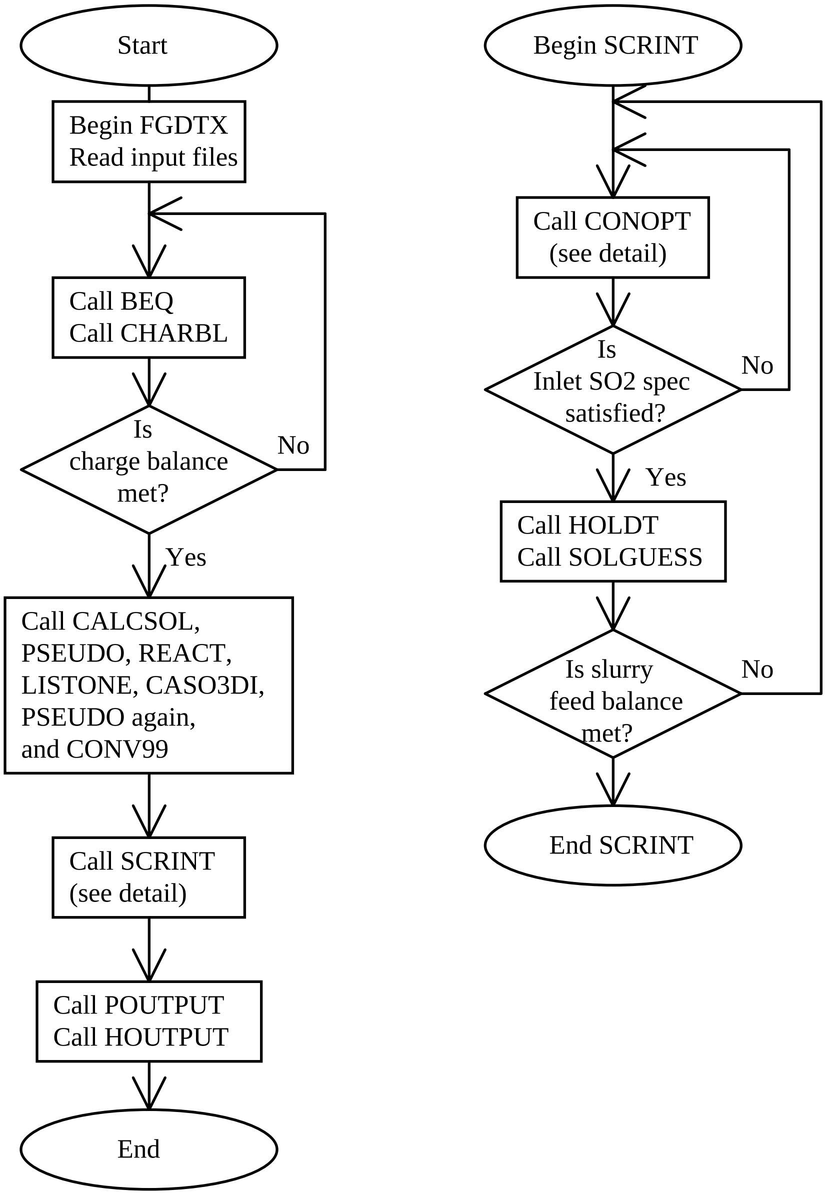

Figure A3-1: The flow of the program through the main driver routine FGDTX and the main convergence driver routine SCRINT

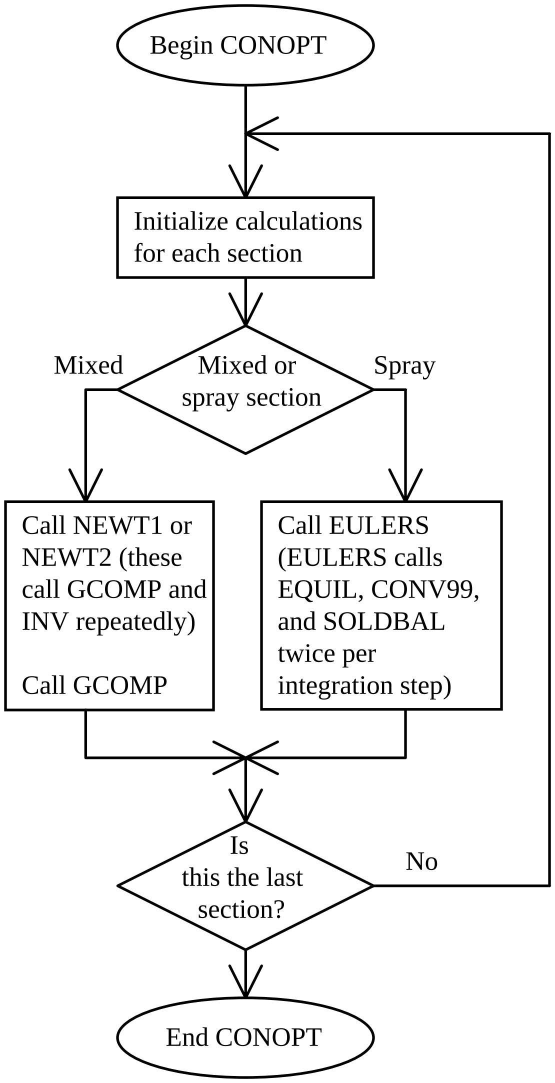

Figure A3-2: The flow of the program through the scrubber calculation routine CONOPT

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