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Project Summary

Effect of Relative Humidity and Additives on the Reaction of Sulfur Dioxide with Calcium Hydroxide

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Previous results with flue gas desulfurization by spray drying of $Ca(OH)_2$ show that a significant amount of SO_2 is removed in the bag filters used to collect the solids. This research program investigates the reaction of SO_2 with $Ca(OH)_2$ at conditions similar to those of commercial scale bag filters: 19-74% relative humidity, 30.4-95°C, and 300-4000 ppm SO_2. This study was carried out in a bench-scale fixed-bed reactor, with powder reagent $Ca(OH)_2$ dispersed in silica sand. The gas phase was a mixture of N_2, SO_2, and water vapor. The effects of $Ca(OH)_2$ loading, temperature, relative humidity, inlet SO_2 concentration, and additives were investigated. Of the additives tried (buffer acids, and organic and inorganic deliquescents), only the deliquescent salts improved $Ca(OH)_2$ reactivity toward SO_2. The improvement depends on the type and amount of salt and on the relative humidity. The experimental data were modelled by a shrinking core model with zero order kinetics in SO_2, using an empirical correlation to account for shape and surface roughness of the $Ca(OH)_2$ particles. The diffusion coefficient of the SO_2 through the product layer (D_e) increases linearly with relative humidity and the amount of additive, and the kinetic rate constant (k_s) increases exponentially with relative humidity and the amount of additive. D_e values ranging from 0.75E-9 to 1.20E-6 cm^2/sec and k_s values ranging from 1.0E-9 to 8.23E-9 $cm^4/gmol$ sec in the model simulated the experimental results.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Flue gas desulfurization by spray drying of a $Ca(OH)_2$ slurry has become increasingly important in recent years as an alternative to the more traditional wet lime or limestone scrubbing. During spray drying, the SO_2-containing flue gas is contacted in the dryer with a finely atomized aqueous solution or slurry of an alkali (typically slaked lime or soda ash), which absorbs and neutralizes the SO_2. Simultaneously, the water is evaporated from the slurry droplets leaving a solid material which can be collected using conventional solids collection equipment such as bag filters or electrostatic precipitators. Bag filters are preferred because the unreacted $Ca(OH)_2$ in the solids reacts with SO_2 in the bag filters, producing additional SO_2 removal. The reaction between lime solids and SO_2 taking place in the ducts and bag filters of a spray dryer system is the subject of the present research.

Most of the information available in the literature for this reaction is reported results of SO_2 removal across the bag filters of pilot and demonstration spray dryer plants. These results are difficult to interpret because the conditions of the flue gas entering the bag filters depend on the spray absorber behavior. Any variable changes that affect the SO_2 removal across the spray absorber will change the concentration of SO_2 entering the bag filters. Therefore, two variables will have effectively been changed in the bag filters and the contribution of each cannot be isolated.

Two bench scale studies regarding the reaction of interest have been reported: one at the Lund Institute of Technology-Sweden, and the other at EPA. However, the characterization of this reaction is far from complete.

The present study was carried out in a bench-scale fixed-bed reactor, operated at conditions similar to those found in bag filters of commercial spray drying systems, and using powder reagent $Ca(OH)_2$ as the sorbent. The effects of $Ca(OH)_2$ loading, temperature, SO_2 concentration, and relative humidity were studied. Also, additives that improve lime's reactivity toward SO_2 were identified.

Experimental Methods

The general design of the experimental apparatus is given in Figure 1. A simulated flue gas was synthesized by combining N_2 and SO_2 from gas cylinders. The gas flow rates were measured using rotameters. Water was added to the system using a syringe pump (Sage Instruments, Model 341A) and evaporated at 120°C in a stainless steel chamber before mixing with the gas stream.

The reactor was glass, 4 cm in diameter, and 12 cm tall. The reactor was packed with a mixture of silica sand and $Ca(OH)_2$ reactant in a weight ratio of 40:1. Sand avoids the channeling caused by lime agglomeration. The silica sand (between 80 and 115 mesh) was obtained from Martin Marietta Aggregates.

The reactor was immersed in a water bath that maintained system temperature within 0.1°C. Tubing upstream from the reactor was heated to prevent the condensation of moisture on the walls. Before being analyzed, the gas was cooled and the water vapor then condensed out by cooling water and an ice bath. The gas was analyzed for SO_2 using a pulsed fluorescent SO_2 analyzer
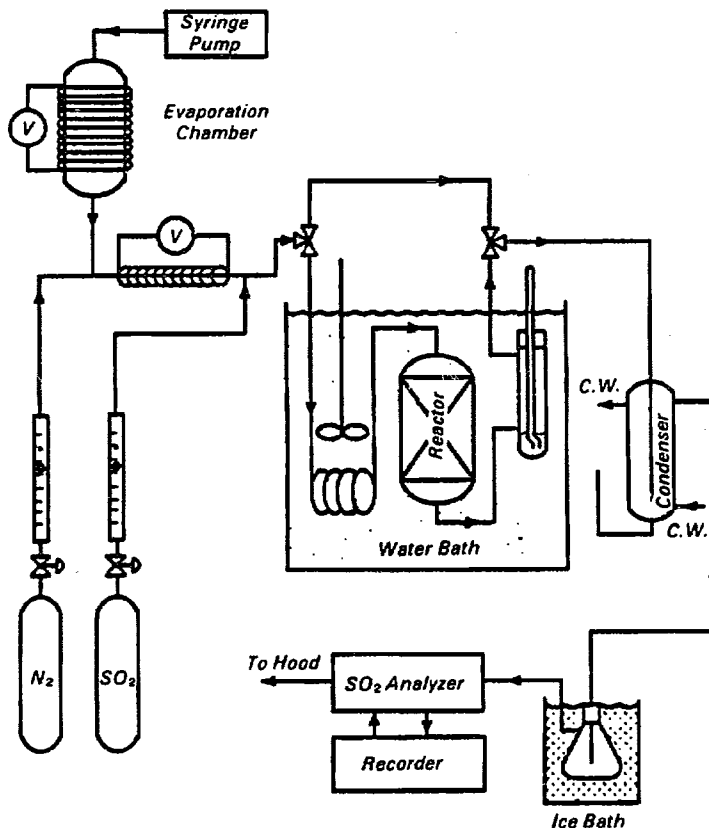

Figure 1.   *Experimental apparatus.*

(Thermoelectron Corporation Model 40), and the SO_2 concentration was continuously recorded. The SO_2 analyzer was calibrated using a calibration standard (a mixture of 2000 ppm SO_2 and N_2). The reactor was equipped with a bypass, to allow the bed to be pre-conditioned and the gas flow stabilized at the desired SO_2 concentration before beginning the experimental run. Before each experimental run, the bed was humidified by flushing with pure N_2, first at a relative humidity of about 98% for 10 minutes, and then for 8 minutes at the relative humidity at which the experiment was to be performed. This humidification simulated moisture conditions encountered in the bag filters where the solids are originally slurry droplets.

The reaction time was normally 1 hr. The raw data from each experimental run were curves of SO_2 concentration leaving the reactor versus time. These

curves were produced by the recorder of the SO_2 analyzer.

The raw data from the experiments were SO_2 concentrations from the reactor as a function of time. By integration of the SO_2 concentration over time and a mass balance on the reactor, the average fraction of $Ca(OH)_2$ converted was calculated at each time. As a backup, the reacted solids were analyzed for sulfite and hydroxide using acid/base and iodine titrations.

Most of the experimental work involved reagent grade $Ca(OH)_2$ as a reactant. Two batches of $Ca(OH)_2$, identified as Lime O and Lime A, were used. These two batches of $Ca(OH)_2$ differ slightly in particle size and BET surface area. The slurrying and drying process caused a slight decrease in the surface area of $Ca(OH)_2$.

An aqueous solution containing the desired additive was prepared. This

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solution (5 ml) was than added to 1 g of $Ca(OH)_2$ and slurried. The sample was placed in an oven to dry at 75°C for about 14 hr, and then sieved to separate the individual $Ca(OH)_2$ particles prior to being mixed with the silica and placed in the reactor.

Model

The equations that describe the absorption of a component from a moving gas stream by a fixed solid in a packed bed consist of two differential equations obtained from material balances in the gaseous and solid phases. Schematically:
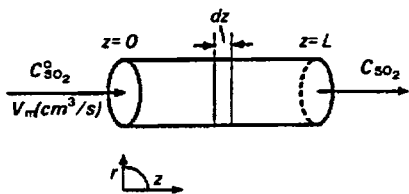
Assuming uniform SO_2 and $Ca(OH)_2$ concentrations in the r and θ directions, and neglecting SO_2 diffusion and dispersion in the z direction as well as the time derivative of the SO_2 concentration, the following equations are obtained:

$$\frac{v_m dC_{SO_2}}{A \, dz} = r_{SO_2} \qquad (1)$$

$$\frac{dC_{lime}}{dt} = r_{SO_2} \qquad (2)$$

with boundary and initial conditions:

$$\text{At } z = 0 \quad C_{SO_2} = C^o_{SO_2} \qquad (3)$$

$$\text{At } t = 0 \quad C_{lime} = C^o_{lime}$$

where:

v_m = volumetric flow rate of gas, cm^3/sec

C_{SO_2} = concentration of SO_2 in the gas phase, $gmol/cm^3$

A = cross sectional area of the reactor, cm^2

z = length of the reactor, cm

r_{SO_2} = rate of disappearance of SO_2, $gmol/cm^3$ sec

C_{lime} = $Ca(OH)_2$ concentration, $gmol/cm^3$

t = time, sec

The rate equation for r_{SO_2} depends on the model selected to represent the kinetics of the reaction.

A shrinking core model with kinetics of zero order in SO_2 was chosen to fit the experimental data. The shrinking (or unreacted) core model assumes that the reaction takes place at the exterior surface of the particle. As the reaction proceeds, the surface of reaction moves into the interior of the solid, leaving behind a layer of inert product. The external radius of the particle remains the same, assuming no shrinkage or swelling of the product layer.

The shrinking core model was originally developed for the isothermal reaction of spherical solid particles. The $Ca(OH)_2$ particles are non-spherical and have a rough surface, so their surface area is much higher than that of spherical particles of the same volume. An empirical expression was introduced to account for the decrease in roughness as the reaction progresses. A dimensionless roughness parameter was defined as:

$$\sigma = \frac{A}{A_\sigma} \qquad (4)$$

where:

A = actual surface area of the lime, m^2/g

A_σ = surface area of spherical particles of equal mass, m^2/g

When the lime is unreacted, σ can be estimated as the ratio of the BET surface area of the lime and the surface area calculated from the Coulter Counter particle size distribution, assuming spherical particles. As the reaction progresses, σ should decrease and approach the limit σ = 1.0 when all the lime has reacted.

An empirical expression of the form:

$$\sigma = 1.0 + \exp(a \, X_{lime} + b) \qquad (5)$$

where X_{lime} is the fraction of lime unreacted, was used to describe the change of roughness with the reaction. Equation (5) must satisfy the condition:

$$\text{At } X_{lime} = 1.0 =$$
$$\sigma_o = BET \, area/A_\sigma \qquad (6)$$

To force σ to decrease more rapidly at high values of X_{lime} and to simulate the experimental results, the following additional condition was imposed:

$$\text{At } X_{lime} = 0.8 \quad \sigma = 2.0 \qquad (7)$$

For the two batches of $Ca(OH)_2$ used in the experiments (Lime O and Lime A), the constants a and b took slightly different values (a = 12.878 for Lime O and a = 13.428 for Lime A, and the values of b were -10.302 and -10.742, respectively).

Using the roughness parameter σ, Equations (8) and (9) can be obtained for the rate of disappearance of SO_2, assuming that chemical reaction (or SO_2 diffusion through the gas film and product layer) is the rate controlling step.

$$r_{SO_2} = \frac{1}{V} 4nR^2 N \sigma \rho_{lime} k_s X_{lime}^{2/3} \qquad (8)$$

$$r_{SO_2} = \qquad (9)$$

$$\frac{1}{V} \frac{C^g_{SO_2}}{\dfrac{X_{lime}^{-1/3} - 1}{4nD_e NR(\sigma\sigma_o)^{1/2}} + \dfrac{1}{4nR^2 k_g No}}$$

where:

V = reactor volume, cm^3

R = radius of the particle, cm

N = number of $Ca(OH)_2$ particles

ρ_{lime} = $Ca(OH)_2$ molar density, $gmol/cm^3$

k_s = kinetic rate constant, cm/sec

$C^g_{SO_2}$ = SO_2 concentration at the gas bulk $gmol/cm^3$

D_e = diffusivity of SO_2 through product, cm^2/sec

k_g = mass transfer coefficient, cm/sec

If the chemical reaction is slow, the rate of disappearance of SO_2 will be given by Equation (8). If the chemical reaction is fast, all of the SO_2 that reaches the surface of the core will be immediately consumed and the concentration of SO_2

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at the surface of the unreacted core will become zero. At these conditions the rates of diffusion of the SO_2 through the gas film and product layer will become the limiting steps, and Equation (9) will become important.

Of Equations (8) and (9), the one that gives the lower rate of SO_2 disappearance will determine the overall kinetic rate. The parameters of the model are k_g, D_e, and k_s. Equations (1) and (2) --with the rate of disappearance of SO_2 given by Equation (8) and (9)-- were integrated by assuming an average particle size of the lime particles which gave the same surface area as the measured particle size distribution, assuming spherical particles. The mass transfer coefficient, k_g, was not used as an adjustable parameter because, at the conditions at which the experiments were performed, gas film diffusion is not likely to be important. The only effect of gas film diffusion is that it limits the rate expression (9) at the beginning of the reaction where product layer resistance is zero, as there is no product formed. The value of k_g (544 cm/sec) was estimated using a Sherwood number of 2, corresponding to mass transfer from spherical particles in a stagnant fluid.

Thus D_e and k_s were the only parameters used to fit the experimental data Depending on whether mass transfer or chemical reaction is the controlling step, only one of these parameters may be important.

A computer program, with variable step size in time and in distance along the reactor, was written to model the reaction. This program uses the IMSL routine DGEAR to carry out the integration, and the IMSL routine ICSCCU to provide interpolated values of lime conversion needed for each time integration step.

Results

The effects of relative humidity, temperature, inlet SO_2 concentration, and the amount of lime in the reactor on the reaction of SO_2 with powdered reagent $Ca(OH)_2$ were studied. The experimental conditions are listed in Table 1.

Relative Humidity

Relative humidity was found to have a dramatic effect on the rate of reaction of SO_2 with $Ca(OH)_2$ as illustrated by Figure 2. The full lines correspond to experimental results at 2000 ppm inlet SO_2 and 66°C using 4 g of Lime 0.

Table 1. Experimental Conditions

|	
Relative Humidity:	17-90%
SO_2 Inlet Concentration:	500-4000 ppm
Reactor Temperature:	30.5-95°C
Nitrogen Flow Rate:	4600 cm³/min (0°C, 1 atm)
Amount of Lime:	1.0-4.0 g

Figure 2 shows that, for all relative humidities, 100% of the SO_2 entering the reactor is being removed during the first 1 or 2 min. of reaction, then the reaction rate (represented by the slope of the conversion versus time curves) decreases quickly at low relative humidities but more slowly at high relative humidities.

The broken lines in Figure 2 correspond to the model prediction for these experiments. Figure 3 shows the dependence of the rate constant and solid diffusion coefficient on relative humidity. At high relative humidity, the chemical reaction is the controlling step and k_s determines the rate of reaction.
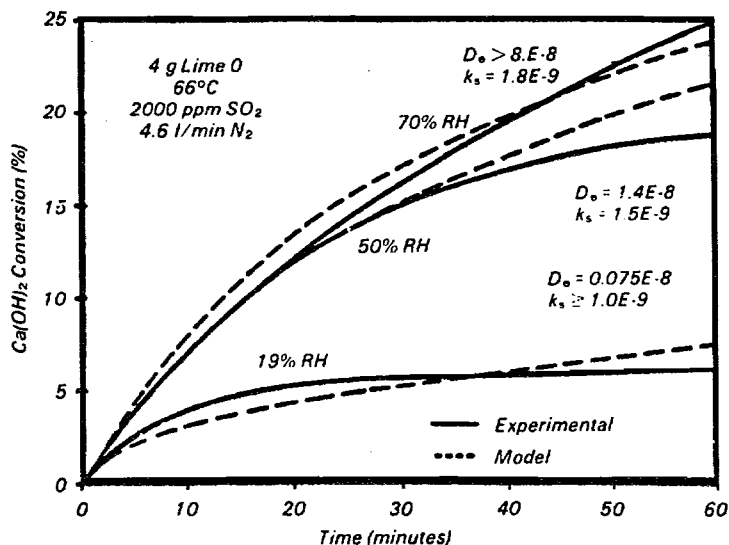
Figure 2. Effect of relative humidity on reaction rate, Lime 0.
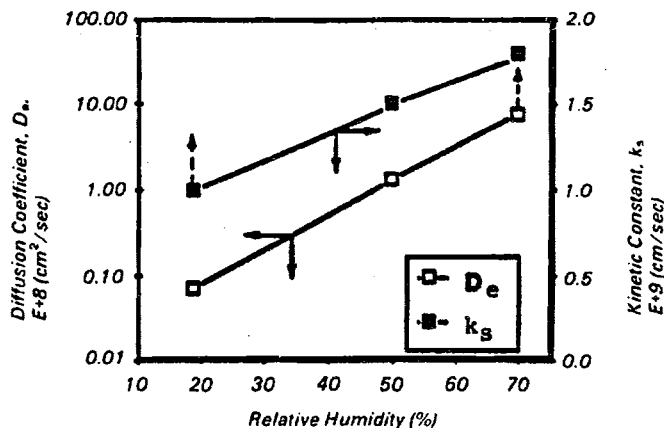
Figure 3. Effect of relative humidity on model parameters.

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Any value of D_e greater than 8.0E-8 cm^2/sec will give essentially the same result. SO_2 diffusion through the product layer becomes more important as the relative humidity decreases. At 19% relative humidity, D_e determines the rate of adsorption of SO_2. At 19% relative humidity, any value of k_s greater than 1.0E-9 cm/sec will give essentially the same results. Both D_e and k_s are affected by the relative humidity but, in the range of relative humidities studied, k_s increases approximately linearly while D_e increases exponentially. Because the SO_2 diffusion coefficient changes more rapidly than the kinetic constant, the controlling mechanism changes when the relative humidity is increased. The strong effect of relative humidity on reaction rate has also been reported by other researchers.

Inlet SO₂ Concentration

The effect of the inlet SO_2 concentration on the reaction rate was found to depend on the relative humidity. Figures 4 and 5 illustrate the effect of inlet SO_2 concentration at 70 and 50% relative humidity, respectively. The full lines in these figures correspond to experimental results, and the broken lines to the model predictions. At 70% relative humidity, the $Ca(OH)_2$ conversion was practically independent of the inlet SO_2 concentration as can be seen in Figure 4. At lower relative humidity the reaction rate is not affected by the SO_2 concentration if the SO_2 concentration is high. However, at lower levels of SO_2 the reaction rate is affected by the SO_2 concentration as illustrated by Figure 5. The observed effect of SO_2 concentration can be explained by assuming that the reaction rate has zero order kinetics in SO_2, but at low relative humidity and/or low SO_2 concentration, SO_2 diffusion (instead of chemical reaction) becomes the controlling step. As can be seen from Figures 4 and 5, the model predicts the SO_2 effect with reasonable accuracy.

Figure 4.   Effect of SO₂ concentration, high relative humidity.
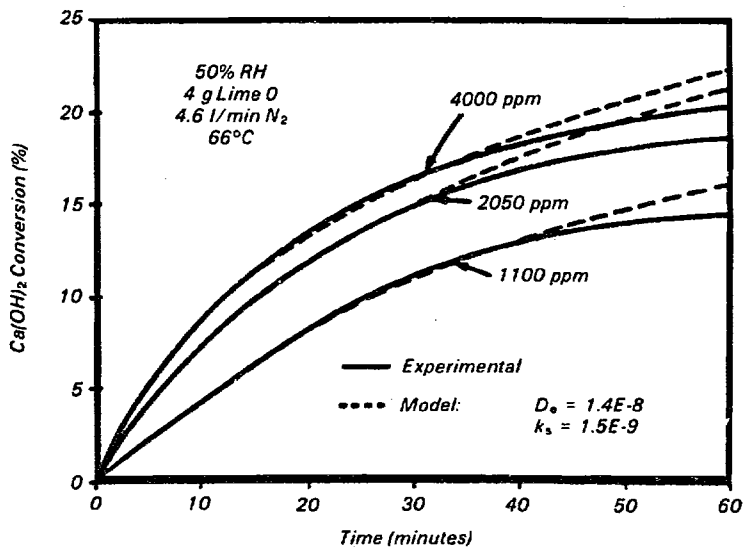
Figure 5.   Effect of SO₂ concentration, moderate relative humidity.

Amount of Ca(OH)₂ in the Reactor

The effect on the average $Ca(OH)_2$ conversion of changing the amount of $Ca(OH)_2$ in the reactor is illustrated by the full lines in Figure 6 which show the experimental $Ca(OH)_2$ conversion when the amount of Lime 0 in the reactor was reduced from 4 to 1 g at 1000 ppm SO_2, 50% relative humidity. Figure 6 shows that the amount of $Ca(OH)_2$ in the reactor
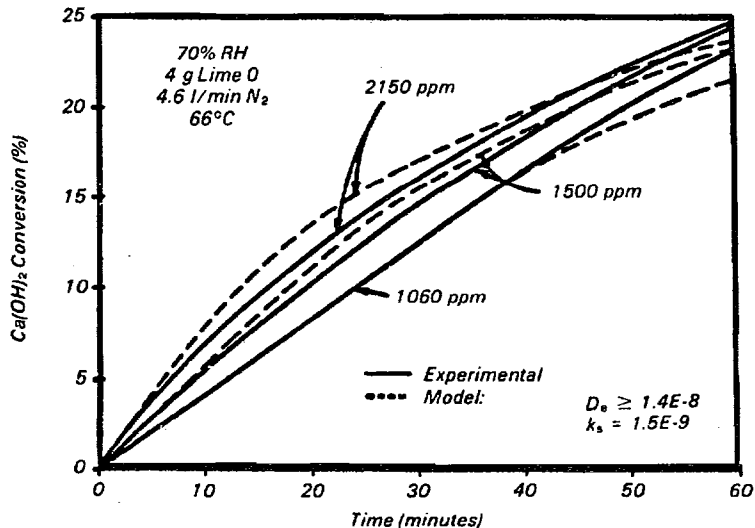
makes a difference during the first minutes of reaction, but the effect is less marked later. These results are consistent with the effect of SO_2 concentration discussed previously. When more $Ca(OH)_2$ is in the reactor, more SO_2 is removed at the entrance of the reactor, so the $Ca(OH)_2$ present farther down in the reactor "sees" a lower concentration of SO_2, and the reaction rate is slower. Later, when the SO_2

removal is lower, the amount of $Ca(OH)_2$ will not be as important.

Reactor Temperature

Reactor temperature has a very moderate effect on $Ca(OH)_2$ reactivity, as illustrated by the full line in Figure 7, which shows the effect on $Ca(OH)_2$ conversion when the reactor temperature was increased from 30.4 to 64.4°C while

keeping all other variables constant. The relative humidity was 74%, so in this region the reaction is expected to be kinetically controlled.

The broken lines in Figure 7 are the model predictions for the experiments run at the two different temperatures. At the conditions at which the experiments were performed, the reaction rate is kinetically controlled, so k_s is the only important adjustable parameter in the model. By using the values of k_s given by the model, an apparent activation energy of 2.9 kcal/gmol can be estimated for $Ca(OH)_2$. This value of activation energy is somewhat lower than the value of 6 kcal/gmol reported by other sources for this reaction.

A very weak dependence of the reaction rate with temperature was also reported by other researchers.

Additives

Two organic acids (adipic acid and glycolic acid) and three organic deliquescents (ethylene glycol, triethylene glycol, and monoethanolamine) were selected as test additives for $Ca(OH)_2$. All of them proved to be detrimental to the reaction of SO_2 with $Ca(OH)_2$.

A number of deliquescent salts were also tested as additives at 74 and 54% relative humidity. The beneficial effect of the salts depends on the type and amount of salt and the relative humidity. At high relative humidity (74%), all the deliquescent salts tried were successful in increasing the reactivity of the $Ca(OH)_2$ toward SO_2. At a lower relative humidity (54%), some of the salts did not perform as well, and some, such as $Ca(NO_3)_2$, did not have any beneficial effect.

The water activity over saturated solutions of the salts (70°C and 1 atm) is about equal to the fractional relative humidity of the gaseous phase that would be in equilibrium with a saturated solution of the salt at that temperature. If one of these deliquescent salts is contacted with a gaseous phase of relative humidity greater than the water activity, the salt will capture water from the gas phase and become a solution. This tendency to capture water has been extensively documented in the literature by studies of the growth of salt containing aerosols as a function of the atmospheric relative humidity. From data in the literature, it is clear that (based on deliquescence alone) most of the salts tested, specifically $NaNO_3$ and all the chlorides except LiCl, should not have any beneficial effect at 54% relative
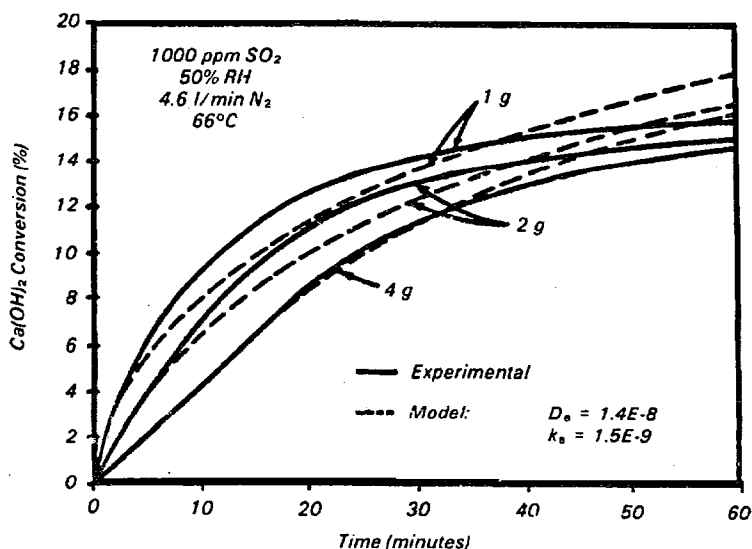

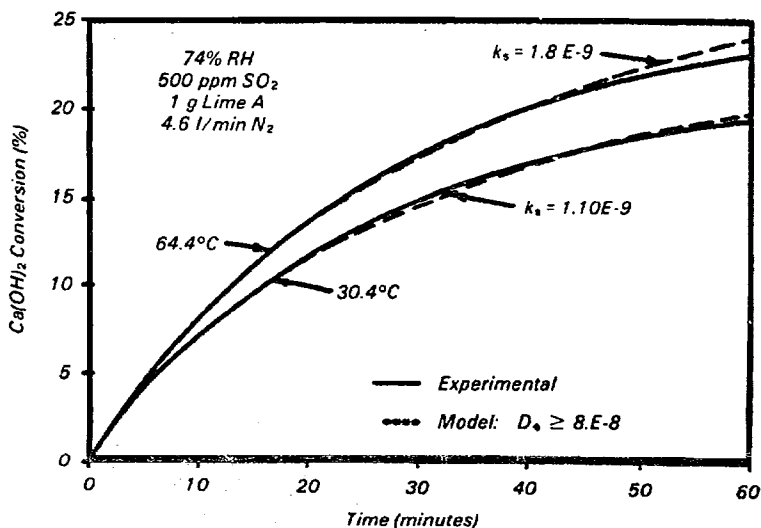Figure 6. Effect of $Ca(OH)_2$ loading, 1000 ppm SO_2.

Figure 7. Effect of reactor temperature, Lime A.

humidity. Nevertheless, these salts are among the ones that behave the best at that moderate relative humidity. A possible explanation for this finding would be a hysteresis phenomenon; this will be discussed later.

The report also shows the values of the diffusion coefficient of SO_2 through the product layer (D_e), and the kinetic constant (k_s) that can be used to simulate the experimental runs using salt additives. D_e values ranging from 1.5E-8 to 120E-8 (cm^2/sec) and k_s values from 1.5E-9 to 8.23E-9 (cm^4/gmol sec) were used in the simulation of the salt experiments. Depending on the amount and type of salt added, chemical reaction or SO_2 diffusion can become the controlling step. A reasonably good agreement was found between the predictions of the model and the experimental results. The maximum percentage of error between the experimental data and predicted values
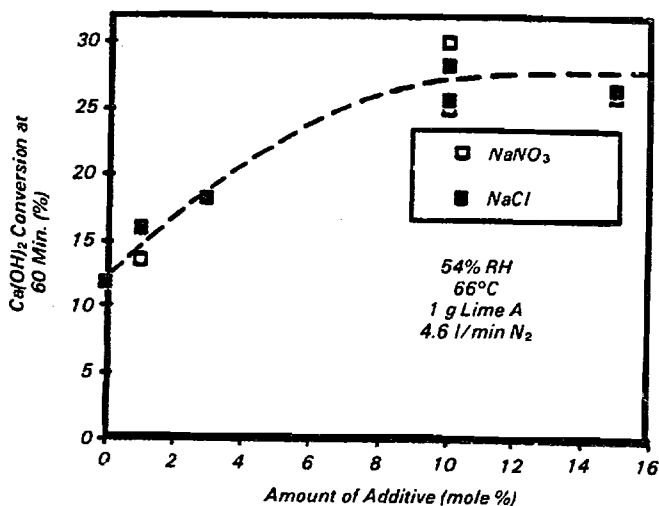
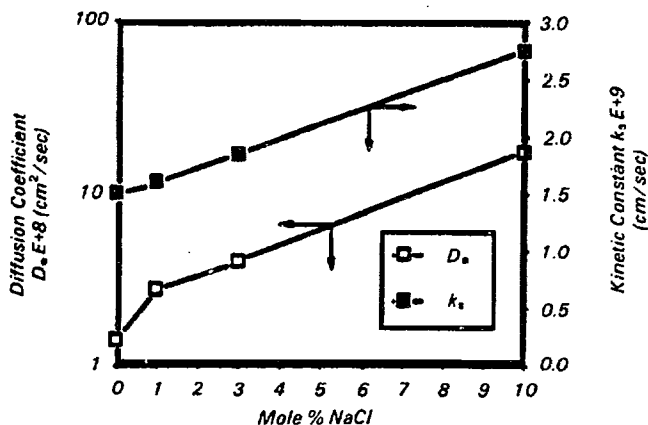**Figure 8.** Effect of amount of additive.

Figure 9. Effect of NaCl on model parameters.

was below 10% in most cases; in a few exceptions, it was below 20%.

The influence of the salt concentration on the SO_2 reaction rate is illustrated by Figure 8. The salts used were NaCl and $NaNO_3$ in concentrations ranging from 1 to 15 mole%. The experiments were carried out at a relative humidity of 54%, and a reactor temperature of 66°C. Figure 8 shows that the conversion increases with increasing concentration of additive until about 10 mole%. After

this the curve levels off. The optimum concentration of additive is then about 10 mole% for 1:1 electrolytes like NaCl and $NaNO_3$.

The deliquescent salts affected the model parameters similarly to the relative humidity: the diffusion coefficient increased more rapidly than the kinetic constant by the addition of the salts. Figure 9 illustrates the effect of NaCl on the model parameters. The kinetic constant increased linearly when NaCl

concentration was increased from 0 to 10 mole%, while the diffusion coefficient increased exponentially after a sharp increase from 0 to 1 mole% NaCl.

As mentioned earlier, before each experimental run the fixed bed was prehumidified by flushing with pure N_2 at a relative humidity of about 98% for 10 minutes before flushing with N_2 at the relative humidity at which the experiment was to be performed.

This prehumidification could be why some of the salts were still effective at a relative humidity lower than the one predicted from equilibrium considerations. Due to hysteresis it is possible that, when the relative humidity was lowered to the experimental conditions after the prehumidification, some excess water remained in the solids. Strong hysteresis effects have been reported in NaCl aerosols.

To check if hysteresis was responsible for the beneficial effect of some salts at low relative humidities, experimental runs were made omitting the prehumidification step. Table 2 shows the results obtained at 54 and 17.4% relative humidity with and without prehumidification of the bed at 98% relative humidity. The additives used were NaCl, $NaNO_3$, and KCl. At 54% relative humidity, even when some decrease of the $Ca(OH)_2$ conversion was found without the prehumidification, the results with additives were still far superior to those with the pure $Ca(OH)_2$. Hysteresis then, cannot explain all of the beneficial effect observed at 54% relative humidity. At 17.4% relative humidity, all the beneficial effect with NaCl appears to be due to prehumidification of the bed; i.e., due to a hysteresis phenomenon.

Conclusions

As shown earlier, the relative humidity of the gaseous phase is the most important variable in the reaction of SO_2 with $Ca(OH)_2$ solids. This result agrees with results reported in the literature for SO_2 removal in the bag filters of spray dryer pilot and commercial plants. The other variables tested (i.e., temperature, amount of $Ca(OH)_2$, and SO_2 concentration) have less impact on the reaction rate. The different effect of SO_2 concentration at low and high relative humidities can be explained by assuming that the reaction has zero order kinetics in SO_2 and that, at low relative humidity, the reaction rate is mass transfer controlled while at high relative humidities the reaction is controlled by reaction kinetics.

500 ppm SO_2, 1.0 g $Ca(OH)_2$ A, 4.6 l/min (0°C, 1 atm) N_2

	Average $Ca(OH)_2$ Conversion after 1 hr (%)			
	54% RH 66°C Prehumidified		17.4% RH 95°C Prehumidified	
Additive (Mole%)	Yes	No	Yes	No
None	11.2	—	4.0	—
10% NaCl	27.0[a]	23.2	9.7	4.0
10% NaNO₃	27.2[a]	23.7	11.9	—
10% KCl	37.3	19.3	3.4	—

[a] Average of two experimental runs.

Most of the deliquescent salts tried effectively increased $Ca(OH)_2$ reactivity toward SO_2. The extent of the beneficial effect was a function of the type of salt, the salt concentration, and the relative humidity. Some salts are effective at a lower relative humidity than would be predicted from their deliquescent properties. Hysteresis due to pre-humidification of the bed appears to be partially responsible for this behavior, but it cannot explain all of the reactivity improvement observed at 54% relative humidity. An alternate explanation proposed is that the chlorides and $NaNO_3$ modify the properties of the product $CaSO_3 \cdot 1/2 H_2O$ layer that is formed as the reaction takes place, thereby facilitating the access of the SO_2 to the unreacted $Ca(OH)_2$ which remains in the interior of the particle. NaCl and $CaCl_2$ have been reported to enhance the SO_2 reactivity of limestones in fluidized-bed combustion by affecting the pore structure of the lime during calcination, which then increases the extent of sulfation of the limestone.

The only previous modelling effort for this reaction used an integral shrinking core model with only reaction kinetics to explain the dependence of reaction rate on lime conversion. That effort's experimental data fit this integral shrinking core model only after a certain lime conversion had been reached. The sharp decrease in reaction rate observed at initial times was attributed to a decrease in surface roughness, but no attempt was made to correlate this decrease in surface roughness with lime conversion. The model neglected the effects of SO_2 diffusion through the product layer, and the SO_2 concentration and lime concentration profiles in the fixed bed reactor. All of these factors will

be more important at initial times, when the SO_2 removal is higher, so it is not surprising that the experimental data could be fit only at later times.

The simple model presented here seems able to predict with reasonable accuracy the effect of all the process variables tested and explain the trends observed in the experimental data. The experimental data was estimated to have ±11% experimental error, so that most predictions of the model are well within the range of experimental error. The values of the diffusion coefficient used in the modelling (from 0.75E-9 to 1.20E-6) seem reasonable for diffusion of SO_2 in a solid, as they are of the same order of magnitude of the diffusivities of gases in polymers.

The relative humidity affects both the diffusion coefficient of SO_2 and the kinetic constant. In the range of relative humidity studied (19 to 74%), the kinetic constant increased linearly with relative humidity, while the diffusion coefficient increased exponentially. This dependence of the parameters on the relative humidity leads to a change in the reaction controlling mechanism as the relative humidity decreases. At high relative humidity and/or high SO_2 concentration, the reaction rate is kinetically controlled and the reaction rate is independent on the SO_2 level. At low relative humidity and/or low SO_2 concentration, the controlling step is the diffusion of the SO_2 through the $CaSO_3 \cdot 1/2 H_2O$ product layer. At these conditions the overall reaction rate becomes affected by the SO_2 concentration which is the driving force for diffusion.

The addition of deliquescent salts increases the diffusion coefficient and the kinetic constant similarly to relative humidity: the diffusion coefficient increases more rapidly than the rate constant. When increasing amounts of the same salt (NaCl) were added, k_s increased linearly and D_e nearly exponentially. Depending on the amount and type of salt additive, chemical reaction or gas diffusion can be the controlling mechanism.

The kinetic constant was a very weak function of temperature. The estimated activation energy was 2.9 kcal/gmol.

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