Theoretical Approach for Enhanced Mass Transfer Effects In-Duct Flue Gas Desulfurization Processes

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**DOE Project Manager
Richard E. Tischer
Environmental Control Division
Pittsburgh Energy Technology Center
U.S. Department of Energy
Pittsburgh, Pennsylvania 15236**

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Prepared by

**Acurex Corporation
Environmental Systems Division
Post Office Box 13109
Research Triangle Park, North Carolina 27709**

and

**University of Texas
Department of Chemical Engineering
Austin, Texas 78712**

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SECTION 1

INTRODUCTION

1.1 OBJECTIVES

While developing dry sorbent duct injection flue gas desulfurization processes may offer significant improvement in capital cost and process simplicity compared to wet scrubbing systems, the economics of this technology can be improved significantly by an improvement in sorbent utilization. The main causes for the current low sorbent utilization rates are the limited inherent reactivity of the sorbent, the short residence times available for reaction in existing power plant ducts, and, for current sorbents to be effective, the need to achieve a close approach to saturation of the flue gas by means of adiabatic humidification. In all the current dry lime-based concepts, the sorbent spends some time both as lime-water slurry particles or lime particles surrounded by a layer of water and dry particles containing absorbed moisture. It is known that reaction with SO_2 can occur in both states, although at different rates. While a general understanding of the mechanism by which the sorbents operate is known, a much more detailed knowledge of reaction rate-controlling phenomena, the role of inherent reactivity, and mass transfer effects and their interaction is needed.

The objectives of this project are threefold:

1. Mass transfer investigation—determine the controlling physical and chemical processes that limit sorbent utilization. In particular, determine whether mass transfer is a controlling factor in in-duct flue gas desulfurization and establish the relative contributions of gas- and liquid- phase mass transfer and inherent sorbent reactivity.
2. Field test support—evaluate various sorbents, operating conditions and process schemes to support large-scale field testings at Meredosia and Beverly.
3. Mass transfer enhancement—examine various techniques that will enable sorbent utilization rates of at least 75 percent to be achieved.

1.2 PROJECT STATUS

During the year from July 1989 through June 1990, experiments have been conducted to measure the mass transfer and kinetic rates at simulated duct injection conditions. Experiments have also been done investigating ways to enhance mass transfer at simulated duct injection conditions.

The stirred tank reactor was used to study absorption of SO_2 into saturated $\text{Ca}(\text{OH})_2$ solutions with varied ionic strengths. The results showed that varying the ionic strength of saturated $\text{Ca}(\text{OH})_2$ solution does not have a significant effect on absorption enhancement. Enhancement in the above solutions was found to be strong function of the SO_2 concentration as predicated by the surface renewal theory. No measurable absorption results were obtained during $\text{Ca}(\text{OH})_2$ slurry test at 25°C , due to the fact that the absorption was still over 70 percent gas film controlled. Experiments were run with different lime types. Tests with 0.1 M Mississippi hydrate and 0.1 M Mississippi slaked lime were run for comparison with 0.1 M reagent $\text{Ca}(\text{OH})_2$ slurry. No significant differences in reactivity were measured among these 3 limes. Additional tests with Mississippi hydrate were run to evaluate the effect of slurry solids content on SO_2 removal. Clear solution saturated with $\text{Ca}(\text{OH})_2$ was tested as the baseline followed by tests with 0.1 M and 0.4 M $\text{Ca}(\text{OH})_2$ slurry. It was found that greater SO_2 removal was obtained with $\text{Ca}(\text{OH})_2$ slurry than with saturated solution. However, no significant differences were found between the two slurries with 0.1 M and 0.4 M $\text{Ca}(\text{OH})_2$. The slurry absorption model for solution compositions which are representative of the tests performed in the stirred tank reactor was run. The slurry absorption model has been run successfully to simulate most of the clear solution experiments. Future model runs will include conditions which simulate the experiments performed in slurry solutions.

Short-time differential reactor (STDR) was used for tests investigating reactivity of sorbents with varying surface area. Several sorbents were produced using Mississippi CaO with surface area ranging from 29-75 m^2/g and porosity ranging from 29-49 percent. Higher reactivities were measured for sorbents with increased surface area following the dry, warm nitrogen conditioning of the sample prior to contact with SO_2 . These reactivities were related to the initial amount of moisture on the sorbent. Reactivity was increasing with increasing amount of initial surface moisture. Fly ash/ $\text{Ca}(\text{OH})_2$ sorbent contained significantly more initial moisture and revealed higher reactivity than any $\text{Ca}(\text{OH})_2$ produced in

the laboratory. The effect of moisture on the pore structure was investigated. Pore volume was decreasing very slightly (less than 2 percent) upon contact with humid nitrogen. The extent of recarbonation of Ca(OH)_2 upon contact with CO_2 was a function of contact time and moisture content of the gas. The decrease of Ca(OH)_2 reactivity with SO_2 when using 10 vol percent CO_2 in the gas was insignificant. Increased initial surface area of Ca(OH)_2 enhanced the extent of carbonation. No significant effect of SO_2 presence on the extent of carbonation of Ca(OH)_2 was found.

Techniques were evaluated for the production of a fine particulate Ca(OH)_2 during slaking. There was no significant effect of slurry solids concentration on median particle size, as measured by x-ray sedimentation. Increased slaking temperature resulted in a decreased median particle size—~3 and ~6 μm for 100 °C (212 °F) and 25 °C (77 °F) slaking, respectively. Two surface active additives—methyl alcohol and calcium lignosulfonate—were tested with the hope of decreasing median particle size of slaked Ca(OH)_2 . There was a marginal decrease of median particle size resulting from methyl alcohol addition. No effect was observed for calcium lignosulfonate. The quality of CaO used for slaking was found to significantly affect slaked Ca(OH)_2 median particle size. Generally, the median particle size of slaked Ca(OH)_2 decreased as the surface area of CaO used for slaking increased.

STDTR has later been modified for experiments with moist solids, in order to investigate the enhancement of mass transfer. Higher conversions were measured for sorbents with increased level of initial surface water than for dry Ca(OH)_2 . For a given contact time, the conversion generally increased with increasing initial surface water contents of solids. Chemically reacted fly ash/ Ca(OH)_2 sorbent consistently had higher conversions than physically mixed fly ash/ Ca(OH)_2 sorbent. The difference between the 2 sorbents was more pronounced for longer contact times (60 and 100 s).

Differential reactor has been modified to allow contact of solids containing varying amounts of surface water with humidified flue gas for 10-120 s. Experiments have been performed using lime/fly ash mixtures containing 5-40 percent initial free moisture. The addition of initial surface moisture to the sorbent significantly enhanced the reactivity of the sorbent towards SO_2 . At 70 °C, 1,000 ppm SO_2 , and 54-62 percent relative humidity, the conversion of solids for 60 and 120 s contact times was nearly 3 times greater for a sorbent containing 40 percent initial moisture than for a sorbent containing 3 percent

initial moisture. In the case of high SO₂ concentration (5,000 ppm), the addition of excess moisture did not increase the conversion (decreased slightly in some cases.)

Pilot plant testing was conducted to evaluate various operating conditions and process schemes to support large-scale field testing at Meredosia and Beverly. Consistent data were obtained from pilot testing of in-duct dry injection downstream of the humidifier. They showed that the recycle operation would not provide significant enhancement of SO₂ removal when the sorbent was injected downstream of the humidifier. The reactivity of the recycle material decreased rapidly after the first pass. Higher SO₂ removal and lime utilization were obtained when sorbent was injected upstream of the humidifier. The operation in this mode was much more difficult than in the downstream injection mode. Special study was conducted investigating the use of Epsom Salt (magnesium sulfate heptahydrate, MgSO₄ • 7H₂O) as an additive for in-duct dry injection to reduce the amount of water needed for humidification. Industrial grade Epsom Salt was injected into a 50-cfm pilot plant at ~3.4 lb/h. Only a 4 °F temperature drop was obtained after Epsom Salt was injected into a ~200 °F duct with 2 s residence time.

Agglomeration of damp Ca(OH)₂-based solids was investigated. Agglomeration of Ca(OH)₂ solids was found to increase as moisture content increased. The effect of the increased moisture was sharp at low values and decreased at greater values.

SECTION 2

TASK 2.1—STIRRED TANK REACTOR EXPERIMENTS

2.1 OBJECTIVE

The ultimate objective of the stirred tank reactor experiments is to simulate the gas/liquid interface of a slurry droplet exposed to SO_2 . The reactor maintains an unbroken, flat interface between SO_2 and the liquid phase. The liquid phase is stirred to simulate surface renewal times of 5-15 s. Absorption of SO_2 into several aqueous and slurry solutions has been measured. These test results will be used to verify the slurry absorption model.

2.2 STIRRED TANK AND MASS TRANSFER PROPERTIES

The design of the stirred tank reactor was described previously. The inside of the reactor was sandblasted to remove surface rust from metal plates and baffles. Also, a new gas mixture containing 1 percent SO_2 in a balance of nitrogen (instead of helium) is now being used as the reaction gas supply.

Gas Film Coefficient Comparison

The gas film mass transfer coefficient, k_g is determined as a function of a droplet's diameter and the diffusivity of the species which is diffusing into the surrounding gas. Fluid mechanics requires that a stagnant droplet (or a droplet traveling at the same velocity as the surrounding gas stream) must have a Sherwood Number ($Sh = k_d/D$) equal to 2. Using this relationship, a slurry droplet of 10 μm would have a k_g of 1.1×10^{-2} moles/ cm^2secbar . A 100 ppm droplet would have a k_g of 1.1×10^{-3} moles/ cm^2secbar . The highest value of k_g measured in the stirred tank was 1.5×10^{-4} moles/ cm^2secbar . This corresponds to a slurry droplet diameter of approximately 800 μm .

Liquid Film Coefficient Comparison

The liquid film mass transfer coefficient, k^l , is a function of the surface renewal time in the liquid. The penetration theory gives a relationship for the dependence of k^l on the surface renewal or contact time as $k^l = 2\sqrt{\pi D/t}$, where D refers to the diffusivity of SO_2 in the liquid. The amount of contact time in a spray dryer is limited to the slurry droplet drying time. This is usually on the order of 1 s and depends on the operating temperature, droplet rate and humidity. A contact time of 1 s is equivalent to a k^l of

1.77×10^{-4} m/s. For comparison, the highest value of k^*l measured in the stirred tank was 7.5×10^{-5} m/s, which is equivalent to a contact time of 5.6 s.

These comparisons show that the stirred tank is capable of representing the mass transfer properties associated with a very large droplet, with an unusually long amount of drying time. However, the ratio of the degree of gas film mass transfer to the amount of liquid film mass transfer in the stirred tank is a useful quantity which better models the properties of a slurry droplet. A k_g/k^*l of up to 30 can be obtained in the stirred tank. These conditions would also simulate a droplet having a diameter of $180 \mu\text{m}$ if a 1 s contact time were specified. Therefore, the k_g/k^*l of the reactor can simulate a reasonable slurry droplet.

2.3 TEST RESULTS

Several experiments were performed which measured the absorption of SO_2 into clear solutions and slurries of $\text{Ca}(\text{OH})_2$. During these tests, SO_2 concentration and liquid agitation speed were varied. The following presents the test results, typically depicted as values of the measured enhancement factor as a function of SO_2 concentration. Also, an attempt was made to compare these data to enhancement predicted by a simple treatment of the surface renewal theory presented by Chang and Rochelle (1979).

Clear Solution Tests

During these tests SO_2 was absorbed into several different solutions at 55°C . Liquid was fed to the reactor at a rate of 205 ml/min to prevent the buildup of species in the bulk liquid which might influence absorption or equilibrium reactions in the reactor. Solution compositions that were studied included water, 0.1 M CaCl_2 , 2.5mM $\text{Ca}(\text{OH})_2$, and 17mM (saturated) $\text{Ca}(\text{OH})_2$. Values of the enhancement factor, $\phi = kl/k^*l$, were calculated from measured absorption. The enhancement factor represents the degree that the reaction occurring in the liquid phase enhances liquid film mass transfer.

Enhancement in these solutions was found to be independent of the liquid agitation speed, but a strong function of the SO_2 concentration. The SO_2 concentration dependence was predicted by the surface renewal theory as interpreted by Chang and Rochelle (1979). The theory predicts that for SO_2 absorption in water and in CaCl_2 solutions, $\phi-1$ is proportional to $1/\sqrt{[\text{SO}_2]_i}$. The proportionality constant is a function of the diffusivities of SO_2 and bisulfite, and the equilibrium constant, K_c , of the reaction,

$\text{H}_2\text{O} + \text{SO}_2 = \text{HSO}_3 + \text{H}^+$. The results of the experiments performed in these solutions, and the predicted results of the theory are shown in Figure 2-1.

Chang and Rochelle (1979) were also able to apply the surface renewal theory to absorption in solutions containing dissolved $\text{Ca}(\text{OH})_2$. This analysis showed that $\phi-1$ for $\text{Ca}(\text{OH})_2$ solutions is proportional to $1/[\text{SO}_2]_i$. The proportionality constant depends upon the same properties listed above, as well as the concentration and diffusivity of hydroxide in the bulk solution. The results of the experiments performed in dissolved $\text{Ca}(\text{OH})_2$ solutions, and the predicted results of the theory are shown in Figure 2-2. In general, the theories overpredict the experimental data. This indicates that the species involved in the theories interact with each other in such a way that the diffusivities are altered. This would especially be true in cases where the CaOH^+ ion pair is being formed.

To investigate the effect of the ionic strength of the solution, saturated $\text{Ca}(\text{OH})_2$ solutions of varying ionic strength were tested. All tests previously run in $\text{Ca}(\text{OH})_2$ solutions and slurries have contained 0.1 M CaCl_2 . One test was run using saturated $\text{Ca}(\text{OH})_2$ solution containing no CaCl_2 . Another test was run with 0.1 M NaCl added, which is one third the ionic strength of 0.1 M CaCl_2 . SO_2 was absorbed into these solutions at 55 °C. Liquid was fed to the reactor at a rate of 205 mL/min to prevent the buildup of sulfur-containing species in the bulk liquid which might influence absorption or equilibrium reactions in the reactor. The results of these experiments were compared to the previous experiment using saturated $\text{Ca}(\text{OH})_2$ solution and 0.1 M CaCl_2 . Values of the enhancement factor, $\phi = k/k^o$, were calculated from measured absorption. The enhancement factor represents the degree that the reaction occurring in the liquid phase enhances liquid film mass transfer. Enhancement in these solutions was found to be a strong function of the SO_2 concentration. The SO_2 concentration dependence was predicted by the surface renewal theory. The theory predicts that for SO_2 absorption in $\text{Ca}(\text{OH})_2$ solutions, $\phi-1$ is proportional to $1/[\text{SO}_2]_i$. Measured enhancement for these tests is plotted as a function of SO_2 concentration in Figure 2-3. The results show that varying the ionic strength of the saturated $\text{Ca}(\text{OH})_2$ solution does not have a significant effect on absorption enhancement.

Figure 2-1. Predicted and Measured Enhancement of SO_2 Absorption in Water and 0.1M CaCl_2 .

Figure 2-2. Predicted and Measured SO_2 Absorption in Dissolved $\text{Ca}(\text{OH})_2$ Solutions with 0.1M CaCl_2 .

Figure 2-3. Absorption of SO_2 In Solutions of Varying Ionic Strength.

Ca(OH)₂ Slurry Tests

During these tests, slurry was fed to the reactor at a rate of 205 ml/min from an agitated mixtank. All slurry tests were run at 55 °C with 0.1M CaCl₂ added to the solutions. A variety of Ca(OH)₂ concentrations and lime sources were used.

The first tests used reagent grade Ca(OH)₂ purchased from a chemical supplier. Two concentrations of slurry were tested with this reagent; 35mM and 0.1M. Absorption of SO₂ was measured and the enhancement factors were calculated for several SO₂ concentrations. The results of these tests are shown in Figure 2-4, along with the test results for the case of saturated Ca(OH)₂ (no solids). Note that a linear relationship between $\bar{\phi}-1$ and $1/[SO_2]_i$ results, similar to the results seen for dissolved Ca(OH)₂. It is clear that an increase in enhancement has resulted by increasing the solids content of the slurry. However, a tripling of the solids content, from 35mM to 0.1M Ca(OH)₂ only increased enhancement by approximately 25 percent.

Calculation of the enhancement factor required a combination of several measured values, each of which has a degree of error associated. Such values include mass flow meter measurements, SO₂ concentrations, and measurement of k_g and k^o_l . Carrying the estimated errors through the calculations for $\bar{\phi}$, we have determined high and low values for the range of experimental error expected for each test run. The results of this analysis are shown in Figure 2-5 for the data taken with 35mM Ca(OH)₂ slurry.

As concentration of SO₂ in the gas phase is decreased, Figure 2-5 shows that the range of error around any data point increases greatly. This is explained by the high degree gas film resistance in the absorption process under these conditions. Gas film resistance is defined by $(P_{SO_2o} - P_{SO_2i})/P_{SO_2o}$. At low SO₂ concentrations, a larger percentage of the available bulk SO₂ is being absorbed by the liquid, causing the difference between the bulk gas and interface concentrations to become large. If the SO₂ concentration in the bulk gas is very low, reasonable measurements of enhancement cannot be obtained.

Next, experiments were run with different lime types to determine if measurement of the enhancement in the stirred tank is sensitive enough to show significant differences from one type to

Figure 2-4. Absorption of SO_2 in Reagent Grade Ca(OH)_2 Slurries (w/0.1M CaCl_2).

Figure 2-5. Estimated Error in Measured Enhancement in a 35mM Ca(OH)_2 Slurry (w/0.1M CaCl_2).

another. Tests with 0.1M Mississippi hydrate and 0.1M Mississippi slaked lime were run for comparison with 0.1M reagent Ca(OH)_2 slurry. The slaked lime was prepared by reacting Mississippi pebble quicklime, CaO , with water at a temperature between 150 - 180 °F. Fresh slaked lime is typically more reactive toward SO_2 because the Ca(OH)_2 particles are small.

Figure 2-6 compares the test results of the three lime types. Unfortunately, significant differences in enhancement were not measured between these three lime types. An analysis of the surface area of the Ca(OH)_2 particles in each slurry has not been performed. Perhaps future tests can compare results of lime types with known large differences in surface area.

Additional tests with Mississippi hydrate were run at higher solids concentrations. Tests at both 0.4M and 1.0M Ca(OH)_2 concentrations were performed. The results of the test with 0.4M Mississippi hydrate are compared to the 0.1M Mississippi hydrate test results and the saturated Ca(OH)_2 solution test results in Figure 2-7. Again, an increase in enhancement was measured, but this increase was only 10-20 percent for a 4-fold increase in solids concentration.

Figure 2-8 summarizes the previously discussed test results for Ca(OH)_2 slurries in a different form. This figure shows the difference in the increase of enhancement with solids concentration at different SO_2 concentrations in the gas phase.

Figure 2-9 shows another representation of the data presented in Figure 2-8. At the given value of k_g/k_l , a particular gas film resistance can be determined based on the measured enhancement. Choosing the k_g/k_l for the reactor that simulates a droplet with a 180 μm diameter and 1 s drying time, values of the gas film resistance are calculated as a function of solids concentration. From this plot it is easy to see the limits of the reactor. At a gas film resistance of >80 percent we have determined that experimental error is too large to measure meaningful data. This condition is reached at low solids concentrations with low concentrations of SO_2 in the bulk gas. At a solids concentration of 0.4M Ca(OH)_2 , meaningful measurements could not be made with SO_2 concentrations in the bulk gas phase less than about 3,000 ppm. It is easy to extrapolate this plot and determine why it was difficult to measure absorption in 1.0M Ca(OH)_2 .

Figure 2-6. Absorption of SO_2 in Three Types of $\text{Ca}(\text{OH})_2$ Slurries (w/0.1M CaCl_2).

Figure 2-7. Absorption of SO_2 in Mississippi Hydrate (w/0.1M CaCl_2) at Higher Concentrations.

Figure 2-8. Effect of Slurry Ca(OH)_2 Concentration on SO_2 Absorption Enhancement.

Figure 2-9. Relationship of Gas Film Resistance to Ca(OH)_2 Concentration in the Stirred Tank.

The same data can be plotted using a different value for the mass transfer ratio. Figure 2-10 shows the results of using a k_g/k_l of 62. Remember that this corresponded to a slurry droplet with a smaller diameter of about 100 μm . This figure shows that gas film resistance becomes less controlling for smaller droplets. We might expect that a 100 μm droplet with a solids concentration of 3 wt percent (0.4M) $\text{Ca}(\text{OH})_2$ would have the characteristics of gas film controlled mass transfer when exposed to a gas stream of <2,000 ppm SO_2 .

2.4 USING THE SLURRY ABSORPTION MODEL

The slurry absorption model consists of 3 parts. The first simulates absorption of SO_2 into the solution, which is enhanced by chemical reaction. Absorption of SO_2 is based on the penetration theory. The second part includes dissolution of $\text{Ca}(\text{OH})_2$ solids in the solution and is based on the film theory. The third part adds CaSO_3 crystallization calculated from a rate expression developed experimentally by Gleason and Rochelle (1987).

The results of the clear solution experiments run in the stirred tank are used to verify the first part of the model. CaSO_3 was precipitated in some of the clear solution experiments that were saturated to $\text{Ca}(\text{OH})_2$. These experiments will be used to verify both the first and third parts of the model. Later, experiments performed in slurry solutions will be used to validate these parts of the model, as well as the second part, which includes dissolution of $\text{Ca}(\text{OH})_2$ solids.

The operating conditions and solution compositions used in the stirred tank experiments had to be specified as inputs to the model. Table 2-1 lists the input variables for the clear solution experiments. The temperature, contact time and gas film coefficient, k_g , remained the same throughout most of the clear solution model runs. Contact time was varied on a few occasions to verify that it does not have an appreciable effect on the absorption rate. Model runs for each solution composition were performed with the bulk gas phase SO_2 concentration, $p\text{SO}_2$, set at 500, 1,000, 2,000, 3,000, 4,000, and 5,000 ppm. Predicted relationship of gas film resistance and total $\text{Ca}(\text{OH})_2$ concentration in a slurry droplet concentrations were set to values which represented the liquid phase at steady state in the stirred tank reactor.

Figure 2-10. Predicted Relationship of Gas Film Resistance and Total Ca(OH)₂ Concentration in a Slurry Droplet.

TABLE 2-1. INPUT VARIABLES FOR THE SLURRY ABSORPTION MODEL USED IN CLEAR SOLUTION TESTS

Operating Conditions	pSO ₂ , kg, contact time, temperature, pH
Solution Composition	Ca ²⁺ , Mg ²⁺ , Na ⁺ , K ⁺ , S(IV), S(VI), CO ₂ , Cl ⁻ , H ₂ A

The initial function of the model is to determine the concentrations, activity coefficients and diffusivities of important species, concentration based equilibrium constants, and the Henry's Law constant. This is done by calling the Bechtel Modified Radian Equilibrium (BMREQ) Program, with the specified solution composition, pH, and temperature. The information returned by BMREQ provides all the necessary input for the main program to perform the absorption calculations. The theory behind the model calculations was described in progress reports issued in December 1988 and April 1989.

The model provides 2 main forms of output. The long version includes concentration profiles of all important species as a function of distance from the interface at incremental fractions of the contact time. The short version reports average the absorption rate of SO₂, NSO₂, at incremental values of contact time.

To arrive at the value of the enhancement factor, the expression for liquid phase absorption is solved for ϕ .

$$N_{SO_2} = \phi k^o_1 A ([SO_2]_i - [SO_2]_o) \quad 2-1$$

Values of the enhancement factor calculated by the model are compared to the enhancement measured in the stirred tank reactor to verify the model.

2.5 RESULTS OF EXPERIMENTS AND MODEL PREDICTIONS

Enhancement measured in the stirred tank was compared to that predicted by solution of the surface renewal theory expressions developed by Chang and Rochelle (1979). The BMREQ program defined more accurately the composition of the liquid phase in the reactor during the experiments. Using this more refined estimate of the liquid composition, the equations for the surface renewal solutions were resolved. These results are compared to the data collected from the stirred tank experiments, and to the new predictions of SO₂ absorption generated by the slurry absorption model.

In general, it was found that the slurry absorption model, as presently written and interpreted, overpredicts measured absorption by 2-10 percent for most of the clear solutions studied. Experimental measurements tend to be predicted well by the surface renewal theory solutions proposed by Chang and Rochelle, except when gas film resistance of the absorption becomes appreciable.

It is expected that, once modified, the slurry absorption model will more closely predict the measured enhancement in clear solutions because of its ability to consider the effects of many species present in the bulk liquid at steady state. It has the advantage of being able to account for gas film resistance, dissolution of $\text{Ca}(\text{OH})_2$ solids, and CaSO_3 crystallization. However, this level of detail makes the model complicated. In fact, because the model initially ran so slowly on the VAX 8600 it is presently configured to run on the Cray X-MP at the University of Texas Center for High Performance Computing.

2.5.1 Enhancement in Water

Enhancement of SO_2 absorption in water was measured in the stirred tank reactor over a narrow range of SO_2 concentrations at varied liquid agitation speeds. The initial pH of the water was adjusted to 5.0 with a small amount of HCl so that absorption would not be biased by the presence of alkaline species in the water. These tests confirmed that varying the liquid agitation speed, (i.e., k^l or contact time) does not have a significant effect on enhancement of SO_2 absorption. The results showed that for SO_2 concentrations between 2,200 and 2,450, the reaction of SO_2 with pure water enhanced SO_2 absorption by a factor of 3 over absorption of SO_2 into a non-reactive solution.

Enhancement of SO_2 absorption in water can be estimated by the surface renewal theory as interpreted by Chang and Rochelle (1979).

$$\phi = 1 + \frac{\sqrt{D_{\text{HSO}_3^-}}}{\sqrt{D_{\text{SO}_2}}} \frac{\sqrt{K_c / 4}}{\sqrt{[\text{SO}_2]_i} - \sqrt{[\text{SO}_2]_o}} \quad 2-2$$

The theory predicts a linear dependence of ϕ on $1 / \sqrt{[\text{SO}_2]_i}$ when $[\text{SO}_2]_o$ can be neglected. The proportionality constant is a function of the diffusivities of SO_2 and bisulfite, and the concentration-based equilibrium constant, K_c , of the reaction:

2-3

In a solution of pure water, the effective diffusivity of HSO_3^- is altered by charge balance constraints. The HSO_3^- and H^+ ions formed by the reaction in Equation 2-3 must diffuse at the same rate to maintain electrical neutrality of the solution. Diffusivities of HSO_3^- and H^+ at 55 °C are 2.54×10^{-5} and $1.78 \times 10^{-4} \text{ cm}^2/\text{s}$, respectively. An effective diffusivity of $4.45 \times 10^{-5} \text{ cm}^2/\text{s}$ for both species is calculated using:

$$\frac{2}{D_{\text{eff}}} = \frac{1}{D_{\text{HSO}_3^-}} + \frac{1}{D_{\text{H}^+}}$$

2-4

The slurry absorption model was run with bulk solution concentrations and other conditions that simulated the absorption experiments in water. The amount of total sulfur in the reactor liquid at steady state was calculated to be about 0.5 mM by material balance. The bulk solution pH was determined by knowing that the H^+ concentration must be approximately equal to the HSO_3^- concentration at steady state as per Equation 2-3. A charge balance performed by the slurry absorption model was checked to assure the correct solution composition.

The remainder of the component concentrations were determined by BMREQ, which is called by the slurry absorption model. Table 2-2 summarizes the conditions and compositions used to simulate the solution in the stirred tank. The results from this model, the surface renewal theory prediction and the measured results in the stirred tank reactor are shown together in Figure 2-11.

The enhancement measured in the stirred tank reactor experiments compares well with the surface renewal prediction at the SO_2 concentrations studied. The slurry absorption model predicts somewhat higher enhancement than the surface renewal theory.

2.5.2 Enhancement in 0.1 M CaCl_2 Solution

The effect that calcium chloride has on SO_2 absorption was studied by absorbing SO_2 into a solution containing 0.1 M CaCl_2 . Absorption in this solution differs from absorption in water because the ionic strength is altered. With CaCl_2 present, the requirement for electrical neutrality permits H^+ and HSO_3^- species to diffuse independently.

Figure 2-11. Enhancement of SO_2 Absorption in Water.

TABLE 2-2. CONDITIONS FOR SLURRY ABSORPTION MODEL FOR ABSORPTION OF SO₂ IN WATER

Concentrations of Important Species (mM)	
H ⁺	0.515
OH ⁻	1.4 x 10 ⁻⁷
SO ₂	3.13 x 10 ⁻²
HSO ₃ ⁻	0.469
SO ₃ ⁻²	4.1 x 10 ⁻⁵
Cl ⁻	0.046
Other Conditions	
Temperature	55 °C
pH	3.3
kg	1.44 x 10 ⁻⁵ mol/Pa m ² s
Contact time	7.53 s
pSO ₂	500-5,000 ppm

Experiments in 0.1 M CaCl₂ solutions measured enhancement at several SO₂ concentrations. Also, experiments were run at similar SO₂ concentrations with varied liquid agitation speeds to confirm that changing liquid agitation speeds (i.e., contact times) had a negligible effect on absorption of SO₂. Again the initial pH was adjusted to 5.0 with a small amount of HCl.

The enhancement factor ranged between 3 at the high SO₂ concentrations near 4500 ppm, to 5.5 at the low SO₂ concentration of 1,000 ppm. At an SO₂ concentration of 2500 ppm, enhancement was improved about 30 percent over enhancement measured in water.

The enhancement factor in CaCl₂ solutions can be estimated by the surface renewal theory as developed by Chang and Rochelle (1979).

$$\phi = 1 + \frac{\sqrt{D_{\text{HSO}_3^-}}}{\sqrt{D_{\text{SO}_2}}} \frac{[\text{HSO}_3^-]_i - [\text{HSO}_3^-]_o}{[\text{SO}_2]_i - [\text{SO}_2]_o} \quad 2-5$$

The bulk concentrations of aqueous SO₂ and bisulfite can be neglected in most cases. The interfacial bisulfite concentration, [HSO₃⁻]_i, is determined from the equilibrium relationship for the reaction in Equation 2-3 and solution of material and charge balances at the interface for the hydrogen ion concentration. Chang and Rochelle (1979) solved these expressions to arrive at

$$[\text{HSO}_3^-]_i = \frac{[\text{HSO}_3^-]_o - R[\text{H}^+]_o + \sqrt{([\text{HSO}_3^-]_o - R[\text{H}^+]_o)^2 + 4 R K_c [\text{SO}_2]_i}}{2}$$

where $R = \frac{\sqrt{D_{\text{H}^+}}}{\sqrt{D_{\text{HSO}_3^-}}}$ 2-6

Because $[\text{HSO}_3^-]_i$ depends on the square root of $[\text{SO}_2]_i$ this theory again shows a dependence of ϕ on $1 / \sqrt{[\text{SO}_2]_i}$.

The slurry absorption model was run with bulk solution concentrations and other conditions that simulated the absorption experiments in 0.1 M CaCl_2 . The amount of total sulfur in the reactor liquid was calculated to range between 0.4 and 2.0 mM by material balance. Again, the bulk solution pH was determined by knowing that the H^+ concentration must be approximately equal to the HSO_3^- concentration as per Equation 2-4, and by checking the charge balance of ionic species. The remainder of the component concentrations were determined by BMREQ.

Two solution compositions were prepared, representing 0.5 and 0.8 mM total sulfur species. Table 2-3 summarizes the conditions and compositions used to simulate the solution in the stirred tank. Enhancement predicted by this model, the surface renewal theory prediction, and the measured results in the stirred tank reactor are shown together in Figure 2-12.

The surface renewal theory slightly overpredicts the measured absorption. Again, the surface renewal solution is based on having only water (with Ca^{+2} and Cl^-) present as an initial condition. Actual absorption in the reactor under steady state conditions takes place in the presence of additional species in the bulk liquid. The presence of sulfur containing species has a measurable effect on enhancement of the absorption of SO_2 .

Figure 2-12. Enhancement of SO_2 Absorption in 0.1 M $CaCl_2$ Solution.

TABLE 2-3. CONDITIONS FOR SLURRY ABSORPTION MODEL FOR ABSORPTION OF SO₂ IN 0.1 M CaCl₂

Concentrations of Important Species (mM)		
	Case 1	Case 2
H ⁺	0.843	0.497
OH ⁻	1.35 x 10 ⁻⁷	2.28 x 10 ⁻⁷
SO ₂	4.75 x 10 ⁻²	1.79 x 10 ⁻²
HSO ₃ ⁻	0.750	0.479
SO ₃ ⁻²	1.32 x 10 ⁻⁴	1.43 x 10 ⁻⁴
Ca ⁺²	100	100
CaSO ₃ o	2.56 x 10 ⁻³	2.78 x 10 ⁻³
CaOH ⁺	9.97 x 10 ⁻⁸	1.69 x 10 ⁻⁷
Cl ⁻	200	200

Other Conditions		
	Case 1	Case 2
Temperature (°C)	55	55
pH	3.15	3.38
kg (mol/Pa m ² s)	1.44 x 10 ⁻⁵	1.44 x 10 ⁻⁵
Contact Time (s)	7.53	7.53
pSO ₂ (ppm)	500-5,000	500-5,000

The slurry absorption model slightly overpredicts the measured results. The results measured in the stirred tank represent solutions with a range of S(IV) concentrations. As the slurry absorption model shows, the S(IV) concentration of the liquid has little effect on enhancement at high SO₂ concentrations, but it has a significant effect at concentrations below about 2,000 ppm SO₂.

The additional enhancement in CaCl₂ solutions predicted by the surface renewal theory and observed in the experiments is a result of Cl⁻ being present, allowing HSO₃⁻ and H⁺ to diffuse independently. In other words, the reaction of SO₂ in the CaCl₂ solution is not inhibited by the ion-pairing effect.

2.5.3 Enhancement in 2.5 mM Ca(OH)₂ Solution Containing 0.1 M CaCl₂

The SO₂ concentrations studied for absorption in 2.5 mM Ca(OH)₂/0.1 M CaCl₂ ranged from 1,070 to 5,450 ppm. Enhancement factors measured during these tests ranged from 5.0, at high SO₂ concentrations, to 17.2 at the low concentrations.

Chang and Rochelle (1979) were also able to apply the surface renewal theory to absorption in solutions containing dissolved $\text{Ca}(\text{OH})_2$. The following general solution for enhancement was derived:

$$\begin{aligned} \phi = 1 + \frac{\sqrt{D_{\text{HSO}_3^-}}}{\sqrt{D_{\text{SO}_2}}} \left(\frac{[\text{HSO}_3^-]_i - [\text{HSO}_3^-]_o}{[\text{SO}_2]_i - [\text{SO}_2]_o} \right) \\ + \frac{\sqrt{D_{\text{SO}_3^{2-}}}}{\sqrt{D_{\text{SO}_2}}} \left(\frac{[\text{SO}_3^{2-}]_i - [\text{SO}_3^{2-}]_o}{[\text{SO}_2]_i - [\text{SO}_2]_o} \right) \end{aligned} \quad 2-7$$

The solution compositions that were determined by the BMREQ program show that some of the bulk solution terms in this equation can be neglected. In all solutions containing $\text{Ca}(\text{OH})_2$ that were modeled, $[\text{SO}_2]_o$ and $[\text{HSO}_3^-]_o$ were found to be insignificant. For all solutions saturated to $\text{Ca}(\text{OH})_2$, the buildup of sulfite in the bulk liquid, $[\text{SO}_3^{2-}]_o$, was also unimportant.

The interfacial concentrations of sulfite and bisulfite are not known, but are related to $[\text{H}^+]_i$ and $[\text{SO}_2]_i$ by equilibrium relations for the reactions. For absorption of SO_2 in $\text{Ca}(\text{OH})_2$, the following reactions are also important:

The equilibrium expression for these reactions and the initial absorption reaction shown in Equation 2-3 are:

$$[\text{HSO}_3^-]_i = \frac{K_{c1} [\text{SO}_2]_i}{[\text{H}^+]_i} \quad 2-10$$

$$[\text{SO}_3^{2-}]_i = \frac{K_{c1} K_{c2} [\text{SO}_2]_i}{[\text{H}^+]_i^2} \quad 2-11$$

$$[\text{OH}^-]_i = \frac{K_w}{[\text{H}^+]_i}$$

2-12

When the appropriate bulk concentrations are neglected and the two equilibrium expressions are applied to Equation 2-7, the equation for the enhancement factor becomes:

$$\phi = 1 + \frac{\sqrt{D_{\text{HSO}_3^-}}}{\sqrt{D_{\text{SO}_2}}} \frac{K_{c1}}{[\text{H}^+]_i} + \frac{\sqrt{D_{\text{SO}_3^{2-}}}}{\sqrt{D_{\text{SO}_2}}} \left(\frac{K_{c1} K_{c2}}{[\text{H}^+]_i^2} + [\text{SO}_3^{2-}]_o \right) \quad 2-13$$

$[\text{H}^+]_i$ can be found by solving the following equation, which was derived by Chang and Rochelle from solution of surface renewal theory material balances for SO_2 and acidity:

$$\begin{aligned} & \sqrt{D_{\text{H}^+}} [\text{H}^+]_i^3 + (\sqrt{D_{\text{HSO}_3^-}} [\text{HSO}_3^-]_o - \sqrt{D_{\text{H}^+}} [\text{H}^+]_o) [\text{H}^+]_i^2 \\ & + 2 \sqrt{D_{\text{SO}_3^{2-}}} [\text{SO}_3^{2-}]_o + \sqrt{D_{\text{OH}^-}} [\text{OH}^-]_o) [\text{H}^+]_i^2 \\ & - (\sqrt{D_{\text{HSO}_3^-}} [\text{SO}_2]_i K_{c1} + \sqrt{D_{\text{OH}^-}} K_w) [\text{H}^+]_i \\ & - 2 \sqrt{D_{\text{SO}_3^{2-}}} [\text{SO}_2]_i K_{c1} K_{c2} = 0 \end{aligned} \quad 2-14$$

The slurry absorption model was run with bulk solution concentrations and other conditions that simulated the absorption experiments in the 2.5 mM $\text{Ca}(\text{OH})_2/0.1 \text{ M CaCl}_2$ solution. Since the addition of $\text{Ca}(\text{OH})_2$ made the solution very alkaline, the bulk solution pH was determined by estimating the OH^- concentration.

The initial amount of OH^- added to the feed was 5.0 mM. The net result of Equations 2-3, 2-11 and 2-12 requires that for every mole of SO_3^{2-} formed, one mole of OH^- is consumed. The amount of total sulfur in the reactor liquid was calculated to range between 0.5 and 2.2 mM by material balance. A typical value of 1.0 mM was chosen as the total steady state S(IV) concentration for modelling purposes. Therefore, the initial pH was chosen such that the sum of OH^- and CaOH^+ concentrations was near 4.0 mM. The pH was then fine tuned to assure a proper charge balance.

The remainder of the component concentrations were determined by BMREQ, which is called by the slurry absorption model. Table 2-4 summarizes the conditions and compositions used to simulate the

TABLE 2-4. CONDITIONS FOR SLURRY ABSORPTION MODEL FOR ABSORPTION OF SO₂ IN
2.5 mM Ca(OH)₂/0.1 M CaCl₂

Concentrations of Important Species (mM)	
H ⁺	5.97 x 10 ⁻⁸
OH ⁻	1.90
SO ₂	negligible
HSO ₃ ⁻	1.97 x 10 ⁻⁵
SO ₃ ²⁻	4.90 x 10 ⁻²
Ca ⁺²	100
CaSO ₃ o	0.95
CaOH ⁺	1.41
Cl ⁻	200
Other Conditions	
Temperature	55 °C
pH	10.3
kg	1.44 x 10 ⁻⁵ mol/Pa m ² s
Contact time	10 s
pSO ₂	500-5,000 ppm

solution in the stirred tank. The results of the slurry absorption model are plotted with enhancement estimated by the surface renewal theory, and enhancement measured in the stirred tank reactor in Figure 2-13.

Several points can be made about the measured absorption data and the models. First, the surface renewal theory does a much better job of predicting enhancement in this solution than it did for the CaCl₂ solution. The slurry absorption model nearly predicts absorption over the range of SO₂ concentrations studied.

We saw in the previous experiments in water at 55 °C that for the range of SO₂ concentration studied, enhancement was strictly a function of SO₂ concentration at the interface. The surface renewal theory, slurry absorption model and experiments performed in CaCl₂ solution showed that the level of absorbed sulfur species (i.e., bisulfite) could influence enhancement. In the experiments involving Ca(OH)₂ liquid phase reactions become more complicated.

Several test runs were made in the stirred tank with 2.5 mM Ca(OH)₂/0.1 M CaCl₂ solution. This was fortunate because so many experimental conditions had the potential to affect the measured

Figure 2-13. Enhancement of SO_2 Absorption in 2.5 mM $\text{Ca}(\text{OH})_2/0.1 \text{ M CaCl}_2$ Solution.

enhancement. Take, for instance, the test runs which resulted in a concentration of $[\text{SO}_2]_i$ near 1.3-1.4 mM. The results of these tests are shown again in Table 2-5 for comparison.

The results suggest that either the change in contact time or the buildup of S(IV) species in the liquid (i.e., CaSO_3) could be influencing the measured absorption. Although a change in contact time should not affect the enhancement factor, the amount of CaSO_3 formed could.

An unknown factor is how much of the CaSO_3 precipitated during the individual runs. The solutions studied quickly reached a supersaturated concentration of CaSO_3 at steady state. During some of the experiments, it was noted that the solution became cloudy, and during experiments where the absorption rate was greatest (i.e., high bulk gas SO_2 concentrations) formation of small, round platelets was observed. These were assumed to be formed from CaSO_3 crystals. Perhaps absorption of SO_2 into solutions that are supersaturated to CaSO_3 as compared to those solutions that are merely saturated to CaSO_3 (i.e., CaSO_3 is precipitating) differs measurably. Once the slurry absorption model is verified for clear solutions it will be run under conditions with varied amounts of CaSO_3 solids present to explore differences in absorption due to CaSO_3 crystallization.

This should, however, only be of concern in describing the absorption of SO_2 in dilute solutions of $\text{Ca}(\text{OH})_2$. In slurry solutions, and solutions saturated to $\text{Ca}(\text{OH})_2$, crystallization and precipitation of CaSO_3 will surely occur, and the bulk liquid will always be saturated to CaSO_3 .

2.5.4 Enhancement in 17 mM $\text{Ca}(\text{OH})_2$ Solution Containing 0.1 M CaCl_2

Another set of experiments was run with $\text{Ca}(\text{OH})_2$ at 17 mM, the level of saturation. This set of conditions is particularly interesting because it represents the same conditions in the dissolved portion of

TABLE 2-5. COMPARISON OF ENHANCEMENT FOR TESTS AT CONSTANT
 $[\text{SO}_2]_i = 1.3 - 1.4 \text{ mM}$

Test #	SO_2 Conc. (ppm)	$K^*l \times 10^5$ (m/s)	Contact Time (s)	$\emptyset$	$[\text{S(IV)}]_0$ (mM)	Gas Film Res. (%)
CD8	3600	7.4	5.9	9.4	2.2	18
CD14	3110	6.5	7.5	9.1	1.8	17
CD17	3140	4.9	13.1	7.4	1.2	11
CD5	2760	3.6	24.0	6.1	0.7	7

a slurry solution. The only difference between it and a slurry solution is the ability of the slurry solution to regenerate the reacted $\text{Ca}(\text{OH})_2$ with dissolution of lime solids.

The SO_2 concentrations studied during experiments in 17 mM $\text{Ca}(\text{OH})_2$ ranged from 580 to 3790 ppm. The enhancement factor measured during these tests ranged from about 13, at the high SO_2 concentrations, up to 60 at a low SO_2 concentration. Some of the test conditions resulted in absorption that was too gas film controlled to accurately determine the enhancement. Typically these were the tests conducted at the lower SO_2 concentrations. Gas film resistance for the test runs varied from 12 percent to 83 percent. Three test runs with gas film resistance of 70 percent and greater resulted in invalid measurements. Measurements made for tests with over 40 percent to 50 percent gas film resistance are more susceptible to error. The tendency for a gas film controlled absorption increased as more $\text{Ca}(\text{OH})_2$ was added to the solutions tested.

The slurry absorption model was run with bulk solution concentrations and other conditions that simulated saturated 17 mM $\text{Ca}(\text{OH})_2/0.1 \text{ M CaCl}_2$ solution. The bulk solution pH was determined by estimating the OH^- concentration, as described previously for the more dilute $\text{Ca}(\text{OH})_2$ solution. The amount of total sulfur in the reactor liquid was calculated to range between 0.9 and 3.8 mM by material balance. A typical value of 2.0 mM was chosen as the total S(IV) concentration for modelling purposes.

The pH of 11.3 was chosen such that the OH^- and CaOH^+ concentrations summed close to 34 mM, however, the charge balance was off by 2 mM. The model had difficulties running under this solution composition. Data could not be generated under for a solution composition with a lower pH which would close the charge balance with more accuracy. Because the pH used is a bit high, the absorption rate will be slightly overpredicted.

The remainder of the component concentrations were determined by BMREQ. The solution was assumed to be saturated to CaSO_3 , since the calcium sulfite precipitated during all of the experiments. Table 2-6 summarizes the conditions and compositions used to simulate the saturated solution in the stirred tank.

As previously mentioned, Chang and Rochelle (1979) used the surface renewal theory to predict that the enhancement factor in $\text{Ca}(\text{OH})_2$ solutions is proportional to $1/[\text{SO}_2]_i$. Using Equations (2-13) and

TABLE 2-6. CONDITIONS FOR SLURRY ABSORPTION MODEL FOR ABSORPTION OF SO₂ IN
17 mM Ca(OH)₂/0.1 M CaCl₂

Concentrations of Important Species (mM)	
H ⁺	6.08 x 10 ⁻⁹
OH ⁻	18.6
SO ₂	negligible
HSO ₃ ⁻	4.07 x 10 ⁻⁶
SO ₃ ²⁻	0.10
Ca ⁺²	101.3
CaSO _{3o}	1.90
CaOH ⁺	13.8
Cl ⁻	198
Other Conditions	
Temperature	55 °C
pH	11.3
kg	1.44 x 10 ⁻⁵ mol/Pa m ² s
Contact time	7.53 s
pSO ₂	500-5,000 ppm

(2-14) with an OH⁻ concentration of 19 mM, enhancement for SO₂ absorption in saturated Ca(OH)₂ solution was estimated. The results of the slurry absorption model are plotted with enhancement estimated by the surface renewal theory, and enhancement measured in the stirred tank reactor in Figure 2-14.

The slurry absorption model appears to overpredict the measured absorption. The surface renewal theory solution only did an adequate job of describing the absorption at very high SO₂ concentrations (i.e., low values of 1/[SO₂]_i).

As previously mentioned, many of the experiments showed high levels of gas film control, especially at lower SO₂ concentrations. The experimental points which are above 1/[SO₂]_i values of 2,000 are 40-60 percent gas film controlled. Since the surface renewal theory can only describe liquid phase phenomena, it is not capable of predicting enhancement of absorption when the gas film control of the absorption becomes appreciable. The slurry absorption model must be used in cases where both gas- and liquid-film resistances are important.

Figure 2-14. Enhancement of SO_2 Absorption in 17 mM $\text{Ca}(\text{OH})_2/0.1 \text{ M CaCl}_2$ Solution.

2.6 FUTURE WORK AND TEST SCHEDULE

A test plan for future work with the stirred tank reactor is presented in Table 2-7.

Modeling efforts will continue. The absorption data produced by the slurry absorption model will be reviewed for computational errors, and computer code will be reviewed. These efforts should produce model data for clear solutions which can be validated by the experiments. Once the model is validated, emphasis will be placed on simulating conditions of the slurry experiments previously performed in the stirred tank.

2.7 REFERENCES CITED

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TABLE 2-7. TEST PLAN

Experiments	Liquid Phase	Temp	SO ₂ Concentration	Up Agitator Speed	Lower Agitator Speed	Additive
Clear Solution Tests	34mM NaOH	55 C	500-5,000ppm	maximum	150 -1400 rpm	0.3M NaCl
CaSO ₃ Slurry Tests	Ca(OH) ₂ sat, 1M CaSO ₃ (s)	55 C	500-5,000ppm	maximum	150 -1400 rpm	0.1M CaCl ₂
	Ca(OH) ₂ slurry, CaSO ₃ (s)	55 C	500-5,000ppm	maximum	150 -1400 rpm	0.1M CaCl ₂
Buffer Additives	Ca(OH) ₂ sat, adipic acid	55 C	500-5,000ppm	maximum	150 -1400 rpm	0.1M CaCl ₂
	Ca(OH) ₂ slurry, adipic acid	55 C	500-5,000ppm	maximum	150 -1400 rpm	0.1M CaCl ₂
	Ca(OH) ₂ sat, MEA	55 C	500-5,000ppm	maximum	150 -1400 rpm	0.1M CaCl ₂
	Ca(OH) ₂ slurry, MEA	55 C	500-5,000ppm	maximum	150 -1400 rpm	0.1M CaCl ₂
Viscosity Modifiers	0.4M Miss Hydrate/inert solids	55 C	500-5,000ppm	maximum	150 -1400 rpm	0.1M CaCl ₂
	0.4M Miss Hydrate/polymer	55 C	500-5,000ppm	maximum	150 -1400 rpm	0.1M CaCl ₂
CO ₂ Effects	Ca(OH) ₂ sat/ CO ₂ in gas phase	55 C	500-5,000ppm	maximum	150 -1400 rpm	0.1M CaCl ₂
	Ca(OH) ₂ sat/ CO ₂ in gas phase	55 C	500-5,000ppm	maximum	150 -1400 rpm	0.1M CaCl ₂

SECTION 3

TASK 2.3—SHORT-TIME DIFFERENTIAL REACTOR

3.1 INTRODUCTION

The objective of this task is to identify rate limiting steps for the reaction of Ca(OH)_2 with SO_2 by measuring rates of gas/solid reaction at contact times of 0.5-5 s using a STDR. Several sorbents were produced from commercial Mississippi CaO employing the so-called "double hydration" method with alcohol. This technique allowed to produce sorbents with nitrogen B.E.T. surface area as high as $75 \text{ m}^2/\text{g}$. The effect of moisture on the structural properties of Ca(OH)_2 was also investigated during this reporting period. Additionally, the effect of CO_2 in the simulated flue gas on the reactivity of Ca(OH)_2 was measured for varying CO_2 concentration. The extent of recarbonation of Mississippi Ca(OH)_2 upon contact with CO_2 -containing moist and dry nitrogen was evaluated by thermogravimetry.

3.2 SORBENT PREPARATION

In order to investigate the solid phase diffusion in the reaction of Ca(OH)_2 with SO_2 , it was necessary to produce sorbents with varying specific surface area. This was accomplished by using the so called "double-hydration" method. According to this method, CaO is hydrated first in a conventional manner. The resulting calcium hydroxide is next calcined in such a fashion as to yield the mixture of $\text{Ca(OH)}_2/\text{CaO}$ with 10-15 wt percent of Ca(OH)_2 after calcination. This product is then hydrated with the mixture of alcohol/water yielding Ca(OH)_2 with high surface area. The final surface area can be controlled by the alcohol/water ratio used during the second hydration.

For the sorbents discussed in this progress report, the hydrator described in the previous quarterly progress report was used. In the first step, commercial Mississippi CaO was hydrated with 2.6 times stoichiometrically required amount of water (alternatively, commercial Mississippi Ca(OH)_2 was used). The CaO was heated to 100°C (212°F) prior to injection of the desired amount of boiling water. Calcination was performed for 16 h in the muffle furnace at 600°C ($1,112^\circ\text{F}$) with nitrogen blanketing. The secondary hydration was also performed with 2.6 times stoichiometrically required amount of water. The $\text{CaO}/\text{Ca(OH)}_2$ calcination product was heated to 74°C (165°F) prior to the injection of 67°C

(153 °F) mixture of methyl alcohol and water at the desired ratio. This ratio was varied from 5:1-0.1:1 by volume.

Alcohol has been selected as an additive capable of increasing the surface area of sorbents because it is believed that by the completion of hydration, the alcohol will have evaporated, leaving residue-free $\text{Ca}(\text{OH})_2$. Other well known means of increasing the surface area of $\text{Ca}(\text{OH})_2$ (such as addition of sugar) result in complex compounds after the hydration is complete. Having residue-free $\text{Ca}(\text{OH})_2$ allows to eliminate side effects of chemical impurities.

3.3 SORBENT CHARACTERIZATION

The sorbents produced in the laboratory were characterized extensively. The characterization included:

- Specific surface area, porosity, pore size distribution by nitrogen adsorption/desorption
- Degree of hydration, amount of surface moisture, degree of recarbonation by thermogravimetry
- Morphology by scanning electron microscopy

The sorbents produced are presented in Table 3-1, giving their structural properties, parameters of hydration, and thermogravimetric data. Specific surface area was increasing with the increasing alcohol/water ratio and reached an experimental maximum of 75 m^2/g for the sorbent produced with 5:1 alcohol-to-water ratio. Porosity was increasing with increasing specific surface area. There was a unique correlation between these two parameters as shown in Figure 3-1. The development pore structure of sorbents produced by "double hydration" is shown in Figure 3-2, giving incremental pore volume for several sorbents. Gradual increase of pore volume was evident for pores in the 100–800 Å size range. For sorbents with surface area in excess of 70 m^2/g , the maximum amount of pore volume was associated with pores in 200–400 Å size range. Sorbents produced by "double hydration" were capable of developing significantly higher pore volume than the ones hydrated conventionally (single hydration without alcohol). This is shown in Figure 3-3 comparing sorbents with maximum surface areas produced as a result of single (conventional) and "double hydration." More pore volume was measured in the

TABLE 3-1 HYDRATION PARAMETERS AND PROPERTIES OF SORBENTS PRODUCED BY "DOUBLE HYDRATION" WITH ALCOHOL
(COMMERCIAL MISSISSIPPI CaO OR Ca(OH)₂ USED)

Sorbent Name	Alcohol/Water ^a [mL/mL]	Surface Area [m ² /g]	Porosity [%]	Median Pore Size [Å]	Amount ^b of Surface water[wt %]	Amount ^c of CO ₂ [wt %]	Degreed of hydration [wt %]
Miss 6	5:1	75	45	229	0.77	0.51	98.29
Miss 7	1:1	48	31	163	0.55	0.33	97.00
Miss 9	0.1:1	29	29	249	0.81	0.47	95.30
Miss 10	3:1	72	48	231	0.42	1.15	95.12
Miss 11	2:1	63	41	192	0.23	0.91	95.72

^aAlways 2.6 times stoichiometrically required amount of water used CaO/Ca(OH)₂ at 74 °C (165 °F), alcohol/water at 67 °C (153 °F)

^bWeight decrease measured by TGA between 20-100 °C (68-212 °F)

^cWeight decrease measured by TGA between 550-700 °C (1022-1292 °F)

^dWeight decrease measured by TGA between 100-550 °C (212-1022 °F)

Figure 3-1. Correlation between specific surface area and porosity of Mississippi Ca(OH)₂.

Desorption Pore Volume Plot Mississippi Ca(OH)₂

Figure 3-2. Development of pore structure by Mississippi Ca(OH)₂ produced by double hydration.

Desorption Pore Volume Plot Mississippi Ca(OH)2

Figure 3-3. Comparison of pore structure developed by sorbents produced by regular (Miss 2) and double (Miss 10) hydration.

50–700 Å size range for the "double hydrate" with alcohol (hydrated with 2.6 times stoichiometrically required amount of water) than for the single hydrate (hydrated with 5 times stoichiometrically required amount of water). The development of pore structure for sorbents produced by laboratory– scale regular hydration is demonstrated in Figure 3-4. The pore volume, even though greater than that measured for the commercial Mississippi Ca(OH)_2 , was lower than pore volume of the Ca(OH)_2 produced by "double hydration."

Based on TGA data presented in Table 3–1, sorbents produced by "double hydration" had less than 1 wt percent of surface moisture. The samples measured were all 95 percent or more Ca(OH)_2 . The amount of recarbonation measured was typical for hydrated lime.

Scanning electron microscope (SEM) evaluation of morphology of sorbents produced by double hydration revealed clusters of submicron particles, typical for Ca(OH)_2 . This is shown in Figures 3-5 and 3-6 for 48 and 75 m^2/g Mississippi Ca(OH)_2 , respectively. Both samples consist of agglomerates of highly irregular grains/particles. However, grains/particles appear to be finer for 75 m^2/g sorbent than for the 48 m^2/g one.

3.4 EFFECT OF SURFACE MOISTURE ON PORE STRUCTURE

The effect on surface moisture on the pore structure of Mississippi Ca(OH)_2 was investigated. The sorbent used for this study was a commercial Mississippi Ca(OH)_2 . Total pore volume, as well as pore size distribution before and after the exposure to the humid nitrogen was determined by nitrogen adsorption/desorption (machine error is 1 percent). The relative humidity was 40 or 80 percent and the conditioning time was 5 or 300 s. The humid gas did not contain SO_2 during this series of experiments which allowed to differentiate between possible changes of pore structure due to the contact with moisture and more plugging due to the deposition of the reaction product. The sample for nitrogen adsorption/desorption was produced in the STDR.

The results of pore volume measurement are presented in Table 3-2, giving the relative change of pore volume and surface area as a result of conditioning. For the 5 s conditioning time at both 40 and 80 percent relative humidity the change was below 2 percent. Increasing the conditioning time with 40 percent relative humidity gas to 300 s resulted in somewhat larger pore volume decrease of

TABLE 3-2 EFFECT OF MOISTURE ON PORE VOLUME AND SURFACE AREA

Relative Humidity of Conditioning Gas [%]	Conditioning Time [s]	Pore volume ^a Change [%]	Surface Area Change [%]
40	5	+0.3	-10.7
80	5	-1.7	-16.0
40	300	-7.0	-8.6

^a Pores smaller than 1181 Å

Figure 3-4. Development of pore structure by Mississippi $\text{Ca}(\text{OH})_2$ produced by regular hydration.

Figure 3-5. SEM photograph of Mississippi $\text{Ca}(\text{OH})_2$, $S_A = 48 \text{ m}^2/\text{g}$, $\times 5,000$.

Figure 3-6. SEM photograph of Mississippi Ca(OH)_2 , $S_A = 75 \text{ m}^2/\text{g}$, x 5,000.

7 percent. Approximately 10 percent decrease of specific surface area was measured as a result of conditioning with 40 percent relative humidity nitrogen. Following 5 s conditioning with 80 percent relative humidity nitrogen, the surface area decreased 16 percent. Pore size distribution was also measured on conditioned samples and results are presented in Figures 3-7 and 3-8. Figure 3-7 gives the differential pore volume after 5 s conditioning with 40 and 80 percent relative humidity nitrogen. Conditioning the sorbent with humid gas resulted in decreased pore volume for 50-300 Å size range. In this size range, the decrease was higher for high relative humidity. The effect of conditioning time was investigated at relative humidity of 40 percent. Increasing the conditioning time did not result in further deterioration of pores in 50-300 Å range, as evident from Figure 3-8. The decrease of pore volume associated with pores in 500-1,000 Å range was responsible for the overall 7 percent decrease of pore volume upon prolonged conditioning time.

Certain decrease of pore volume associated with 50-300 Å pore size took place upon conditioning described above. For conditioning representative of duct conditions (5 s), the decrease of the overall pore volume was insignificant.

3.5 EFFECT OF MOISTURE ON REACTIVITY

In previous reports, the data was presented indicating relatively significant effect of sorbent conditioning on the reactivity with SO₂. During this reporting period the amount of moisture was measured by the TGA for different conditioning schemes and for sorbents with varying surface area. The results are presented in Table 3-3, giving the amount of weight loss over 20-100 °C (68-212 °F) temperature range, as measured by TGA.

This weight loss may be related to the so-called free moisture (or surface moisture) that can potentially be evaporated upon the contact of sorbent with dry gas. The conditioning time was fixed at 2 min and following conditioning schemes were investigated:

- Dry nitrogen, 61 °C (142 °F)
- Room air

TABLE 3-3 THE EFFECT OF SORBENT TYPE AND CONDITIONING SCHEME ON THE AMOUNT OF MOISTURE

Sorbent	Surface Area [m ² /g]	Porosity [%]	Conditioning	TGA wt Loss ^a [%]
Commercial Mississippi	17	19	room air warm, dry N ₂	0.73 0.73
Mississippi 2	32	30	room air warm, dry N ₂	N/A 0.47
Mississippi 7	48	31	room air warm, dry N ₂	0.70 0.54
Mississippi 6	75	49	room air warm, dry N ₂	0.70 0.66

a Upon heating from 20-100 °C (68-212 °F)

Effect of RH at 5 Seconds Mississippi Ca(OH)2

Figure 3-7. The effect of relative humidity on the pore size distribution of commercial Mississippi Ca(OH)2 (5 s conditioning with N2).

Effect of Time at 40% RH Mississippi Ca(OH)₂

Figure 3-8. The effect of conditioning time with 40 percent relative humidity N₂ on the pore size distribution of commercial Mississippi Ca(OH)₂.

For both conditioning schemes and for all Ca(OH)_2 the amount of surface moisture after 2 min conditioning was below 1 wt percent. Except for the commercial Mississippi Ca(OH)_2 , the amount of moisture was increasing with increasing specific surface area of Ca(OH)_2 for conditioning with 61 °F (142 °F), dry nitrogen. For all sorbents tested, the amount of moisture detected by the TGA following the room air conditioning was approximately the same.

Conditioned sorbents were exposed to SO_2 in the STDR operated at 60 percent relative humidity and with 2,000 ppm SO_2 . Figure 3-9 presents calcium conversion after 5 s in the STDR as a function of sorbent surface area for both conditioning schemes. There appears to be little sensitivity of Ca(OH)_2 conversion with SO_2 to the surface area of the sorbent following the conditioning with room air. The sensitivity of Ca(OH)_2 conversion to the original surface area of sorbent was higher when sorbents were conditioned with dry, 61 °C (142 °F) nitrogen. Figure 3-10 was constructed to explain the effect of conditioning on reactivity in more detail. It presents the Ca(OH)_2 conversion as a function of a measured TGA weight loss. The amount of TGA weight loss following the dry, 61 °C (142 °F) conditioning varied from 0.47-0.66 wt percent. The amount of loss following room air conditioning was approximately 0.7 wt percent for 3 sorbents tested. The conversion ranged from 2.1-3.5 percent following dry, 61 °C (142 °F) conditioning and from 2.7-3.5 percent following room air conditioning.

Based on data presented in Figures 3-9 and 3-10, it appears that there is a combined effect of surface area and initial moisture content of the sorbent on its reactivity with SO_2 . The reactivity was increasing with both increasing surface area and initial moisture content. Sorbent with lower surface area could become more reactive by increasing its initial moisture content. However, for samples tested the amount of initial moisture content of Ca(OH)_2 resulting from conditioning techniques applied was always below 1 wt percent, regardless of the sorbent's surface area.

One other sorbent was tested and it was produced by slurring fly ash from coal-fired power plant with Ca(OH)_2 at the weight ratio of 3:1 at 90 °C (194 °F) for 16 h. Following 2 min conditioning with room air, 1.25 wt percent loss was measured for this sorbent by TGA. The conversion of Ca(OH)_2 measured after 5 s in the STDR operated under conditions previously described was 7.6 percent. This comparison of fly ash/ Ca(OH)_2 and Ca(OH)_2 sorbent is shown in Figure 3-11.

Figure 3-9. Combined effect of sorbent surface area and conditioning techniques on sorbent's reactivity with SO₂.

Figure 3-10. Reactivity of Ca(OH)_2 as a function of initial moisture content as measured by TGA.

Figure 3-11. The effect of surface moisture on reactivity of sorbents with SO_2 .

3.6 EFFECT OF CO₂ ON REACTIVITY

Typical flue gas contains CO₂, which can potentially react with Ca(OH)₂ under conditions of duct injection for the removal of SO₂. By reacting with CO₂, the sorbent can be partially recarbonated. Since it is known that limestone is not reactive with SO₂ under duct conditions, the presence of CO₂ could potentially decrease the reactivity of sorbent with SO₂.

In order to investigate the extent of recarbonation, the sorbent was placed in STDR under N₂/CO₂ flow for a desired contact time and later analyzed by TGA for the amount of CaCO₃. The weight loss by the sample between 550-700 °C was assumed to be indicative of the amount of CaCO₃ in the sample. The baseline content of CaCO₃ in the untreated commercial Mississippi Ca(OH)₂ (6.0 or 6.4 wt percent, depending upon the batch used) was then subtracted. The resulting number is reported as the percent carbonation in Figure 3-12. Figure 3-12 presents the percent carbonation as the function of the exposure time to CO₂-containing gas. Two levels of CO₂ concentration were tested: 10 and 20 vol percent. The CO₂-containing gas was dry or humidified (relative humidity of 60 percent) and it did not contain SO₂. Mississippi Ca(OH)₂ was used for experiments. The contact time range tested was 0.5-300 s. For humidified gas, the percent of carbonation increased with increasing contact time. For dry gas, the percent carbonation increased with contact time up to 5 s and later levelled off. For any contact time with either dry or humidified gas, there was no significant difference in the extent of carbonation for gas containing 10 or 20 vol percent CO₂. Significantly less recarbonation occurred in the dry gas than in the humidified gas, especially for contact times longer than 50 s. Data presented in Figure 3-12 indicates that the presence of moisture in the flue gas can increase the amount of CO₂ combined with Ca(OH)₂.

Several sorbents were produced in the laboratory to investigate the effect of specific surface area on the extent of carbonation. The specific surface range investigated was from 17-78 m²/g. Carbonation conditions were constant at 5 s contact time and 10 vol percent CO₂ concentration. Both dry and humid (60 percent relative humidity) carbonation was tested. The results are presented in Figure 3-13 giving the percent carbon after 5 s as a function of initial Ca(OH)₂ surface area. Measured percent carbonation was

- 10 vol% CO₂, dry gas (6.0% baseline)
- ✕ 20 vol% CO₂, dry gas (6.0% baseline)
- + 10 vol% CO₂, 60% RH (6.0% CaCO₃ baseline)
- 20 vol% CO₂, 60% RH (6.4% CaCO₃ baseline)

Figure 3-12. Recarbonation of Mississippi Ca(OH)₂ upon contact with CO₂.

Figure 3-13. Carbonation of Mississippi $\text{Ca}(\text{OH})_2$ as a function of Initial surface area (10 vol percent of CO_2).

increasing with the increasing initial surface area of Ca(OH)_2 . For any sorbent tested, the percent of carbonation was higher for humid than for dry N_2/CO_2 gas. Data presented in Figure 3-13 indicates that increased initial surface area of Ca(OH)_2 can increase the amount CO_2 combined with the sorbent.

In the actual environment of duct, the carbonation of dry injected Ca(OH)_2 due to the presence of CO_2 would take place in the presence of SO_2 . To investigate the possible effect of SO_2 on the extent of carbonation, the sample of Mississippi Ca(OH)_2 was exposed to the humid $\text{N}_2/\text{CO}_2/\text{SO}_2$ gas. The concentration of CO_2 was 10 vol percent and the concentration of SO_2 was 2,000 ppm. After 5 s exposure the sample was analyzed for the amount of CaCO_3 by TGA. Additionally, the sample was analyzed with C, H, N elemental analyzer to avoid the interference of CaSO_3 with CaCO_3 analysis. The extent of carbonation in the presence of SO_2 and at the conditions described above was measured to be 8.08 and 8.31 wt percent by the TGA and C,H,N, elemental analysis methods, respectively. Previously measured extent of carbonation in humid N_2/CO_2 gas and after 5 s contact time in the STDR was 8.72 wt percent of CaCO_3 . Based on the above set of data, there was no significant effect of SO_2 presence on the extent of carbonation of Ca(OH)_2 .

In the next step, the reactivity of Mississippi Ca(OH)_2 with SO_2 in the presence of CO_2 was investigated in the STDR. The sorbent was conditioned for 2 min with dry 61 °C (142 °F) nitrogen and later injected into gas stream with 2,000 ppm SO_2 at 11 °C (20 °F) approach to saturation and with between 10 and 40 vol percent of CO_2 . The results are presented in Figure 3-14, giving conversion as a function of residence time for 3 different concentrations of CO_2 . The effect of CO_2 presence on Ca(OH)_2 reactivity varied with the concentration of CO_2 . There was moderate decrease of Ca(OH)_2 reactivity in the presence of CO_2 for high concentration of CO_2 . For example, after 5 s exposure to 2,000 ppm SO_2 at 11 °C (20 °F) approach to saturation the conversion was 2.1 and 1.6 percent for nitrogen/ SO_2 and nitrogen/ SO_2 /40 vol percent CO_2 gas, respectively. However, for the practical range of CO_2 concentration (0-10 vol percent) its effect on reactivity of Ca(OH)_2 was insignificant.

Figure 3-14. The effect of CO₂ on reactivity of Mississippi Ca(OH)₂ with SO₂ (dry, warm N₂ conditioning, 2000 ppm SO₂, 11% approach to saturation).

3.7 CONCLUSIONS

- There was a correlation between surface area and porosity of Mississippi Ca(OH)_2 .
- Pore volume of commercial Mississippi Ca(OH)_2 decreased slightly upon contact with humid nitrogen. For 5 s conditioning time the decrease was less than 2 percent.
- Initial moisture content of sorbent (as measured by TGA) is a function of conditioning scheme. For dry, warm nitrogen conditioning, the moisture content was increasing with increasing surface area of sorbent. Following the conditioning methods used, the initial moisture content for Ca(OH)_2 sorbents was below 1 percent.
- Conversion in the STDR was increasing with the initial amount of moisture on the sorbent (as detected by TGA) conditioned with dry, warm nitrogen.
- There was more initial moisture on the fly ash/ Ca(OH)_2 sorbent than on any Mississippi Ca(OH)_2 sorbent. Reactivity of fly ash/ Ca(OH)_2 was approximately twice that of Ca(OH)_2 .
- The recarbonation of commercial Mississippi Ca(OH)_2 upon contact with CO_2 was enhanced by the presence of moisture in the flue gas (60 percent relative humidity). The extent of recarbonation upon contact of Ca(OH)_2 with humid N_2/CO_2 gas was a function of contact time. For dry N_2/CO_2 gas, the recarbonation levelled off after 5 s. There was no significant effect of the CO_2 concentration (10 and 20 vol percent tested) on the amount of recarbonation.
- Moderate decrease of reactivity of Ca(OH)_2 with SO_2 took place as a result of high CO_2 concentration (40 vol percent). For practical range of concentration (0-10 vol percent), the effect of CO_2 on reactivity of Ca(OH)_2 with SO_2 was insignificant.
- Increased initial surface area of Ca(OH)_2 could increase the amount of CO_2 combined with the sorbent. For any surface area sorbent tested, the percent carbonation was higher for humid than dry N_2/CO_2 gas.
- No significant effect of SO_2 presence on the extent of carbonation of Ca(OH)_2 was found.

SECTION 4

TASK 3—PILOT PLANT TESTING

4.1 OBJECTIVES

The objectives of Task 3 are to conduct pilot plant testing to evaluate various sorbents, operating conditions and process schemes to support large-scale field testings at Meredosia and Beverly. Duct dry injection recycle tests were performed during this reporting period. Very few data are available such that the benefit of recycle operation for in-duct dry injection is still not clear. Because of the low sorbent utilization expected, the majority of the lime initially injected into the duct remains unused after the particulate collector. It is likely that the unused lime, when reinjected into duct, should react and absorb SO_2 . However, it absorbed SO_2 forms CaSO_3 crystal on the surface of the lime, the active surface area and average pore size of the sorbent would be substantially reduced. Therefore, even though the lime is only partially used, it may have lost its reactivity. As a result, the reinjection of the partially used lime might not result in any significant additional SO_2 removal.

Pilot plant testing (50 cfm) was conducted to evaluate the effectiveness of in-duct dry injection recycle operation. If the data shows that recycle operation is beneficial, parametric pilot plant tests are going to be performed. The pilot plant tests were conducted in such a way that the real process occurring in-duct dry injection can be bracketed. That is, the sorbent was injected before the humidifier to determine the maximum limits for dry injection. On the other hand, the sorbent was also injected after the humidifier to determine the lower limit for SO_2 absorption at equilibrium moisture case.

4.2 EXPERIMENTAL APPARATUS

The pilot plant facility used in the present work incorporates a Niro Atomizer Mobile Minor spray dryer facility. The spray dryer has been retrofitted with additional ductwork downstream of the spray dryer vessel, plus a dry sorbent injection system, a Dustex pulse-jet baghouse for particulate collection, and a stainless steel fan (Cincinnati Fan & Ventilator Co.) for exhausting the cleaned gas into the atmosphere. The pilot plant arrangement is depicted in Figure 4-1.

Air flow is drawn from ambient through an air filter and an electrical heater. The heated air enters the spray dryer chamber through an air disperser located in the center of the chamber roof. The air

Figure 4-1. Schematic of duct injection pilot plant facility.

dispenser is designed to swirl the air flow around the rotary atomizer wheel from which water, or slurry, is atomized. The rotary atomizer is equipped with an abrasion resistant stainless steel wheel with 4 silicon carbide inserts, with an inside diameter of 2 mm (0.08 in). The wheel is mounted on a high speed spindle which is driven by a compressed air turbine. The compressed air is supplied at a pressure of around 5 bar (75 psig), which normally provides an atomizer speed around 40,000 rpm. Feed liquid (slurry or water) is pumped to the atomizer wheel and atomized into a fine spray of droplets. The droplet spray into the hot air causes very rapid evaporation of the water and simultaneously cools the air stream inside the insulated chamber. The spray dryer diameter is 800 mm (31.5 in) and its total volume is 0.42 m³ (15 ft³), providing for a gas retention time of approximately 15-20 s based on the outlet gas conditions. For dry injection tests, the spray dryer served as a humidifier to condition the flue gas humidity and temperature to desired level.

The gas (and any dried sorbent) is drawn off at the base of the chamber through a 50 mm (2 in) diameter heat traced and isolated duct section. Different lengths of duct section, 9.8 m (32 ft) in length or, alternatively, 24.4 m (80 ft), provide gas retention times of 0.8 s or 2 s. A dry sorbent injection system is installed at the vertical duct section just downstream of the spray dryer vessel upstream of the main duct section). The injection system consists of a Vibra Screw or AccuRate Model 604 volumetric feeder, equipped with a helix [19-44 mm (0.75-1.75 in) diameter] for feeding the dry or semidry sorbent directly into the duct. Another dry sorbent injection point is located on the top of the spray dryer vessel (upstream of the spray dryer).

The dry particulates are collected by the pulse-jet baghouse equipped with 4 polyester bags, providing a total solids collection area of 2.3 m² (25 ft²). A rotary air lock discharges, batchwise, the collected solids from the baghouse hopper. Alternatively, a cyclone separator (from Niro Atomizer's Mobile Minor unit) with a cut size of about 3 µm can be inserted just upstream of the baghouse to collect a large fraction (normally 80-95 percent) of the particulates. This cyclone has been equipped with a vortex breaker and a bucket for continuously discharging the particulates from the flue gas system. Both the baghouse and the cyclone are insulated, and the baghouse hopper is also equipped with electrical heaters to minimize heat loss.

An induced draft fan located downstream of the baghouse provides negative pressure in the entire simulated flue gas system. It also exhausts the cleaned gas into the atmosphere through the roof of the building via a 3 in PVC pipe stack [inside diameter 78 mm (3.1 in)].

The SO₂ concentrations throughout the system were determined by extractive sampling from the spray dryer inlet duct, the spray dryer outlet duct, and cyclone outlet duct/baghouse inlet duct. The extractive sampling system was made of a filter which separates the solid and gas in the gas samples. The filter was heat traced and the temperature was maintained above 100 °C (212 °F). The gas samples were constantly pumped through heated sample lines at 150 °C (300 °F) to continuous SO₂ monitors. A DuPont 411 ultraviolet spectrophotometer and a Thermo Electron Model 40 pulsed fluorescent analyzer were used. Calibrations were conducted on a daily basis using commercially available span gases (Airco Industrial Gases) of SO₂ in nitrogen or air for the DuPont analyzer, and SO₂ in air for the Thermo Electron analyzer.

Temperatures, pressures, flowrates, SO₂ concentrations, etc. were recorded every 1/2 h during a 4-8 h test run at fairly stable conditions. An average value was calculated for each test parameter at the end of the test run and reported for that particular test.

4.3 TEST RESULTS

4.3.1 Duct Dry Injection Downstream of Water Spraying

Baseline performance test was first conducted to establish the lime utilization and data reproducibility of once-through operation. The major operating parameters are listed Table 4-1. Fly ash from the Meredosia Power Plant (provided by Radian Corporation) was injected into the flue gas at a rate equivalent to 1.1 gr/acf dust loading. Mississippi hydrated lime was used as the sorbent and was injected into the duct after the humidifier. Therefore, no sorbent wetting by water droplet/sorbent particulate collision was expected.

The average SO₂ removal observed after 6 runs on the pilot plant was about 27 percent at a calcium to sulfur ratio of 2.0. Therefore, the lime utilization was about 13.5 percent. The results are presented in Figure 4-2. In addition, 2 runs were conducted to evaluate the reactivity of Meredosia fly ash toward SO₂.

Figure 4-2. DOE dry duct Injection (Meredosia Ash/Lime Mixture).

TABLE 4-1. PILOT PLANT OPERATING CONDITIONS

Flue gas temperature	300 °F
Flue gas SO ₂ concentration	2,000 ppm
Simulated fly ash loading	1.1 gr/acf at 300 °F
Duct residence time	~2 s
Calcium to sulfur ratio	2.0
Approach to saturation	20 °F

As shown in Figure 4-2 by the data point represented by the triangle, almost no SO₂ removal was obtained by injecting only Meredosia fly ash as the sorbent. It is apparent that Meredosia fly ash is quite inert toward SO₂. This conclusion is further supported by the evidence that no difference in SO₂ removal was obtained between runs with and without fly ash.

After the baseline was established, recycle operation was performed. The product collected from the baseline tests was used as the recycle material. The recycle material was mixed with fresh lime and fly ash before duct injection. The ratio of mixing was controlled so that the fresh calcium to sulfur ratio would be 2.0 at a recycle ratio of 2.0. As shown in Figure 4-3, approximately 42 percent SO₂ removal efficiency was obtained during the first recycle test. However, the SO₂ removal declined to 28 percent during the second and the third recycle tests which used the product from the first and the second recycle test as the recycle material, respectively. Compared with baseline SO₂ removal (27 percent), the pilot plant data show that very little improvement in SO₂ removal was obtained by recycle operation during the third recycle test which should provide a fairly close simulation of the long term, steady state recycle operation. To further investigate the effect of recycle operation, pilot plant tests were conducted with recycle material only (i.e., no fresh lime). As shown in Figure 4-3 by crosses, the recycle material used by the first recycle test yielded approximately 15 percent SO₂ removal. However, the recycle materials used by the second and the third recycle tests yielded only 2 percent SO₂ removal. The pilot plant data indicate that the recycle material lost its reactivity toward SO₂ rapidly after the first pass. It is suspected that the absorbed SO₂ forms CaSO₃ crystals on the surface of lime which tends to blind the active surface and plug the pores. As a result, the recycled lime, although less than 30 percent of it was utilized, became almost nonreactive toward SO₂ after the second pass.

Figure 4-3. Effect of recycle operation SO_2 removal for duct dry injection after (downstream) of the humidifier.

4.3.2 Duct Dry Injection Upstream of Water Spraying

The sorbent injection point was moved to the top of the spray dryer vessel for this test series. Considerable operating difficulties were encountered. Those included wet deposit on the walls, pluggage of sorbent dispersion section, and sorbent build-up around the spraying section. After significant hardware modification and several trial-and-error tests, stable operation of pilot testing was sustainable for up to 4 h at an approach to saturation temperature of 25-30 °F. Figure 4-4 compares the baseline performance of dry injection before (upstream) and after (downstream) the humidifier at a calcium to sulfur ratio of 2.0. It is shown that higher SO₂ removal was obtained when the sorbent was injected upstream than downstream.

4.4 SUMMARY

- Consistent, reproducible data were obtained from pilot testing of in-duct dry injection downstream (after) the humidifier.
- Pilot plant data showed that recycle operation would not provide significant enhancement in SO₂ removal when the sorbent was injected downstream of the humidifier.
- The reactivity of recycle material decreased rapidly after the first pass which accounts for the little effect of recycle operation on SO₂ removal enhancement.
- In-duct dry injection upstream of (before) the humidifier turned out to be a much more difficult operation when compared with dry injection downstream of (after) the humidifier.
- Higher SO₂ removal and lime utilization were obtained from the pilot testing when the sorbent was rejected upstream rather than downstream of the humidifier.

Figure 4-4. Comparison of dry injection before and after humidifier.

SECTION 5

TASK 4.1—ENHANCEMENT OF SLURRY INJECTION

5.1 SLAKING MODIFICATION

Conventional slaking processes aim at fast and efficient conversion of CaO to Ca(OH)_2 , which is an exothermic reaction, with the purpose of producing a suspension of 3-5 μm particles of Ca(OH)_2 in water. This is normally done by optimizing the temperature and the solids content in the slurry, i.e., using a temperature of 85-95 °C and a solids content of about 25 percent (use of a paste slaker even allows handling of 30-35 percent solids). The particle size of the produced Ca(OH)_2 can normally be controlled to some extent by adjusting temperature and solids content during slaking. A too low slaking temperature, however, would normally entail the risk of producing a coarse particle suspension with a significant amount of unconverted CaO .

A test program was undertaken to evaluate techniques for producing very fine particulate Ca(OH)_2 during slaking with the assumption that fine Ca(OH)_2 slurry would be very reactive towards SO_2 . Slaking was conducted in a laboratory-scale slaker consisting of a 0.4 L Pyrex beaker suspended in a constant temperature oil bath. Similarly to the dry hydration technique, a mechanical stirrer was used to mix the water and CaO . Each slaking was conducted by loading 10 g of Mississippi Quicklime into the slaker and allowing CaO to achieve thermal equilibrium in the bath. The stirrer was then started, and a single, rapid addition of water was syringed into the slaker at the desired ratio of $\text{H}_2\text{O}/\text{CaO}$. The amount of water used was such as to yield 10-50 percent solids in a slurry. The temperature of solids and of water was 25 or 100 °C. The particle size distribution of slaked lime was measured by the x-ray sedimentation technique. After completion of slaking, the sample was vacuum filtered and microwave dried. Particle size distribution was determined on the sample prepared in such a way.

The results of slaking experiments are presented in Figure 5.1, giving median particle size of slaked lime as a function of a slurry concentration for two slaking temperatures investigated. No significant effect of slurry solids percent on median particle size could be found (except for 40 percent slaking at 25 °C). Slaking at 100 °C resulted in a significantly finer product than that obtained as a result

Figure 5-1. Combined effect of slurry solids percent and slaking temperature on the median particle size of slaked lime.

of slaking at 25 °C. For the range of slurry solids percent tested, the median particle size of slaked lime was approximately 3 and 6 µm for 100 and 25 °C slaking, respectively.

The source of the quicklime used in the slaking modification experiments was a commercial Mississippi CaO. In the next set of experiments, 3 quicklimes with dissimilar structural properties were produced. The production involved calcination of Mississippi CaCO₃ and subsequent slaking under conditions that yielded 2.92 mm Ca(OH)₂ when the commercial Mississippi CaO (100 °C, 26 percent solids slurry) was used also. Structural properties of 3 CaO and of commercial Mississippi CaO are given in Table 5-1. The median particle size of Mississippi CaCO₃ used for calcinations at 1,000, 800, and 700 °C was 11.9 mm. As shown in Table 5-1, 3 CaO produced in-house had higher surface area than commercial CaO. The high surface area CaO (11.1 m²/g) was probably combining significantly more water vapor and CO₂ from the room atmosphere than the remaining 3 CaO. The last column of Table 5-1 gives a median particle size of Ca(OH)₂ resulting from slaking at 100 °C in 26 percent solids slurry. Generally, the median particle size of slaked Ca(OH)₂ was decreasing with increasing surface area of CaO used for slaking. Somewhat larger median particle size of Ca(OH)₂ resulting from

TABLE 5-1 STRUCTURAL PROPERTIES OF CaO USED FOR SLAKING

CaO Type	Surface Area m ² /g	Porosity --	CaO ^b D50 [mm]	Surface H ₂ O [wt (%)]	Combined H ₂ O [wt (%)]	CO ₂ ^c [wt (%)]	Ca(OH) ₂ ^f D50 [mm]
Commercial	1.2	0.03	6.45	0.05	2.8	0.7	2.92
1,000 °C, 16 h ^a	2.0	0.02	6.99	0.02	0.2	0.2	1.37
800 °C, 16 h ^a	8.5	0.08	4.30	0.09	1.1	0.2	0.66
700 °C, 16 h ^a	11.1	0.14	5.83	0.12	1.1	1.8	0.88

a CaCO₃ calcination conditions

b Median particle size of CaO

c TGA weight loss 20-100 °C

d TGA weight loss 300-540 °C

e TGA weight loss 540-700 °C

f Median particle size of Ca(OH)₂ resulting from slaking (100 °C and 26 percent slurring)

slaking of 11.1 m²/g CaO can be a result of higher initial amounts of surface water and CO₂ on this CaO as compared with 8.5 m²/g CaO. It should also be pointed out that a commercial CaO revealed the highest degree of rehydration among 4 CaO under consideration (2.8 wt percent, as detected by TGA). The extent of rehydration combined with relatively low surface area (1.2 m²/g) might have been the reason for considerably larger median particle size of slaked Ca(OH)₂ produced with commercial CaO.

Two surface active additives were tested with the hope of decreasing median particle size of the resulting slaked Ca(OH)₂. Methyl alcohol was used to reduce the surface tension of slaking water. Reduced surface tension of water in turn would tend to increase the nucleation rate. Another additive tested was calcium lignosulfonate (trade name "Lignosite"), known to enhance dispersion of dry hydrated Ca(OH)₂. The source of quicklime was a commercial Mississippi CaO.

In the first series of experiments, methyl alcohol and D.I. water were used for slaking. The ratio of alcohol-to-water varied from 1:10-2:1, and the slaking temperature was maintained at 74 °C. The results are presented in Figure 5-2 showing the effect of alcohol-to-water ratio on median particle size of slaked Ca(OH)₂, as measured by x-ray sedimentation of a dried slurry powder. The lowest median particle size of 2.8 mm was measured for solids slaked with a mixture of alcohol-to-water at the ratio of 1:2. Slaking with water only produced slaked Ca(OH)₂ with a median particle size of 3.14 mm.

In the second series of experiments, 0.1-9 wt percent (CaO based) calcium lignosulfonate was used. Calcium lignosulfonate was dissolved in water first and the solution was added to CaO. Slaking temperature was 100 °C. The results are presented in Figure 5-3 giving the median particle size of slaked Ca(OH)₂ as a function of calcium lignosulfonate concentration.

Figure 5-2. The effect of alcohol-to-water ratio on median particle size of slaked $\text{Ca}(\text{OH})_2$.

Figure 5-3. The effect of calcium lignosulfonate concentration on the median particle size of slaked $\text{Ca}(\text{OH})_2$.

SECTION 6

TASK 4.2—ENHANCEMENT OF DRY INJECTION - SHORT TIME DIFFERENTIAL REACTOR

6.1 HYDRATION MODIFICATIONS

In the process of "lime hydration," dry calcium hydroxide is produced by the addition of water in an amount sufficient to chemically complete the hydration of CaO plus account for water losses due to evaporation. The amount of water of hydration is usually limited by the need of having dry powder at the completion of hydration. The temperature of hydration can affect the efficiency of hydration and fineness of product Ca(OH)_2 .

Several sorbents were produced in order to investigate the effect of temperature on the structural properties and reactivity of sorbents with SO_2 . Hydrates discussed in this section were produced in a laboratory-scale hydrator consisting of a 0.4-L Pyrex beaker suspended in a constant temperature oil bath. A mechanical stirrer was used to mix the water and CaO. Each hydration was conducted by loading 10 g of Mississippi quicklime into the hydrator and allowing CaO to achieve thermal equilibrium in the bath. The stirrer was started, and a single, rapid addition of water was syringed into the hydrator at the desired molar ratio of $\text{H}_2\text{O}/\text{CaO}$. After 15 min, the hydration vessel was purged of remaining water vapor with nitrogen, leaving a thoroughly dry product. The amount of water used was 2.6 times the amount stoichiometrically required, and the temperature of solids and of liquid was varied from 25-100 °C.

Structural properties of dry hydrated sorbents produced in the laboratory and using Mississippi CaO are given in Table 6-1. For the hydration parameters used there was little effect of temperature of solids or of temperature of water on the surface area and porosity. The surface area varied from 31-32 m^2/g and porosity from 0.23-0.31.

Each sorbent produced was characterized by thermogravimetry to measure the amount of surface moisture, chemically bound water, and amount of recarbonation. The weight loss at 100, 545, and 700 °C was assumed to correspond to the amount of surface water, chemically bound water, and recarbonation, respectively. As evident from Table 6-2, the amount of surface water measured was always below 1 weight percent. The extent of hydration varied from 74 percent for sample prepared at

TABLE 6-1. STRUCTURAL PROPERTIES OF DRY HYDRATED SORBENTS

Sor bent	Temperature		Stoichiometric Ratio (mol H ₂ O/ mol C ⁺)	Specific Surface Area (m ² /g)	Porosity
	Solids (°C)	Water (°C)			
Miss12	100	100	2.6	31	0.23
Miss13	100	25	2.6	32	0.28
Miss14	25	100	2.6	37	0.31
Miss15	25	25	2.6	36	0.30

25/25 °C conditions (18.03 percent weight loss at 545 °C). The weight loss resulting from the decomposition of recarbonated sorbent varied between 0.51-1.63 percent.

Sorbents produced during the hydration experiments were tested in the Short-Time Differential Reactor (STDR) operated at 10 °C (18 °F) approach to saturation (approximately 60 percent relative humidity). The concentration of SO₂ was 2,000 ppm and the contact time was 5 s in the STDR. The conversion of sorbents varied from 3.57-4.68 percent after 5 s contact time in the STDR.

6.2 SOLIDS WITH EXCESS MOISTURE

6.2.1 Reactor and Solids Preparation

The STDR, previously used to identify a rate limiting step for the reaction of dry Ca(OH)₂ with SO₂ was modified to allow for testing of solids with free moisture. The miniature fixed bed reactor (0.5 in OD and 1.0 in. h) with stainless steel mesh bottom is now inserted into the STDR. No conditioning of solids prior to the contact with SO₂ has been implemented. The schematic of modified STDR is shown in Figure 6-1.

Wet solids were prepared by weighing a known amount of solids and water in a glass vial. The solids and water were then mixed thoroughly with a spatula, vial enclosed and stored in an ice bath.

TABLE 6-2. THERMOGRAVIMETRIC CHARACTERIZATION OF DRY HYDRATED SORBENTS

Sor bent	Weight Loss (%)		
	at 100 °C	at 545 °C	at 700 °C
Miss12	0.33	23.09	0.88
Miss13	0.21	22.89	0.85
Miss14	0.35	22.70	1.63
Miss15	—	18.03	0.51

Figure 6-1. The schematic of modified short-time differential reactor.

Moist solids were dispersed on quartz wool and placed in the miniature sand-bed reactor. Exposure to the SO₂ containing process gas was proceeded by a thorough dispersion of solids on quartz wool. The amount of an excess moisture (free moisture) is reported here on a total solids basis based on a thermogravimetric measurement (TGA), i.e. weight loss detected by TGA upon heating from room temperature to 100 °C. The amount of free moisture detected by TGA agrees fairly well with actual moisture contents, indicating that most of the moisture is given off when the wet solids are heated up to 100 °C in the TGA. The comparison of TGA-detected amount of moisture and actual moisture contents is shown in Figure 6-2. The solid line in Figure 6-2 indicates 100 percent detection of actual moisture by the TGA.

6.2.2 Sorbents

Two types of sorbents were used to study the effect of initial free moisture on the conversion with SO₂: Ca(OH)₂ physically mixed with fly ash and Ca(OH)₂ reacted with fly ash. Even small amounts of free moisture are known to deteriorate the handling properties of hydrated lime, which tends to agglomerate and become a paste unsuitable for dry duct injection. Since previous work on fundamental mass transfer mechanisms indicated that the conversion of Ca(OH)₂ increased with the increasing amount of initial moisture on the solids, an alternative means of moisture delivery was used. The modified STDR was used to simulate the moist duct injection (MDI) moisture delivery system. To simulate the MDI, 6 mg of dry Mississippi Ca(OH)₂ (actual TGA-Detected moisture contents of a commercial Mississippi Ca(OH)₂ was 0.55 wt percent) were physically mixed with 20 or 30 mg of moist fly ash that were prepared in the manner described in the previous chapter. Meredosia fly ash was used for MDI experiments.

Another sorbent tested was chemically reacted fly ash with Ca(OH)₂. This sorbent was produced by slurring ground Clinch River fly ash with reagent grade Ca(OH)₂ at the weight ratio of 3:1 at 90 °C for 3 h. Previous work indicated that slurring ground fly ash can significantly increase the reactivity of sorbet for any given slurring conditions, compared to the unground fly ash. It was also known that sorbents produced by slurring fly ash with Ca(OH)₂ (calcium silicate sorbent) were capable of holding 20-30 wt

Figure 6-2. The comparison of TGA-detected moisture contents with actual moisture contents.

percent moisture without significant deterioration of handling properties. No ground Meredosia fly ash was available in the beginning of testing. Ground Clinch River fly ash was therefore selected in place of Meredosia fly ash, since it is also a eastern bituminous coal fly ash.

6.2.3 Results and Discussion

Moist sorbents were exposed to 2,000 ppm SO₂ in the STDR operated at 11 °C (20 °F) approach to saturation which corresponded to approximately 60 percent relative humidity (RH). The contact time in the STDR varied from 0.5-5 s with occasional experiments performed at 60 and 400 s. Baseline experiments were done first with 6 mg of dry Mississippi Ca(OH)₂ only and then with 6 mg of dry Mississippi Ca(OH)₂ physically mixed with 20 mg of dry Meredosia fly ash. The results are shown in Figure 6-3. There was no significant difference (except for an outlying datapoint for 3 s contact time) in conversion of dry Ca(OH)₂ and dry Ca(OH)₂ physically mixed with the dry fly ash. Following baseline tests, solids were prepared by physically mixing Ca(OH)₂ and moist Meredosia fly ash to yield 3 levels of initial free moisture: 3.9, 12.4, and 18.3 percent. The results are presented in Figure 6-4 giving the conversion of calcium as a function of contact time. Baseline results for dry Ca(OH)₂ are also shown in Figure 6-4 for comparison. Higher conversions were measured for sorbents with increased level of initial free moisture than for dry Ca(OH)₂. For a given contact time, the conversion was generally increasing with increasing initial free moisture contents of solids. Additional experiments were performed at 60 and 400 s contact time and these results are also shown in Figure 6-4. The effect of initial free moisture was more pronounced at longer contact times (60 and 400 s). For example, the conversion at 5 s contact time was 2.18 and 4.72 percent and at 400 s contact time was 7.27 and 36.3 percent for dry Mississippi Ca(OH)₂ and a physical mixture of dry Mississippi Ca(OH)₂ and moist Meredosia fly ash with 18.3 percent initial free moisture, respectively.

In the next series of experiments, chemically reacted fly ash with Ca(OH)₂ was used. The dryness of sorbent was assured by microwaving it immediately following completion of slurring. Baseline experiments were done first with dry solids produced by slurring Ca(OH)₂ and ground fly ash (32 m²/g overall dry sorbent surface area). Considerably higher conversions were measured for dry sorbent produced by slurring Ca(OH)₂ and ground fly ash than previously measured for dry Ca(OH)₂

Figure 6-3. Baseline tests with dry Meredosia fly ash added to dry Mississippi $\text{Ca}(\text{OH})_2$ (STDR, 2,000 ppm SO_2 , 60 percent RH).

Figure 6-4. Effect of initial free moisture on the reactivity of Ca(OH)₂ physically mixed with Meredosia fly ash (STDR, 2,000 ppm SO₂, 60 percent RH).

alone. For example, following the 5 s contact time the conversion of dry fly ash/Ca(OH)₂ sorbent was 7.35 percent, compared to 2.18 percent for dry Mississippi Ca(OH)₂.

Following baseline tests, solids were prepared by re-wetting chemically reacted fly ash/Ca(OH)₂ sorbent to yield 3 levels of initial free moisture: 8.5, 12, and 40 percent. The results are shown in Figure 6-5, giving the conversion of calcium as a function of contact time with 2,000 ppm SO₂ at approximately 60 percent RH. For each initial moisture content tested the conversion increased with increasing contact time. Except for 0.3 s contact time, the conversion after any contact time increased with increasing initial free moisture contents.

The comparison of conversion measured for 2 types of sorbent is shown in Figure 6-6. Both sorbents had a comparable amount of initial free moisture: 12 percent in the case of the chemically reacted sorbent and 12.4 percent in the case of physically mixed fly ash and Ca(OH)₂. For the contact time range tested, chemically reacted fly ash/Ca(OH)₂ sorbent consistently had higher conversions than physically mixed fly ash/Ca(OH)₂ sorbent. The difference between the 2 sorbents was more pronounced for longer contact times (60 and 400 s). It should be pointed out that the 2 sorbents tested had different surface area (32 m²/g overall for chemically reacted fly ash/Ca(OH)₂ sorbent and 17 m²/g for Mississippi Ca(OH)₂ used for physical mixture). However, preliminary results with a physical mixture of fly ash and Ca(OH)₂ using in-house produced 70 m²/g surface area Ca(OH)₂ indicate only marginally increased conversion due to the increased specific surface area of Ca(OH)₂ (5.2 and 4.7 percent conversion after 5 s contact time with 70 and 17 m²/g Ca(OH)₂ was used for physical mixture, respectively).

More data comparing the effect of the initial free moisture on the conversion of 2 sorbents under consideration is shown in Figure 6-7. The physical mixture of fly ash/Ca(OH)₂ was tested with up to approximately 20 percent initial free moisture. Chemically reacted fly ash/Ca(OH)₂ was tested with up to approximately 40 percent initial free moisture. Attempts to produce a physical mixture of Ca(OH)₂ and fly ash with initial free moisture contents above 20 percent were unsuccessful thus far. Chemically reacted fly ash/Ca(OH)₂ appeared to be a free-flowing powder even with 40 percent initial free moisture. Figure 6-7 gives calcium conversion after 5 s contact time in the STD 1 with 2,000 ppm SO₂ and approximately 60 percent RH. For any initial free moisture tested, reacted Ca(OH)₂/fly ash sorbent revealed higher

Figure 6-5. The effect of initial free moisture on the reactivity of chemically reacted fly ash/ $\text{Ca}(\text{OH})_2$ (STDR, 2,000 ppm SO_2 , 60 percent RH).

Figure 6-6. Reactivity comparison for physically mixed and chemically reacted fly ash/ $\text{Ca}(\text{OH})_2$ (STD, 2,000 ppm SO_2 , 60 percent RH, 12-14.7 percent at limited moisture contents).

Figure 6-7 . The effect of an initial moisture on the reactivity of physically mixed and reacted fly ash/ Ca(OH)_2 (STD, 2,000 ppm SO_2 , 60 percent RH, 5 s contact time).

conversion than physically mixed Ca(OH)_2 and fly ash. The 5 s conversion of reacted Ca(OH)_2 /fly ash appears to be levelling off at 30 percent initial moisture contents.

A complete set of results for experiments with moist solids is given in Table 6-3.

TABLE 6-3 SUMMARY MR-STD

Test No.	Sorbent* (mg)	Fly ash** (mg)	Surface H ₂ O (wt %)	Conversion (%)				1.0 m	6.75 m
				0.5 s	1.0 s	3.0 s	5.0 s		
23	6	30(e)	12.07	1.08	2.00	5.32	4.45	—	—
29	6	20	2.78	—	—	—	—	5.07	10.39
30	6	30(e)	12.46	—	—	—	—	16.55	21.96
31	6	0	—	—	—	—	—	4.47	7.27
33	6	30(e)	12.59	1.23	2.06	3.67	4.47	—	—
34	6	20	3.98	1.81	2.54	3.49	3.76	—	—
35	6	30(e)	13.24	—	—	—	—	15.16	21.51
36	6	30(e)	12.55	0.91	2.28	3.11	4.10	—	—
37	6	30(d)	14.89	—	—	—	—	17.12	20.75
38	6	20	3.67	—	—	—	—	6.94	12.79
39	6	30(d)	18.45	1.94	1.95	4.47	4.91	—	—
40	6	20(e)	11.65	—	—	—	—	9.23	15.28
42	6	30(d)	18.03	2.88	3.63	4.58	4.53	—	—
43	6	0	0.55	0.80	1.33	1.83	1.69	—	—
44	6	20(e)	12.71	0.49	2.07	4.08	4.49	—	—
46	6	20(c)	0.63	0.78	1.47	1.15	2.21	—	—
48	6	30(d)	17.25	—	—	—	—	15.82	30.67
49	6	20	3.86	1.44	1.44	2.07	2.41	—	—
50	(a)	(a)	8.47	2.09	3.14	4.88	6.49	—	—
51	(a)	(a)	14.13	2.37	5.07	7.95	12.90	—	—
52	(a)	(a)	20.93	2.13	2.96	5.86	7.63	—	—
53	(a)	(a)	39.53	2.14	4.37	10.48	15.59	—	—
54	6	0	—	1.02	1.43	1.67	2.66	—	—
55	6	20(e)	13.04	—	—	—	—	17.81	35.71
58	6	30(d)	17.72	—	—	—	—	24.34	41.88
59	(a)	(a)	11.95	2.77	3.76	6.08	9.08	—	—
60	(b)	(b)	52.27	1.36	1.26	6.89	7.99	—	—
61	(a)	(a)	42.27	—	—	—	—	59.05	80.87
62	(a)	(a)	14.67	—	—	—	—	39.38	64.83
63	(b)	(b)	52.00	—	—	—	—	21.68	77.66
64	(a)	(a)	9.40	—	—	—	—	32.56	—

Continue

TABLE 6-3 SUMMARY MR-STD (CONCLUDED)

Test No.	Sorbent* (mg)	Fly ash** (mg)	Surface H ₂ O (wt %)	Conversion (%)	0.5 s	1.0 s	3.0 s	5.0 s	1.0 m	6.75 m
65	(a)	(a)	4.38	3.79	3.98	4.36	7.35	—	—	—
66	(a)	(a)	20.68	—	—	—	—	—	33.48	82.37
71	(a)	(a)	50.47	2.10	1.97	5.56	11.72	—	—	—
72	(a)	(a)	20.91	2.62	3.24	6.35	9.98	—	—	—
73	(a)	(a)	30.90	4.25	5.52	10.70	15.53	—	—	—
75	(a)	(a)	32.03	1.45	2.65	4.73	4.36	—	—	—
76	(a)	(a)	59.96	—	—	—	—	—	19.05	64.97
80	(a)	(a)	48.07	3.45	4.16	7.95	10.28	—	—	—

* MR-200 Mississippi Ca(OH)₂, dry, unless stated otherwise

** Meredosia fly ash with 10 percent moisture unless stated otherwise

*** For all runs, Twet = 122 °F and Tdry = 142 °F

a 20 mg Sorbent (Cinch River Fly ash & Reagent Grade Ca(OH)₂, 3:1 ratio respectively, 90 °C, 3 h slurry, microwaved dry)Surface Area = 30.1985 m²/g, Porosity = 0.22

b Same as (a) except 30 mg of sorbent used

c Dry, no moisture added

d 30 percent moisture

e 20 percent moisture

SECTION 7

TASK 4.2--ENHANCEMENT OF DRY INJECTION DIFFERENTIAL REACTOR

7.1 INTRODUCTION

Previous pilot and bench-scale work has determined that $\text{Ca}(\text{OH})_2$ and Ca-based sorbents have significant potential for application in dry duct injection SO_2 abatement systems. The effectiveness of these solids can be enhanced by increasing the surface moisture content of the sorbent as a function of the relative humidity of the ductwork. Operational difficulties which arise when flue gas is treated with reactive sorbent at high relative humidities limit the applicability of such processes to tightly controlled conditions (Babu, et al., 1988; Yoon, et al., 1988; Drummond, et al., 1988). Improvements to sorbent reactivity are possible by increasing the surface area of the sorbent and the availability of reactive species which may fix the SO_2 in a condensed state (White, et al., 1989; Peterson, et al., 1987; Drummond, et al., 1988; Jozewicz and Chang, 1986, 1987; Jorgensen, et al., 1987). Even with these enhancements, lime-based sorbents do not approach appreciably the reactivity of similar lime-based sorbents applied in spray-dryers (Blythe, 1988).

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

The reactivity of damp sorbent towards SO_2 has not been investigated at the bench scale, and both pilot-scale work and spray dryer work indicate that excess surface moisture significantly enhances the reactivity of lime-based sorbents towards SO_2 . It would be beneficial to study the performance of various, damp, lime-based sorbents at the bench level, in order to investigate the mechanism by which reaction with SO_2 occurs and to quantify the enhancement in reactivity due to the excess moisture. It

may be possible to develop a predictive model for the performance of damp sorbents based upon the similarity of the damp sorbent reaction and the reactions which occur in spray dryer or wet slurry scrubbing.

This work investigates the reactivity of several lime-based sorbents towards SO_2 in the presence of equilibrium and excess moisture on the sorbent. Sorbents of varying surface area and surface structure are studied in a differential reactor under conditions of 0-90 percent relative humidity, 1,000-5,000 ppm SO_2 in the flue gas, 70 °C reaction temperature, 3-50 percent initial excess moisture, and 10-120 s RH.

7.2 THEORY

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

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

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

Mass transfer theory may be applied to the gas-solid reaction system in the presence of moisture in excess of equilibrium on the surface of a reactive sorbent. The theoretical model below describes the

reaction occurring when a wet solid is drying and relates the evaporative drying and the SO₂ capture mechanisms.

7.2.1 Assumptions for Theoretical Development

The reaction between damp sorbent and SO₂ is assumed to be fast compared to gas phase mass transfer of SO₂ to the particle surface. The transfer is assumed to occur by Knudsen diffusion within the pores of the reactive sorbent. The following assumptions also are necessary for the development of the model:

- Liquid water present on the damp solid is present predominantly in the pores of the solid
- The resistance to mass transfer for both the evaporation process and the SO₂ capture process is controlled by diffusion in the gas phase
- Reaction between SO₂ and a damp sorbent which dries during the course of reaction occurs in two separate stages, the effects of which are additive. These two stages are; reaction in the presence of excess surface moisture (damp sorbent), and reaction in the presence of equilibrium moisture (sorbent in equilibrium with flue gas relative humidity) and
- the bulk flow contribution to the overall mass flux of the exchanged species is negligible during pore diffusion.

7.2.2 Derivation

The evaporation of water from the pores of the solid and the transport of SO₂ through the pores to the gas-liquid interface can be represented by:

$$\frac{d(H_2O/area)}{dt} = N_{H_2O} = -(D_{H_2O}) * \frac{dC_{H_2O}}{dx} \quad (7.1)$$

$$\frac{d(SO_2/area)}{dt} = N_{SO_2} = (D_{SO_2}) * \frac{dC_{SO_2}}{dx} \quad (7.2)$$

where:

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

x = diffusion distance ; [length],

D = mass diffusion coefficient; [length²/time], and

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

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

Transport of H₂O and SO₂ are assumed to occur by Knudsen diffusion, which is a valid assumption if the gas/liquid interface is located within small pores in the sorbent. Knudsen diffusion is applicable when the mean free path over which a molecule can travel is greater than the pore diameter through which it is diffusing. The mean free path of a molecule is defined as follows (Bird, et al., 1960):

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 n} \quad (7.3)$$

where:

λ = mean free path; [length],

π = particle diameter; [length], and

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

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

$$D_{AK} = 97.0 r \sqrt{\frac{T}{M_A}} \quad (7.4)$$

where:

D_{AK} = Knudsen diffusion coefficient; [length²/time],

r = radius of diffusing particle ; [length],

T = system temperature, and

M_A = diffusing particle molecular weight; [mass].

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

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

$$\frac{dSO_2}{dH_2O} = \frac{D_{SO_2K} (dSO_2/dx)}{-D_{H_2OK} (dH_2O/dx)} \quad (7.5)$$

The relationship between the water evaporated from the solid surface and the SO₂ captured is obtained by integrating this expression, as follows:

$$\frac{\Delta SO_2}{\Delta H_2O} = \frac{D_{SO_2K} (P_{SO_2})}{D_{H_2O}K (P_{H_2O}^* - P_{H_2O})} \quad (7.6)$$

where:

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

The model allows one to predict the conversion of the porous sorbent as a function of the quantity of water evaporated from the sorbent while in contact with SO₂. This representation does not account for reaction which occurs when the sorbent contains water in equilibrium with the flue gas relative humidity.

When experiments are conducted, the initial weight percent water on the reactive sorbent, the relative humidity of the flue gas, and the SO₂ content of the flue gas are noted. The expression above is modified to predict the Ca utilization of the sorbent based on these parameters. The modified predictive expression is:

$$\frac{\Delta SO_2}{Ca} = \frac{D_{SO_2K} (P_{SO_2})}{D_{H_2O}K (P_{H_2O}^* - P_{H_2O})} \left(\frac{\Delta H_2O}{Ca} \right) \quad (7.7)$$

where:

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

Figure 7-1 shows the conversions predicted by the model under typical experimental conditions. These results assume that all H₂O initially present on the surface of the solid evaporates from the solid. The results do not include reaction between the sorbent and SO₂ in the absence of excess moisture on the surface of the sorbent. The model predicts a linear increase in conversion of sorbent as a function of its initial moisture. The slope of this increase is dependent on the relative humidity of the system and the SO₂ concentration in the gas phase.

The accuracy of this model will be studied using damp hydrated lime and hydrated lime/fly ash sorbents with flue gases of varying SO₂ content and relative humidity. Hydrated lime sorbents of varying surface area and porosity will be studied to determine the effects of surface properties on the sorbent reactivity, although the model indicates that the reaction with damp sorbent will be independent of the

Figure 7-1. Predicted Conversion in the Presence of Liquid H₂O: (Lime/Fly Ash sorbent containing 3.65×10^{-3} moles Ca/g sorbent).

sorbent surface properties. The surface area effects will be observed when the reactive sorbent contains equilibrium moisture, and such effects will be reflected by a changing y-intercept in the plot above. The slope of the plot of Ca-utilization versus initial moisture is a function of relative humidity and SO₂ concentration for a reaction between damp sorbent and flue gas.

When the model is applied to predict the conversion of a damp sorbent, the conversion attained by that sorbent with no excess moisture present will be required to predict the total conversion. If there is no interaction between the wet reaction and the reaction when the sorbent contains moisture in equilibrium with the flue gas relative humidity, this combination will accurately predict the total conversion of damp sorbent which is dried as it reacts.

7.2.3 Effects of Equilibrium Reaction

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

It is believed that the conversion predicted as a function of excess moisture on the surface of the sorbent is correct, but that the magnitude of the contribution of the equilibrium-moisture reaction must be adjusted to reach a correct total conversion. To calculate the conversion which will occur by the equilibrium-moisture reaction, the results of equilibrium-moisture reaction studies will be analyzed to determine the instantaneous rate of sorbent conversion as a function of sorbent conversion. For each experiment to be modelled, the conversion expected due to liquid water will be noted, and the instantaneous conversion rate corresponding to this conversion level will be used to calculate the conversion due to equilibrium-moisture reaction. If it is assumed that the excess moisture on the sorbent surface will evaporate instantly during reaction, the differential expression for conversion due to reaction in the presence of equilibrium moisture must be integrated over the entire reaction time. The resulting

conversion predicted due to reaction in the presence of equilibrium moisture will be added to the conversion expected due to wet reaction in order to determine the total conversion of the sorbent.

7.2.4 Derivation of Modified Equilibrium Conversion Estimate

The expression which predicts sorbent conversion due to excess moisture is shown above in Equation 7.7. The expression for total sorbent conversion is:

$$\text{Pred. Conversion} = f_{\text{H}_2\text{O}} + g_{\text{EQ}} \quad (7.8)$$

where:

$f_{\text{H}_2\text{O}}$ = conversion due to excess H_2O : [mole SO_2 /mole Ca], and

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

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

$$g_{\text{EQ}} = h_{\text{EQ}}(t + t_0) - f_{\text{H}_2\text{O}} \quad (7.9)$$

where:

t_0 = time required to achieve $f_{\text{H}_2\text{O}}$ conversion by the equilibrium-moisture mechanism; [s],

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

$h_{\text{EQ}}(t + t_0)$ = instantaneous rate of conversion by equilibrium-moisture mechanism evaluated at $(t + t_0)$; [(moles S/mole Ca)/(s)].

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

7.3 Apparatus and Procedures

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

7.3.1 Flue Gas Preparation and Delivery System

The flue gas preparation/delivery system is shown in Figure 7-2. This apparatus included:

- 4 mass flow controllers, which were used to maintain constant flowrates of the various gases used in the simulated flue gas
- A furnace and evaporator, to evaporate water and mix the steam into the flue gas
- A pressure control valve, to set the flue gas relative humidity after the water and gas flowrates were established

- A constant-rate syringe pump, to provide water to the evaporator
- A water bath and several heat exchangers, to maintain the flue gas and
- Reactor at a constant temperature during reaction,
- A scrubber, to remove any unreacted SO₂ from the gas stream, and
- an analyzer, to determine the SO₂ concentration in the gas.

House air, N₂, CO₂, and a mixture of 1 percent SO₂ in N₂ were metered through Brooks Series 5580 Mass Flow Controllers, marked "FC" in Figure 7-2, to provide a flue gas of accurately known composition. CO₂ was drawn from a gas cylinder of pure CO₂, while N₂ was drawn from a cylinder of liquid N₂.

The SO₂/N₂ mixture and the CO₂ were provided by either Wilson Oxygen of Austin, TX or Big Three Industrial Gases of Houston, TX. The N₂ was provided by the Cryogenics Lab at The University of Texas at Austin.

The flue gas was a mixture of N₂, CO₂, air, and the SO₂/N₂ gas mixture, and after the flue gas was formed, steam was injected to achieve a desired water content in the gas. The steam was generated and injected within an evaporator housed in the furnace (Not shown in Figure 7-2). Water was fed into the evaporator, and thus into the flue gas, at a constant rate of 0.03 ± 0.002 mol/min with a single-speed pump, labelled "H₂O" in Figure 7-2. The water injection system is discussed in detail in Section 3.1.1.

7.3.1.1 Water Injection System

Water was delivered to the flue gas system by a constant-speed pump made by Kernisk Teknologi of Sweden and two plastic syringes manufactured by Becton-Dickinson and Co. of Rutherford, NJ. The pump was designed to provide constant pressure on the syringes, and when 2 60 cm³ plastic syringes were attached, the liquid flowrate out of the pump was 0.54 cm³/min (0.03 mol H₂O/min). After leaving the pump, the water was evaporated in a glass evaporator manufactured in the Glassblowing Shop at The University of Texas at Austin, which was itself housed in a furnace provided by Tracor Co. (Stone Furnace model FD-1).

The evaporator consisted of a narrow glass tube wrapped around a large contacting barrel containing glass beads, as shown in Figure 7-3. The flue gas entered the top of the evaporator while the

Figure 7-2. Flue Gas Preparation/Delivery System.

Figure 7-3. Evaporator.

water was forced into the outer tube, beginning at the bottom of the evaporator. The water evaporated as it travelled through the tube, so that the steam exited the top of the tube and entered the mixing chamber, where it mixed with the flue gas. The humid flue gas left the bottom of the evaporator after passing through the glass beads, to guarantee adequate mixing. The furnace was typically run at temperatures ranging from 200-250 °C.

For a constant water flow rate, the flue gas relative humidity was controlled by changing the total flowrate of the flue gas and adjusting the pressure of the gas stream using the pressure control valves labelled "PC" in Figure 7-3. The total overall gas flowrates, considering the flowrates of the individual gases in the flue gas on a dry basis, are presented in Table 7-1. The gas flowrates were set to achieve a desired relative humidity at a pressure of 2 psig.

7.3.1.2 SO₂ Analyzer

The SO₂ content of the flue gas was measured using a Columbia Scientific Industries ambient-level flame photometric SO₂ analyzer (model SA295E). The SO₂ concentration was determined prior to the onset of reaction by bypassing the fixed-bed reactor unit and sending the simulated flue gas to the analyzer.

The analyzer was calibrated with a calibration gas mixture of approximately 1,000 ppm (by volume) SO₂ in N₂, which was provided by either Wilson Oxygen or Big Three Industrial Gases. The SO₂ content of the calibration gas always was known, although several cylinders of calibration gas were used, each with a slightly different SO₂ content.

The analyzer operated in the 1 ppb range so it was necessary to dilute both the calibration gas and the flue gas to this level prior to analysis. This dilution was accomplished by metering house air (dilution air) through a rotameter (Matheson model 7630-C) into the analyzed gas. When calibrating, house air was introduced so that the analyzer output for the 1,000 ppm calibration gas was at either 90 or 45 percent of full-scale. If experiments were to be conducted using 2000 ppm SO₂ in the flue gas, the dilution air rate was set so that the analyzer read 45 percent of full scale when the 1,000 ppm calibration gas was being analyzed, while if 1,000 ppm flue gas was to be used in the experiments, the dilution air flowrate was set so that the analyzer read 90 percent of full-scale during calibration.

TABLE 7-1. EXPERIMENTAL GAS FLOWRATES.

SO ₂ content (ppm)	flue gas RH (%)	total gas flow (slpm)	CO ₂ c ontent (vol %)	O ₂ content (vol %)
1000	55-63	4.1	10	12
1000	55-63	4.6	9	10
2000	80-90	2.5	10	11
2000	80-90	2.8	9	10
5000	55-63	4.1	10	12
1000, 2000, or 5000	0	4.1	10	12

When the simulated flue gas was being prepared, the same flowrate of dilution air was used as during the calibration step. After the carrier gas flowrate was set, the flowrate of the SO₂-N₂ mixture into the carrier gas was modified so that the analyzer read either 90 or 45 percent of full-scale, depending on the calibrated value. For example, to accurately attain flue gas SO₂ levels of 2,000 ppm, the analyzer was calibrated so that the 1,000 ppm calibration gas read 45 percent of full-scale, then the carrier gas and SO₂ flowrates were set so that, with the same flowrate of dilution air as in the calibration, the analyzer read 90 percent of full-scale. In all cases, the flue gas concentration was within 100 ppm of the desired level, with the exception of the 5,000 ppm experiments.

When experiments were conducted using 5,000 ppm SO₂ in the flue gas, the SO₂ content of the flue gas could not be checked with the analyzer. To dilute the calibration gas so that the 5,000 ppm flue gas was within the functional range of the analyzer, great quantities of dilution air were required. The flue gas delivery system was adversely affected by this high dilution air flowrate, as dilution air was found to penetrate upstream into the flue gas delivery system. This leak upstream into the delivery system caused unmanageable pressure fluctuations which inhibited the operation of the mass flow controllers.

To operate the reaction system with 5,000 ppm SO₂ in the flue gas, a mass flow controller was inserted between the SO₂/N₂ cylinder and the delivery system. The flowrates of the Air, N₂, CO₂, and SO₂/N₂ streams were adjusted to obtain 5,000 ppm SO₂ in the flue gas while maintaining the O₂ and CO₂ levels and preserving the overall total gas flowrate required to achieve the desired relative humidity in the flue gas. When the system was operated in this manner, it is estimated that the flue gas SO₂ content ranged from 4,800-5,200 ppm SO₂.

7.3.2 Fixed-Bed Reactor

The fixed-bed reactor is presented in Figure 7-4. This system was inserted into the flue gas line in the space marked "REACTOR" shown in Figure 7-2.

The fixed-bed reactor was composed of three individual reactor units, with common intake and outlet manifolds. The individual reactors were isolated from each other and the manifolds by stainless steel ball valves, and the interior volume of each of the three reactors was approximately 5.7 cm³. The reactors were constructed from 1/2 in stainless steel tubing with Swagelok® fittings and ball valves

Figure 7-4. Fixed-Bed Reactor.

mounted on each end of the individual reactor chambers. The inlet and outlet manifolds were constructed of 1/4 in stainless steel tubing and Swagelok® fittings. The reactor unit was rigid, and the steel construction was airtight and allowed for excellent heat transfer. The design allowed for three experiments to be run consecutively under the same conditions of temperature, gas-phase SO₂ content, and sorbent H₂O content.

Wet sorbents which were loaded into the three reactors were equilibrated to the reaction temperature without being exposed to hot, unsaturated (to H₂O) flue gas. As a result, while the water evaporated from the sorbent to saturate the vapor space of each individual reactor unit, the sorbents still retained a significant quantity of their initial surface moisture until reaction was initiated. The interior volume of each reactor was accurately known, making it possible to quantify the amount of H₂O which would evaporate from the wet sorbent prior to reaction.

Using this reactor design, three experiments could be run consecutively at nearly identical conditions of sorbent H₂O content, relative humidity, and SO₂ concentration. The most variation between consecutive experiments arose as a function of the density of the wet sorbent/sand mixture packed in the three reactors. During different experiments, pressure changes through the different individual reactor housings ranged from 2-5 psig, altering the relative humidity condition from one experiment to the next. In all cases, the relative humidity during an experiment was known accurately as a function of the H₂O and gas flowrates and the reactor pressure, measured as a change in the pressure upstream of the reactor.

7.3.3 Wet Sorbent Preparation

Wet sorbents were prepared by weighing approximately 10 mg of sorbent and H₂O into a small glass vial (approximately 15 cm³) which accepted a screw-on cap. The sorbents and H₂O were mixed using a stainless steel spatula, and a sample of damp sorbent was removed. The sample was weighed immediately to determine its mass while wet, and then oven-dried at approximately 100 °C. The initial H₂O content of the sample was determined by weight difference.

The vial containing the wet sorbent was capped and stored in a refrigerator at approximately 50 °F. When wet sorbent was required for experiment, two samples were extracted. One was placed in

the reactor and the other was weighed, dried, and reweighed to determine the initial moisture content of the reacted sample.

7.3.4 Reaction Procedure

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

It was assumed that H₂O evaporation from the sorbent occurred during the mixing with the sand. This evaporation was assumed to saturate the interior vapor space of the mixing vial. An estimate of the interior volume of the mixing vials was made to account for this H₂O loss. It also was assumed that evaporation occurred from the sorbents to saturate the interior vapor space of the reactor units, but that no additional H₂O loss from the reactive sorbents occurred. As stated previously, the interior volume of each reactor unit was known, so that all evaporative losses could be calculated. In total, a maximum loss of 0.0012 g of H₂O from the sorbent was expected due to evaporation during the mixing, loading, and equilibration processes.

After the reactor was loaded, it was inserted into the flue gas delivery system and allowed to equilibrate to the reaction temperature. During the equilibration step, flue gas flow bypassed the reactor. To initiate an experiment, flue gas was directed into the reactor housing, and one reactor unit was opened by opening its two ball valves. The pressure in the flue gas line during the reactions was controlled by

both the pressure-control valve downstream of the reactor outlet and the pressure drop inherent in the reactor packing. The pressure was monitored, upstream of the reactor, throughout the course of reaction, so that the relative humidity during reaction was known.

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

7.3.5 Analytical Procedure

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

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

The mother liquor from the filtration process was mixed with water in a 100 ml volumetric flask to make a 100 ml stock solution, which is referred to later in this document as the undiluted stock solution. This solution was diluted by withdrawing a 5 ml aliquot and adding it to 45 ml of H₂O in a 50 ml volumetric flask. This diluted liquid was injected into a Dionex Ion Chromatograph (IC) to determine sulfate content. A second 5 ml aliquot was removed from the stock solution, and it was added to 5 ml of 1 M NaCl and 40 ml of H₂O in a second 50 ml volumetric flask. This second diluted sample was used in a Varian Atomic Absorption Spectrophotometer (AA) to determine Ca content.

7.3.6 Analytical Equipment

7.3.6.1 Ion Chromatograph

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

- Separator column; Dionex HPIC-AS4A; p/n 037041,
- Guard column; Dionex HPIC-AS4A; p/n 037042,
- Eluent; 0.75 mM NaHCO₃, 2 mM Na₂CO₃ in H₂O,
- Cation suppressor solution; 0.005 M H₂SO₄,
- Suppressor module; Dionex Anion Micro Membrane Suppressor, p/n 038019, and
- Output conductivity range; 30 s (microsiemens).

The integrator was operated at the following settings:

- attenuation 2; 10,
- peak width; 0.04,
- threshold; 4, and
- area rejection; 0.

During operation, the IC first was calibrated with two standard solutions, after which the solutions of unknown sulfate content were analyzed. The standards were 0.05 mM NaSO₄ and 0.001 mM NaSO₄. In this concentration range, the IC responded in a linear fashion to concentration differences in the analyzed solution, and a least-squares fit to the two standards outputs and an assumed zero output for a

sulfate-free solution was used to determine the concentration of sulfate in the unknown samples. With the operating conditions presented above, the sulfate peak was eluted from the column after slightly less than 6 min.

7.3.6.2 Atomic Absorption Apparatus

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

- Acetylene, AA grade, and
- Nitrous oxide, medical grade.

The AA was operated at the following settings:

- lamp mode; double beam,
- wavelength monitored; 422.7 nm,
- slit width; 0.5 nm, and
- lamp current; 10 mA.

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

7.3.6.3 Total Carbon Analyzer

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

- acid source: 15 percent H_3PO_4 in H_2O ,
- carrier gas: N_2 ,
- water sorbent: $\text{Mg}(\text{ClO}_4)_2$,
- integrating device: Horiba PIR-2000 Infrared CO_2 Analyzer,
- CO_2 standard: 0.1 M NaHCO_3 , and
- injection volume of unknown: 1 ml.

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

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

7.3.6.4 SO_2 Sorbents

Several different sorbents were utilized in this study. Their properties are presented in Table 7-2. The reactivities of Mississippi Hydrated Lime and the lime/fly ash material have been studied by previous researchers at The University of Texas at Austin (Peterson and Rochelle, 1988; White and Rochelle, 1989). The other two sorbents, which are made from lime which has been hydrated in the presence of alcohol to promote the formation of high surface area, high porosity $\text{Ca}(\text{OH})_2$, were selected to determine the effects of surface area and porosity on the reaction with SO_2 . All of the sorbents used in this study were provided by Acurex Corp, with the exception of the Mississippi Hydrated lime, which was provided by the Mississippi Lime Co.

7.4 RESULTS AND CONCLUSIONS

The experimental work addressing the SO_2 -removal performance of damp lime-based sorbents under duct-injection conditions was performed in two stages. In the first stage, sorbents containing moisture in equilibrium with laboratory relative humidity (~ 50 percent) were exposed to flue gas of

TABLE 7-2. SORBENT PROPERTIES

<u>Sorbent Name</u>	<u>Surface Area</u> (m ² /g)	<u>Porosity</u> (cm ³ /g)	<u>Formation Conditions</u>
Lime/Fly Ash	16	.21	3:1 ratio Clinch River Flyash:Miss. Hydrated Lime slurried at 90°C for 12 hours
Mississippi Hydrated Lime	17	.19	
Promoted Lime "A"	74	.47	hydrated (alcohol present) at 74 °C for 50 min., N ₂ blanket for 41 min.
Promoted Lime "B"	51	.25	hydrated (alcohol present) at 74 °C for 35 min., N ₂ blanket for 26 min.

varying relative humidity and SO₂ content. In the second stage, water was added to the sorbent so that its water content was above that attained through equilibrium with the room humidity. Four sorbents, of varying surface properties and chemical composition, were used, and the flue gas SO₂ content and relative humidity were varied during both stages of testing.

In this work, two different gas-phase SO₂ concentrations were utilized, 1,000 and 5,000 ppm. At 1,000 ppm, it was expected that significant Ca-utilizations could be achieved in the lime/fly ash sorbent when both equilibrium moisture and moisture in excess of the equilibrium condition were applied to the reaction system. It was expected that the sorbent would not approach 100 percent Ca-utilization under these conditions. When 5,000 ppm SO₂ was present in the flue gas, it was expected that significant Ca-utilizations would be attained in all of the sorbents for reactions utilizing sorbent containing both equilibrium moisture and moisture in excess of the equilibrium quantity. Due to the possibility that the lime/fly ash sorbent would approach 100 percent Ca-utilization if significant quantities of moisture were present on the sorbent during reaction with 5,000 ppm flue gas, the amount of water added to this sorbent was limited during the 5,000 ppm testing. Tables 7-3 and 7-4 present the test plans followed in this work.

It was expected that lime/fly ash sorbent could hold up to 30 percent initial moisture (by mass), and still remain free-flowing. Water contents in excess of this amount would result in agglomerated sorbent which would show inhibited reactivity towards SO₂. The hydrated lime sorbents were expected to lose their free-flowing nature in the presence of quantities of moisture exceeding 10-15 percent (by mass). For both sorbent types, the amount of moisture present on the sorbent during experimental work was limited so that the sorbents remained free-flowing, although a limited number of experiments were performed utilizing sorbents containing moisture in excess of these levels.

7.4.1 Stage 1: Sorbent with Ambient Moisture

The experimental work performed with sorbents containing moisture in equilibrium with laboratory temperature and relative humidity are presented below.

The results presented in Figures 7-5, 7-6, and 7-7 complete the work done to investigate sorbent reactivity when the sorbent contains moisture in equilibrium with laboratory relative humidity. Initially, the sorbents contained moisture in equilibrium with the laboratory relative humidity. When the flue gas was

TABLE 7-3. TEST PLAN: STAGE 1. AMBIENT REACTION

<u>Sorbent Type</u>	<u>Initial Moisture (%)</u>	<u>Flue Gas SO₂ content (ppm)</u>	<u>Reaction Time (s)</u>	<u>Flue Gas RH (%)</u>
Lime/Fly Ash	3.5	1000	10,60,120	0,55,80
	3.5	5000	10,60,120	0,55
Miss. Hydrate	1.0	5000	10,60,120	55
Promoted Lime Hydrate "A"	1.0	5000	10,60,120	55
Promoted Lime Hydrate "B"	1.0	5000	10,60,120	55

TABLE 7-4. TEST PLAN: STAGE 2. SORBENT WITH EXCESS MOISTURE

Sorbent Type	Initial <u>Moisture</u> (%)	Flue Gas SO ₂ Content (ppm)	Reaction Time (sec)	Flue Gas RH (%)
Lime/Fly ash	15, 30	1000	10, 60, 120	0, 55, 80
	15, 30	5000	10, 60, 120	0, 55
Miss. Hydrate	15	5000	10, 60, 120	55
Promoted Lime Hydrate "A"	15	5000	10, 60, 120	55
Promoted Lime Hydrate "B"	15	5000	10,60,120	55

Figure 7-5. Conversion of Lime/Fly Ash Sorbent Containing Ambient Moisture: (1,000 ppm SO₂ in flue gas, 70 °C, 3.5 percent initial moisture on sorbent).

Figure 7-6. Conversion of Hydrated Lime Sorbents Containing Ambient Moisture: (5,000 ppm SO₂ in flue gas, 70 °C, 1.0 percent initial moisture on sorbents, 58-67 percent RH in flue gas).

Figure 7-7. Comparison of Lime/Fly Ash and Mississippi Hydrated Lime Sorbent: (5,000 ppm SO₂ in flue gas, 70 °C, 1.0 percent initial moisture on Miss. Hydrate, 3.5 percent on Lime/Fly Ash, 60-67 percent RH in flue gas).

Introduced into the reactors, the sorbents' moisture content shifted to attain equilibrium with the flue gas relative humidity. It was expected that the magnitude of the change in the surface moisture content of the sorbent was negligible during this process.

It can be seen in Figure 7-5 that increasing the relative humidity of the flue gas and increasing the gas-sorbent contact time enhances the conversion (moles S captured/mol Ca) of the lime/fly ash sorbent. At the higher relative humidities, conversions reach 0.50 and 0.20 for 120 and 10 s reactions, while the average sorbent conversion for 120 s gas/solid contact time is 0.30 at approximately 60 percent RH. The increase in sorbent conversion with increasing reaction time is not as significant for the lower relative humidities as for the higher relative humidities, implying that for a given reaction time, the greater the surface moisture content of the sorbent, the greater the conversion.

The surface area of hydrated lime sorbent "A" is 74 m²/g, of hydrated lime sorbent "B" is 51 m²/g, of Mississippi Hydrated Lime sorbent is 17 m²/g, and of lime/fly ash is 16 m²/g. There is a corresponding increase in sorbent porosity with increasing surface area for all of the sorbents. Figure 7-6 shows that the equilibrium conversion of the hydrated lime sorbents increases with increasing sorbent surface area, and the conversion of lower surface area sorbents does not approach that of the high surface area sorbents at short or long times. The conversion of the hydrated lime sorbents increases slightly with increasing reaction time, although the effect is not as significant as for the lime/fly ash sorbent in the 1,000 ppm flue gas (Figure 7-5).

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

In Figure 7-7, a comparison of the reactivity of lime/fly ash sorbent with that of Mississippi Hydrated Lime is presented. 5,000 ppm SO₂ were in the flue gas during these tests, which were conducted at approximately 60 percent RH. The conversion of the lime/fly ash composite was superior to that of the Mississippi Hydrate at all reaction times, although the surface areas of the two sorbents are similar. In contrast to its performance in the presence of low concentrations of SO₂, the conversion of the

lime/fly ash sorbent does not increase drastically with increasing reaction time in the presence of 5,000 ppm SO₂. The conversion of the lime/fly ash sorbent is approximately the same for the 120 s reaction, although the 10 and 60 s reactions provide significantly higher conversions in the presence of the 5,000 ppm SO₂ than in the presence of the 1,000 ppm SO₂, which was not expected. It appears that, with 5,000 ppm SO₂ in the flue gas, the conversion occurring during the short time reactions of all the sorbents studied is the dominant conversion, with incremental reaction occurring at long times.

It is possible that the gas-solid reaction in the presence of equilibrium moisture on the sorbent surface is controlled by the effective surface area of the sorbent. Increasing sorbent conversion reduces the rate of additional conversion, probably due to product precipitation on the reactive surface. The instantaneous conversion of a sorbent of high surface area is high, but additional conversion is incremental by comparison when 5,000 ppm SO₂ are in the flue gas. With lower SO₂ contents in the flue gas, the instantaneous reaction is not as significant as for the high-SO₂ cases, but the additional conversion is more significant at the low SO₂ contents than at the high levels. The conversions of the high surface area hydrated lime and the lime/fly ash sorbent are approximately the same at all conditions, implying that the sorbent conversion is controlled by the dispersion of Ca throughout this surface area. Such a mechanism would result in:

- higher SO₂ capture on high surface area sorbents compared to low surface area sorbents,
- for a given surface area, an inverse relationship between the Ca content of sorbents and their conversion, and
- high sorbent conversions for short-time reactions, which occur when the sorbent surface area is not blocked by the formation of a product layer, followed by incremental increases in conversion for longer-time reactions, when the sorbent surface area has been reduced by product layer formation.

Figure 7-8 presents a comparison between the m² sorbent/mole Ca(OH)₂ and sorbent conversion in 5,000 ppm SO₂ flue gas when the sorbent contains moisture in equilibrium with flue gas relative humidity. The lime/fly ash and hydrated lime sorbents fall approximately on the same curves,

Figure 7-8. Effect of Ca Dispersion on Sorbent Conversion: (5,000 ppm SO₂ in flue gas, 70 °C, 1.0 percent initial moisture on Miss. Hydrate, 3.5 percent on Lime/Fly Ash, 60-67 percent RH in flue gas.

implying that the dispersion of the $\text{Ca}(\text{OH})_2$ over the sorbent surface area is more important than the quantity of $\text{Ca}(\text{OH})_2$ applied.

7.4.2. Stage 2: Reaction of Damp Sorbents

7.4.2.1 Damp Lime/Fly Ash Sorbent in 1,000 ppm SO_2

Figures 7-9, 7-10, and 7-11 present the results obtained using damp lime/fly ash sorbent in 1,000 ppm SO_2 for 10, 60, and 120 s. The results shown are for work performed at 0, 54-64, and 80-91 percent relative humidity. For all cases shown, the sorbent conversion increases with increasing moisture content and increasing flue gas relative humidity. While the straight lines drawn on the plots accentuate the increase in conversion with increasing moisture content, the increase is not linear, except at the high relative humidity.

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

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

Figure 7-9. Conversion of Damp Lime/Fly Ash Sorbent: (1,000 ppm SO₂ in flue gas, 70 °C, 10 s reaction).

Figure 7-10. Conversion of Damp Lime/Fly Ash Sorbent: (1,000 ppm SO₂ in flue gas, 70 °C, 60 s reaction).

Figure 7-11. Conversion of Damp Lime/Fly Ash Sorbent: (1,000 ppm SO₂ in flue gas, 70 °C, 120 s reaction).

moisture content than at the lower levels, although the intermediate-moisture results support the trend that conversion levels off with increasing moisture.

It is possible that the excess moisture evaporates very rapidly at the lower relative humidities, resulting in high instantaneous conversion of the sorbent but blockage of the surface area by product and limited reaction due to equilibrium moisture after the sorbent has dried. It also is possible that the evaporation rate at the low relative humidities is competitive with the rate of dissolved SO₂ migration within the free moisture, resulting in a saturated liquid phase and limitation of the absorption of SO₂ into the free moisture. At the higher relative humidity, the free moisture will remain on the particle for longer time periods, resulting in increased H₂O available for SO₂ absorption.

7.4.2.2 Damp Sorbents in 5,000 ppm SO₂

Figures 7-12 through 7-17 present the results obtained using damp sorbents in 5,000 ppm SO₂. Neither the lime/fly ash sorbent nor the hydrated lime sorbents reacting in 5,000 ppm flue gas showed a significant increase in conversion with increasing moisture content, as was expected. With the hydrated lime sorbents, the conversion increase with increasing initial moisture content is not significant, and within the spread of the data the conversion can be considered essentially constant with increasing initial moisture content of the moderate surface area hydrated limes. Conversion of the highest surface area hydrated lime is seen to decrease with increasing initial moisture content of the sorbent, while for the low surface area hydrated lime the conversion increases with increasing initial moisture content.

These results indicate that, for the hydrated limes, the presence of excess moisture on the sorbent surface interferes with the reaction occurring by the equilibrium-moisture mechanism on the sorbent surface. For the high surface area materials, the surface reaction occurring with the equilibrium moisture is significant and results in high sorbent conversions. The addition of excess moisture reduces the sorbent surface area available for equilibrium-type reaction, and after the free moisture has evaporated, the product formed blocks the sorbent surface area and continues to inhibit the equilibrium-moisture reaction. While the reaction is very fast in the presence of free moisture, the reaction occurring after the free moisture has evaporated is greatly reduced by the surface products, reducing the net benefit of adding excess moisture to the high surface area hydrated lime. For the low surface area

Figure 7-12. Conversion of Damp Lime/Fly Ash Sorbent: (5,000 ppm SO₂ in flue gas, 70 °C, 10 s reaction, 58-63 percent RH).

Figure 7-13. Conversion of Damp Lime/Fly Ash Sorbent: (5,000 ppm SO₂ in flue gas, 70 °C, 60 s reaction, 58-68 percent RH).

Figure 7-14. Conversion of Damp Lime/Fly Ash Sorbent: (5,000 ppm SO₂ in flue gas, 70 °C, 120 s reaction, 58-62 percent RH).

Figure 7-15. Conversion of Damp Hydrated Lime Sorbents: (5,000 ppm SO₂ in flue gas, 70 °C, 10 s reaction, 56-66 percent RH).

Figure 7-16. Conversion of Damp Hydrated Lime Sorbents: (5,000 ppm SO₂ in flue gas, 70 °C, 60 s reaction, 58-69 percent RH).

Figure 7-17. Conversion of Damp Hydrated Lime Sorbents: (5,000 ppm SO₂ in flue gas, 70 °C, 120 s reaction, 58-64 percent RH).

hydrated lime, where the equilibrium moisture conversion is not significant, the addition of excess moisture increases the sorbent conversion. It is clear that the conversion of all of the hydrated lime sorbents is approximately the same when large quantities of initial moisture are added. This implies that the reaction due to excess moisture is independent of sorbent surface area and that overall conversion in the presence of significant quantities of excess moisture is dominated by the wet reaction mechanism.

For the lime/fly ash sorbent, the conversions at low moisture contents are significantly greater in the 5,000 ppm flue gas than for the 1,000 ppm flue gas for both the 10 and 60 s reactions at 56-68 percent relative humidity. The conversions at higher sorbent moisture contents are approximately equal between the 5,000 and 1,000 ppm SO₂ flue gas. It appears that there is an instantaneous reaction occurring when there is 5,000 ppm SO₂ in the flue gas and upon completion of this reaction, additional sorbent conversion, with increasing reaction time or increasing moisture content, provide incremental additional conversion. In the presence of 1,000 ppm SO₂, the instantaneous reaction is not significant, so that significant additional conversion can be accomplished by increasing the reaction time or moisture content of the sorbent.

With the lime/fly ash sorbent, experiments conducted at lower SO₂ content but higher relative humidities attained significantly higher conversions for the same initial moisture content than the experiments run at the high SO₂ content and lower relative humidity. The higher relative humidity changes the drying time of the sorbent, and it appears that the amount of time liquid moisture is present on the surface of the sorbent is more significant than the gas-phase SO₂ content.

It is expected that the sorbent dries very rapidly when exposed to flue gas. Changing the gas-phase SO₂ concentration will increase the rate of transfer of SO₂ to the sorbent surface, but this effect may not be visible over the very brief period of time that the liquid water is present. Raising the drying time, and consequently increasing the period of gas-phase control, appears to have a more significant effect on sorbent conversion.

7.4.3 Comparison: Additive Model vs. Experiment

In Section 7.2: Theory, an expression describing the effect of excess moisture on the conversion of damp sorbent is presented. The predictive expression is shown here:

$$\frac{\Delta \text{SO}_2}{\text{Ca}} = \frac{D_{\text{SO}_2 \text{K}} (P_{\text{SO}_2})}{D_{\text{H}_2\text{O} \text{K}} (P_{\text{H}_2\text{O}}^* - P_{\text{H}_2\text{O}})} \left(\frac{\Delta \text{H}_2\text{O}}{\text{Ca}} \right)$$

where:

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

The total conversion of the sorbent is the combination of reaction occurring due to the moisture in excess of the equilibrium (with the flue gas relative humidity) quantity and the reaction occurring due to moisture in equilibrium with the flue gas relative humidity. The Additive Model assumes that the presence of excess moisture on the sorbent does not interfere with the equilibrium-moisture reaction. In order to predict the total conversion of the sorbent with the Additive Model, conversion values from equilibrium-moisture studies must be added to the conversion predicted due to the excess moisture on the sorbent.

Selected examples of the conversions attained by the various sorbents when reacted without the addition of excess moisture are presented in Tables 7-5 and 7-6. The values, which are added to the conversion predicted due to wet reaction in the Additive Model, are grouped according to the approximate relative humidities of each experiment.

The comparison of theoretical and observed conversions of damp solids for various conditions of SO_2 concentration, relative humidity and contact time is given in Figures 7-18 through 7-23.

The Additive Model correctly predicts the conversion of the lime/fly ash sorbent at 0 percent relative humidity in 1,000 ppm SO_2 flue gas for 60 s reaction. At this condition, the effect of the equilibrium-moisture reaction is nearly negligible, and the sorbent conversion was seen to increase linearly with increasing moisture content. For the other conditions presented, the Additive Model consistently overpredicts the sorbent conversion at high sorbent moisture contents. At low initial moisture contents, the observed effect of excess moisture is small compared to the equilibrium-moisture reaction. At these low moisture contents, the Additive Model is essentially the equilibrium moisture conversion. With this consideration, it is not surprising that the data are correctly modelled in this regime. Considering the results at high moisture contents, the overpredictions are usually less than the magnitude of the equilibrium-moisture contribution to the overall predicted conversion. This implies that the effect of excess moisture is correctly approximated, but the effect of the wet reaction the equilibrium-moisture reaction is not correctly handled. The results of the 5,000 ppm study with damp lime/fly ash sorbent do not fall into this category. The model grossly overpredicts the sorbent utilization, implying that the effect

TABLE 7-5. CONTRIBUTION OF AMBIENT REACTION TO TOTAL CONVERSION OF LIME/FLY ASH AND HYDRATED LIME SORBENTS (ADDITIVE MODEL): (5,000 PPM SO₂ IN FLUE GAS, 70 °C).

<u>Reaction Time (s)</u>	<u>Sorbent Type</u> *	<u>RH (%)</u>	Equilibrium- Moisture Conversion (add to pred. value)
10	MH	56-63	0.08
10	A	58-66	0.21
10	B	58-60	0.10
60	MH	55-65	0.13
60	A	80-90	0.24
60	B	0	0.14
120	L/FA	58-68	0.30

* (MH = Mississippi Hydrated Lime, A = Hydrated Lime "A",
B = Hydrated Lime "B", L/FA = Lime/Fly Ash)

TABLE 7-6. CONTRIBUTION OF AMBIENT REACTION TO TOTAL CONVERSION OF LIME/FLY ASH AND HYDRATED LIME SORBENTS (ADDITIVE MODEL): (1,000 PPM SO₂ IN FLUE GAS, 70 °C).

<u>Reaction Time (s)</u>	<u>RH</u>	Equilibrium-Moisture
		Conversion (<u>add to pred. value</u>)
10	80-90	0.14
60	0	0.03
120	55-65	0.23

Figure 7-18. Comparison: Theoretical and Observed Conv. of Damp Lime/Fly Ash Sorbent (Additive Model): (1,000 ppm SO₂ in flue gas, 70 °C, 120 s reaction, 5565 percent RH).

Figure 7-19. Comparison: Theoretical and Observed Conv. of Damp Lime/Fly Ash Sorbent (Additive Model): (1,000 ppm SO₂ in flue gas, 70 °C, 60 s reaction, 0 percent RH).

Figure 7-20. Comparison: Theoretical and Observed Conv. of Damp Lime/Fly Ash Sorbent (Additive Model): (1,000 ppm SO₂ in flue gas, 70 °C, 10 s reaction, 8090 percent RH).

Figure 7-21. Comparison: Theoretical and Observed Conv. of Damp Hydrated Lime Sorbents (Additive Model): (5,000 ppm SO₂ in flue gas, 70 °C, 10 s reaction, 8090 percent RH).

Figure 7-22. Comparison: Theoretical and Observed Conv. of Damp Hydrated Lime Sorbents (Additive Model): (5,000 ppm SO₂ in flue gas, 70 °C, 60 s reaction, 8090 percent RH).

Figure 7-23. Comparison: Theoretical and Observed Conv. of Damp Lime/Fly Ash Sorbent (Additive Model): (5,000 ppm SO₂ in flue gas, 70 °C, 120 s reaction, 55-60 percent RH).

of excess moisture is not as significant with the lime/fly ash sorbent at these conditions as is expected in the model.

The assumption that the excess moisture on the surface of the sorbents does not interfere with the equilibrium-moisture reaction mechanism (basis for the Additive Model) appears to be erroneous. Significant quantities of moisture on the sorbent surface significantly reduce the surface area available for equilibrium-moisture reaction, and it is likely that the equilibrium-moisture reaction does not begin until significant portions of the free moisture have evaporated and the product has blocked the sorbent surface.

In the Additive Model, the sorbent conversion expected for a sorbent reacting in the presence of equilibrium moisture is added to the conversion predicted due to the free moisture. It is probably more accurate to adjust the equilibrium-moisture component to account for the reduced surface area and reduced reaction time available for reaction in the presence of equilibrium moisture. The fact that the model correctly predicts sorbent conversions when either the free-moisture or equilibrium-moisture reactions are dominant indicates that properly adjusting the magnitude of the two additive portions of the model will provide accurate predictions.

7.4.4 Comparison: Interactive Model vs. Experiment

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

The Interactive Model requires expressions for the rate of conversion by the equilibrium-moisture mechanism as a function of sorbent conversion. The plots used to generate these expressions are presented in Figures 7-24 and 7-25. The expressions are presented in Table 7-7.

To use the Interactive Model, the conversion attained by the wet reaction mechanism is noted and the expressions presented in Table 7-7 are manipulated to determine the time required to attain this conversion by the equilibrium-moisture mechanism (t_0). It is then assumed that the excess moisture evaporates instantly from the sorbent surface upon introduction of the flue gas, so that the time available for reaction by the equilibrium-moisture mechanism is approximately the original reaction time (t). The rate expressions presented in Table 7-7 are evaluated twice, at time = ($t_0 + t$) and time = (t_0). The conversion expected at t_0 is then subtracted from that expected at $t_0 + t$ to determine the conversion occurring by the equilibrium-moisture mechanism after the wet reaction is complete.

Figures 7-26 through 7-40 present a comparison between the conversions predicted by the Interactive Model and the experimentally observed conversions.

The Interactive Model underpredicts system performance for all reaction times at 0 percent relative humidity and 1,000 ppm SO_2 in the flue gas. At this condition the contribution of equilibrium reaction is relatively insignificant, although the overall magnitude of the sorbent conversion is small. The model also underpredicts lime/fly ash conversion with 1,000 ppm SO_2 in the flue gas at long times for both the 55-65 and 80-90 percent relative humidities. At these conditions, the equilibrium-moisture conversions are significant. The Additive Model overpredicted the system performance at these conditions, while the Interactive Model, which incorporates a significantly lower contribution due to the equilibrium-moisture reaction into the final result, underpredicts system performance. This implies that the wet reaction influences the equilibrium-moisture reaction and that the model has overcompensated for this effect.

Figure 7-24. Determination of Instantaneous Sorbent Conversion Rate Hydrated Lime Sorbents: (5,000 ppm SO_2 in flue gas, 70 °C, 55-65 percent RH).

Figure 7-25. Determination of Instantaneous Sorbent Conversion Rate Lime/Fly Ash Sorbent: (1,000, 5,000 ppm SO₂ in flue gas, 70 °C, 55-65 percent RH).

TABLE 7-7. RATE OF SORBENT CONVERSIONS FOR INTERACTIVE MODE.

<u>Sorbent Type</u>	ppm SO ₂ in <u>flue gas</u>	<u>RH (%)</u>	<u>value of slope</u>	<u>value of intercept</u>
Lime/Fly Ash	1000	0	3.6217×10^{-2}	-2.364×10^{-2}
Lime/Fly Ash	1000	55-65	0.18938	-0.14235
Lime/Fly Ash	1000	80-90	0.26199	-0.10919
Lime/Fly Ash	5000	55-65	3.6416×10^{-2}	0.17771
Hydrate "A"	5000	55-65	7.3167×10^{-2}	0.15487
Hydrate "B"	5000	55-65	0.11566	1.6071×10^{-2}
Miss. Hydrate	5000	55-65	4.6061×10^{-2}	5.3755×10^{-2}

Figure 7-26. Interactive Model of Lime/Fly Ash Conversion: (1,000 ppm SO₂ in flue gas, 70 °C, 0 percent RH).

Figure 7-27. Interactive Model of Lime/Fly Ash Conversion: (1,000 ppm SO₂ in flue gas, 70 °C, 0 percent RH, 60 s reaction).

Figure 7-28. Interactive Model of Lime/Fly Ash Conversion: (1,000 ppm SO₂ in flue gas, 70 °C, 0 percent RH, 120 s reaction).

Figure 7-29. Interactive Model of Lime/Fly Ash Conversion: (1,000 ppm SO₂ in flue gas, 70 °C, 55-65 percent RH, 10 s reaction).

Figure 7-30. Interactive Model of Lime/Fly Ash Conversion: (1,000 ppm SO₂ in flue gas, 70 °C, 55-65 percent RH, 60 s reaction).

Figure 7-31. Interactive Model of Lime/Fly Ash Conversion: (1,000 ppm SO₂ in flue gas, 70 °C, 55-65 percent RH, 120 s reaction).

Figure 7-32. Interactive Model of Lime/Fly Ash Conversion: (1,000 ppm SO₂ in flue gas, 70 °C, 80-90 percent RH, 10 s reaction).

Figure 7-33. Interactive Model of Lime/Fly Ash Conversion: (1,000 ppm SO₂ in flue gas, 70 °C, 80-90 percent RH, 60 s reaction).

Figure 7-34. Interactive Model of Lime/Fly Ash Conversion: (1,000 ppm SO₂ in flue gas, 70 °C, 80-90 percent RH, 120 s reaction).

Figure 7-35. Interactive Model of Lime/Fly Ash Conversion: (5,000 ppm SO₂ in flue gas, 70 °C, 55-65 percent RH, 10 s reaction).

Figure 7-36. Interactive Model of Lime/Fly Ash Conversion: (5,000 ppm SO₂ in flue gas, 70 °C, 55-65 percent RH, 60 s reaction).

Figure 7-37. Interactive Model of Lime/Fly Ash Conversion: (5,000 ppm SO₂ in flue gas, 70 °C, 55-65 percent RH, 120 s reaction).

Figure 7-38. Interactive Model of Hydrated Lime Conversion: (5,000 ppm SO₂ in flue gas, 70 °C, 55-65 percent RH, 10 s reaction).

Figure 7-39. Interactive Model of Hydrated Lime Conversion: (5,000 ppm SO₂ in flue gas, 70 °C, 55-65 percent RH, 60 s reaction).

Figure 7-40. Interactive Model of Hydrated Lime Conversion: (5,000 ppm SO₂ in flue gas, 70 °C, 55-65 percent RH, 120 s reaction).

The model inaccuracy may be attributed to inaccuracy in determining the instantaneous rate of sorbent conversion. In Figures 7-25 and 7-26, the best-fit lines do not always represent the data accurately. Errors in the projected slopes of these lines will propagate into the expected equilibrium-moisture conversion used in the Interactive Model.

The Interactive Model overpredicts the conversions attained in the work done using lime/fly ash sorbent in 5,000 ppm SO₂ flue gas, as did the Additive Model. This implies that the overprediction is generated within the expression for conversion as function of initial moisture content, which has proven reliable with the other sorbents and with the lime/fly ash sorbent at low SO₂ content. The wet reaction occurring on lime/fly ash in the presence of high SO₂ contents is inhibited and does not fall within the gas-phase controlled regime.

Considering the hydrated lime sorbents, the Additive Model is seen to slightly overpredict the conversion of the high surface area sorbent and underpredict the conversion of the low surface area sorbent at high moisture contents, independent of reaction time. The high surface area sorbent achieved high conversion due to the equilibrium-moisture reaction, which was inhibited by the wet reaction to a greater degree than the Interactive Model allowed. The low surface area hydrated lime achieved minimal conversion due to the equilibrium-moisture reaction, but the Interactive Model overcompensated for the reduction in this reaction.

In general, the Interactive Model is a significant improvement over the Additive Model. The data support the model reasonably well in all cases with two exceptions. In the high SO₂-lime/fly ash system, in which the wet reaction appears to be outside the realm of gas-phase control, the model does not fit the data. In the 0 percent relative humidity studies with the 1,000 ppm SO₂-lime/fly ash system, the model does not fit the data, although the magnitude of the sorbent conversion is too low to provide a reasonable test of the model.

7.4.5 Conversion of Lime/Fly Ash Sorbent by Reaction with CO₂

The lime/fly ash sorbent contained CO₂ in the form of carbonate, prior to reaction with the 1,000 ppm SO₂, 10 percent CO₂ flue gas. The initial carbonate content of the sorbent was 2×10^{-4} moles CO₂/mol Ca. Significant additional CO₂ capture was not discovered for short or long time reactions in the

presence of excess moisture on the sorbent surface (Figure 7-41). Within the ability to experimentally determine CO₂ capture on the sorbent, no CO₂ capture occurred, and more importantly, the magnitude of Ca-conversion by CO₂ is several orders of magnitude lower than for conversion by SO₂ with 10 percent CO₂ and 1,000 ppm SO₂ in the flue gas.

7.5 CONCLUSIONS

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

- In the presence of low concentration SO₂, the addition of excess moisture to lime/fly ash sorbents significantly increases their conversion over that attained in the absence of excess moisture.
- In the presence of high concentrations of SO₂, the addition of excess moisture to lime/fly ash sorbents does not increase significantly, and may decrease slightly, the sorbent conversion in comparison with that attained in the absence of excess moisture.
- The conversion of low surface area hydrated limes increases with increasing initial moisture content of the sorbent, while the conversion of high surface area hydrated limes remains the same or decreases slightly with the addition of excess moisture.
- The reaction between damp lime/fly ash sorbent and low concentrations of SO₂ is gas-phase mass-transfer controlled until the moisture has evaporated from the sorbent surface.
- The reaction between damp hydrated lime sorbent and high concentrations of SO₂ is gas-phase mass-transfer controlled until the moisture has evaporated from the sorbent surface.
- The reaction between damp lime/fly ash sorbent and high concentrations of SO₂ is not gas-phase mass-transfer controlled.
- Sorbent conversion due to wet reaction is not a strong function of sorbent surface area.
- Overall damp lime/fly ash conversion at times ranging from 10-120 s is a stronger function of relative humidity (sorbent drying time) than of SO₂ content in the flue gas.
- The reaction occurring between lime/fly ash and hydrated lime sorbents in the presence of excess free moisture is a combination of the equilibrium-moisture reaction and the wet reaction.

Figure 7-41. Reaction of Lime/Fly Ash Sorbent with CO₂ (1,000 ppm SO₂ in flue gas, 70 °C, 55-65 percent RH).

- The conversion of the hydrated lime and lime/fly ash sorbents due to wet reactions affects the surface properties of the sorbents and the extent of equilibrium-moisture conversion which occurs upon evaporation of the free moisture.
- The equilibrium-moisture conversion of the hydrated lime and lime/fly ash sorbents increases with increasing surface area/mole $\text{Ca}(\text{OH})_2$ of the sorbent.
- Sorbents which attain high conversions due to equilibrium-moisture reaction do not show increased reactivity at long times in the presence of excess moisture, although the wet reaction occurs much more quickly than the equilibrium-moisture reaction.
- Reaction occurring between damp lime/fly ash and low conc. SO_2 and damp hydrated lime sorbents and high conc. SO_2 can be adequately modelled assuming the wet reaction is gas-phase mass-transfer controlled and the products of the wet reaction affect the progress of the equilibrium-moisture reaction.
- Damp hydrated limes and lime/fly ash sorbents can be prepared, loaded and reacted with SO_2 without losing their initial moisture and without agglomerating.
- Up to 10 percent CO_2 in flue gas containing 1,000 ppm SO_2 does not inhibit the sorbent- SO_2 reaction.

SECTION 8

FIELD TEST SUPPORT

8.1 SPECIAL STUDY--EPSOM SALT

Considerable operational problems may be encountered in the dry-duct injection process when the buildup of wall deposits occurs. The likelihood of wall deposits occurrence can be reduced by decreasing the amount of moisture in the duct (increasing approach to saturation). Since the conversion of Ca(OH)_2 in the duct is strongly affected by the approach to saturation, operation at decreased approach to saturation would need to be accompanied by delivery of additional moisture with the injected solids. It was suggested that if waters of hydration would be evaporated at a desirable rate, the Epsom Salt (magnesium sulfate heptahydrate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), might be used as an additive for in-duct dry injection to reduce the amount of water needed for humidification and relieve the concerns of wall deposits.

To test the possibility of moisture delivery by means of injected solids, the decomposition of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was investigated. Figure 8-1 presents TGA data acquired at 54 F/min heating rate. The sample of a reagent-grade $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was placed in the TGA and exposed to dry N_2 . The weight loss equal to the theoretical weight decrease upon evaporation of $7\text{H}_2\text{O}$ (51.2 percent) was measured at 610 F. The decomposition rate of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was measured at temperatures ranging from 158-482 F and data is presented in Figure 8-2. The decomposition rate was increasing with the temperature of the gas (N_2). Less than 10 percent weight loss was measured following 10 min exposure to 212 F dry N_2 . Based on data presented in Figure 8-2, the application of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ as a moisture carrying agent for dry duct injection seems unlikely.

Industrial grade Epsom Salt was injected into the pilot plant at ~3.4 lb/h. Since Epsom Salt contains about 51 percent hydrate water, it is estimated that the flue gas temperature should decrease ~40-50 F if all the hydrate water is released and evaporated from liquid to vapor phase. Figure 8-3 shows the effect of Epsom Salt injection on in-duct temperature. The duct temperature reported was measured downstream of the Epsom Salt injection point. In the first test, the duct temperature was maintained at ~200 °F before Epsom Salt injection. The temperature measurement device was placed at

Figure 8-1. Thermal Decomposition of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

Figure 8-2. Decomposition Rate of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

Figure 8-3. Effect of Epsom Salt Injection on In-duct Temperature.

the point which allowed ~2 s gas residence time downstream of the injection point. Figure 8-3 shows that only a 4 F temperature drop was obtained after Epsom Salt injection. The second test was conducted by injecting the Epsom Salt before the humidifier which provided ~10 s more gas residence time. The flue gas temperature was controlled at 300 F before injection. Fifty minutes after Epsom Salt injection, only a 3 F temperature drop was obtained.

SECTION 9

AGGLOMERATION OF DAMP CALCIUM HYDROXIDE BASED SOLIDS

9.1 INTRODUCTION

This section documents progress made on a study of the moisture capacity of SO₂ sorbents. Mississippi hydrate and lime/fly ash solids have been sieved through a series of sieves. The solids contained moisture from 0-32 percent. The sieve tests reflect the effect of moisture on agglomeration of the solids. Planned work includes sieve tests on high surface area solids prepared in the laboratory. Additionally, aerodynamic size distributions of the materials will be determined.

9.2 MATERIALS STUDIED

Sieve tests were conducted on 2 sorbents: Hydrated lime and a lime/fly ash slurry product. The properties of the 2 sorbents are summarized in Table 9-1. The hydrated lime was supplied by the Mississippi Lime Company. The lime/fly ash material was prepared by Acurex in March 1987 by slurring Clinch River fly ash with calcium hydroxide in a 3-1 weight ratio. The components were slurried for 12-16 hours at 80-90°C, then filtered and dried in an atmospheric oven.

9.3 EXPERIMENTAL PROCEDURE

This section describes the procedure used to obtain the reported test results. Sixteen-gram samples of sorbent were used for sieve tests. In the future, 5 g samples will be used because sorbents produced in the laboratory are not produced in a large enough quantity. The exact weight was determined at ambient moisture conditions: Less than 0.8 wt percent moisture. Ambient moisture was

TABLE 9-1. PROPERTIES OF THE HYDRATED LIME AND LIME/FLY ASH MATERIALS
(Rochelle et al., 1990)

Property	Lime/Fly Ash	Mississippi Hydrate
Surface area - m ² /g	16	17
Median particle diameter - μm		
Sedigraph	3.8	2.9
Impactor	6.0	18.6
Porosity - cm ³ /g	0.21	0.19
True density - g/cm ³	2.62	2.24

determined by drying a 14 g sample in an oven at 110 °C. In the future sorbent samples will be initially dried at 110 °C in an atmospheric oven for at least 10 h and then placed in a desiccator to cool before weighing and testing.

Water was added drop-by-drop to the sorbent and mixed in by hand with a spatula to achieve the desired moisture content. The sample was weighed again to determine its moisture content. The sample was then placed on the uppermost sieve of a series of 3 sieves, 3 standard 8 in diameter sieves and designated by No. 80 (177 micron openings), No. 120 (125 micron openings), and No. 270 (53 micron openings). A collection pan was placed below the series of sieves and a cover used. The sieves were shaken for 15 min on a Portable Sieve Shaker Model RX-24 from W.S. Tyler, Incorporated. After shaking, the material from each sieve and the pan was collected and the 4 splits weighed. If moisture had been added to the initial sample, the splits were dried in an oven at 110 °C until constant weight was achieved (this usually took less than 30 min). In the future the splits from all tests will be placed in the oven, even if no water was added to the initial sample.

9.4 RESULTS

Figure 9-1 shows the results of tests conducted on the Mississippi hydrate. As the initial moisture content of the material increased, more of the material was retained by the No. 80 sieve. This reveals increasing agglomeration of the material as the moisture content increased. The effect of increased moisture was sharp at low values and decreased at greater values. It was observed that the moist hydrate forms spherical agglomerates. Figure 9-2 shows the results of tests conducted on the lime/fly ash material. Again, the amount retained by the coarsest sieve increased as the initial moisture content increases. However, in this case much less of the material was retained relative to the hydrate at low moisture content. More than 97 percent of the material was retained on the No. 80 sieve at moisture contents of 20 percent and above. In this case the material sat on the sieve similar in appearance to dried clay which cracks to form platelets. Figure 9-3 shows the moisture content of each split. The results indicate that the material, which passes through to the smaller sieve openings, contains less moisture. This may occur because the smaller material contained less

Figure 9-1. Percentage of Mississippi Hydrate passing through each sieve. The values at 0 percent moisture are averages of 6 tests. The range of values for the No. 8 sieve is indicated.

Figure 9-2. Percentage of Lime/Fly Ash material passing through each sieve.

Figure 9-3. Moisture content of each sieve split versus initial moisture content of the lime/fly ash material.

Figure 9-4. Comparison of sieve tests results. 5 g sample of lime/fly ash material which was initially sieved through a No. 8 sieve versus results for a 16 g sample which was not initially sieved.

moisture throughout the entire test or, if initially the moisture was evenly distributed among all size particles, the smaller particles may have lost their moisture more rapidly than the larger particles.

In preparation for the next tests, a 5 g sample of the lime/fly ash material was dried in a 110 °C oven for more than 6 h and cooled in a desiccator. The material was then sieved by hand through a No. 80 sieve. The small fraction that did not pass through the sieve on the first pass, was broken up by hand with a spatula and passed through again. The material was then returned to the desiccator where it remained overnight. The next day it was subjected to the standard sieve test with no moisture added. Figure 9-4 shows the results from that test compared to a test on 16 g of the lime/fly ash material. The effect due to initial sieving through a No. 80 sieve is negligible.

9.5 PLANNED TESTS

High surface area sorbents and those resembling recycle material will be prepared in a manner identical to that used by Peterson. The surface area of the solids will be determined and sieve tests will be conducted at moisture contents ranging from 0-30 percent or more. The intent is to determine which conditions produce solids with high moisture handling capabilities.

Additionally, a cascade impactor will be used to determine the aerodynamic size distribution of the solids when they are dry. An effort will be made to determine the size distribution of moist solids also.

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