DOE(PC) 888 74..T11

OCT 29 1990

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

Quarterly Report No. 9
Report Period July 1, 1990 through September 30, 1990

DOE/PC/88874--T11

DE91 004221

Prepared for:

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

Under Contract No. DE-AC22-88PC88874
Date Prepared: October 24, 1990

Prepared by:

Acurex Corporation
Environmental Systems Division
P.O. Box 13109
Research Triangle Park, NC 27709

and

University of Texas at Austin
Department of Chemical Engineering
Austin, TX 78712

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
List of Figures	ii
List of Tables	iii
1.0 Project Status	1
2.0 Task 2.1. Stirred-Tank Reactor Experiments	3
2.1 Objective of Current Work	3
2.2 Slurry Absorption Model	3
2.2.1 Changes to the Model	3
2.2.2 Inputs that Establish Slurry Properties	3
2.3 Comparison of Model and Experimental Results	4
2.3.1 Enhancement Predicted by Slurry Absorption Model	4
2.3.2 Effect of Solids Concentration on Enhancement and Gas-Film Resistance	9
2.4 Future Work	11
3.0 Task 4.2. Enhancement of Dry Injection: Moist Solids	13
3.1 Short Time Differential Reactor (STDR)	13
3.1.1 Reactor and Solids Preparation	13
3.1.2 Sorbents	13
3.1.3 Effect of Fly Ash Source	17
3.1.4 Effect of the Amount of Initial Free Moisture	20
3.1.5 Effect of the Approach to Saturation	20
3.1.6 Combined Effect of Initial Free Moisture and Approach to Saturation	22
3.1.7 Effect of the Sorbent's Surface Area	22
3.1.8 Conclusions	26
3.2 Grinding for Recycle Reactivation	26
4.0 Task 4.2. Enhancement of Dry Injection: Solids Moisture Capacity	28
4.1 Introduction	28
4.2 Experimental Procedure	28
4.2.1 Sieve Tests	28
4.2.2 Critical Moisture	29
4.2.3 Solids Preparation	31
4.2.4 Materials Tested	31
4.3 Results and Discussion	31
4.4 Future Work	32
4.4.1 Slurry Reactants	32
4.4.2 Other Slurry and Solid Conditions	34
5.0 Special Study	35
5.1 Bench-Scale Evaluation	35
5.2 Pilot-Plant Testing	37

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
2-1 Enhancement Predicted by Slurry Absorption Model for 35mM $\text{Ca}(\text{OH})_2$ Slurry	5
2-2 Effect of Particle Size on Enhancement Predicted by Slurry Absorption Model for 0.1M $\text{Ca}(\text{OH})_2$ Slurry	7
2-3 Enhancement Predicted by Slurry Absorption Model for 0.4M $\text{Ca}(\text{OH})_2$ Slurry	8
2-4 Effect of $\text{Ca}(\text{OH})_2$ Concentration in Slurry on Enhancement Predicted by Slurry Absorption Model	10
2-5 Effect of $\text{Ca}(\text{OH})_2$ Concentration on Gas-Film Resistance Predicted by Slurry Absorption Model	12
3-1 SEM Photomicrograph of "as received" Clinch River fly ash sample, x 5,000	15
3-2 SEM Photomicrograph of ground Clinch River fly ash sample, x 5,000	16
3-3 The effect of fly ash source on reactivity of sorbent with SO_2	18
3-4 Combined effect of fly ash source and initial free moisture content on sorbent's reactivity with SO_2	19
3-5 Conversion as a function of initial free moisture content	21
3-6 The effect of approach to saturation on the conversion of sorbent with an initial free moisture content of 30 weight percent	23
3-7 Combined effect of the approach to saturation and initial free moisture on 5 s conversion of sorbent with SO_2	24
3-8 The effect of sorbent surface area on 5 s conversion of Meredosia fly ash/ $\text{Ca}(\text{OH})_2$ sorbent	25
4-1 Sieve test data for solids produced by slurrying Clinch River fly ash with hydrated lime at the weight ratio of 3:1 for 8 h	30
4-2 Correlation of critical moisture content with solid surface area.	33
5-1 Bench-scale testing of ISGS sorbents	36
5-2 Pilot-plant testing of air classified BH-101 sorbent from ISGS.	38

LIST OF TABLES

<u>Table</u>		<u>Page</u>
2-1	Predicted gas-film resistance in 1.0M $\text{Ca}(\text{OH})_2$ slurry at various SO_2 concentrations	9
3-1	Structural properties of fly ashes used to produce fly ash/ $\text{Ca}(\text{OH})_2$ sorbents	13
3-2	Structural properties of fly ash/ $\text{Ca}(\text{OH})_2$ sorbents	14
3-3	Structural properties of pilot-plant solids	27
4-1	Materials tested and range of values for critical moisture and surface areas	32
5-1	Properties of ISGS sorbents	35

SECTION I

PROJECT STATUS

During the reporting period of July 1 to September 30, 1990, bench- and pilot-scale experiments were conducted to measure mass transfer and kinetic rates under simulated duct-injection conditions.

Section 2 describes the results of stirred-tank modeling experiments. The slurry absorption model predicts the correct absorption in the stirred tank by adjusting the diffusivity of hydroxide to 40 percent of the referenced value. The results of the model were compared to absorption measured for saturated $\text{Ca}(\text{OH})_2$ solutions and $\text{Ca}(\text{OH})_2$ slurries.

Section 3 presents the results of experiments with moist solids in the short-time differential reactor (STDR). When compared with equilibrium solids, the presence of an initial free moisture greatly enhanced SO_2 conversion in the STDR. Maximum conversion for 5 s contact time and 11 °C approach to saturation was measured for solids with 30-40 weight percent initial free moisture. Both the preferred initial free moisture content and the corresponding level of maximum sorbent conversion with SO_2 varied with the surface area of the sorbent. A sorbent was prepared with ground recycled material for use in bench-scale tests of recycle reactivation.

Section 4 summarizes the status of an investigation into the agglomeration of damp $\text{Ca}(\text{OH})_2$ -based solids. The critical moisture content of solids prepared by chemically reacting $\text{Ca}(\text{OH})_2$ with fly ash correlated well with their surface area. Critical moisture content increased as the surface area of fly ash/ $\text{Ca}(\text{OH})_2$ solids increased. The addition of calcium sulfite to the slurry during preparation did not affect the correlation. Hydrated lime did not follow the correlation.

Section 5 presents the evaluation of specialty sorbents prepared by the Illinois State Geological Survey (ISGS). Compared to commercial Mississippi $\text{Ca}(\text{OH})_2$, the ISGS sorbents yielded a significant increase in calcium conversion during bench-scale tests measuring BH-101 and BH-130. Pilot-plant testing of BH-101 sorbent revealed 44 percent SO_2 removal in-duct and 50 percent SO_2 removal through the system. The Mississippi $\text{Ca}(\text{OH})_2$ removed 28 percent in-duct and 46 percent through the system.

SECTION 2

TASK 2.1 - STIRRED-TANK REACTOR EXPERIMENTS

2.1 OBJECTIVE OF CURRENT WORK

Current work focuses on running the slurry absorption model using inputs for Ca(OH)_2 slurries. The results are compared to absorption measured in the stirred-tank for saturated Ca(OH)_2 solutions and Ca(OH)_2 slurries.

2.2 SLURRY ABSORPTION MODEL

2.2.1 Changes to the Model

Application of the slurry absorption model for simulating conditions in the stirred-tank reactor has been described in previous progress reports. The slurry absorption model overpredicted (by a factor of 2) the results of experiments performed in a 17mM Ca(OH)_2 saturated clear solution. It also overpredicted enhancement measured in Ca(OH)_2 slurries by about the same amount. Although a physical reason for this discrepancy has not been determined, it was found that the model predicts the correct measured absorption by adjusting the diffusivity of hydroxide (D_{OH}) to 40 percent of the referenced value. This adjusted D_{OH} was used for predicting the enhancement in slurry solutions presented in this report. Additional tests may be necessary to determine why such a correction is necessary.

2.2.2 Inputs that Establish Slurry Properties

The solution composition of the slurry was assumed to be the same as the saturated Ca(OH)_2 solution, with additional solid Ca(OH)_2 . Therefore, the input for the model resulted in the same conditions for the saturated Ca(OH)_2 clear solution. Only 2 additional inputs were required for the slurries: solids concentration and particle size. Solids concentration was specified as the same concentrations used in the stirred-tank absorption experiments. The model was run for slurries containing 35mM, 0.1M, 0.4M, and 1.0M Ca(OH)_2 in 0.1M CaCl_2 . It was run at several particle sizes to

determine which represented the conditions of the slurry used in the stirred-tank experiments. Particle sizes of 0.5, 1, 5, and 10 μm were used as input to the model.

At present, particle size is the only input that establishes the solid's level of reactivity in the slurry absorption model. Large particles are typically less reactive, because the amount of exposed surface area per volume is small. Therefore, changing the particle size of the solid determines the reactivity of the slurry.

In practice, particle size alone is not the only factor that influences the reactivity of the $\text{Ca}(\text{OH})_2$ solids in the slurry. Porosity can also increase the amount of exposed surface area and the reactivity of the solids. Also, contamination of the solids (typically by exposure to CO_2 over long periods) can influence reactivity. Reagent purity and the source of the $\text{Ca}(\text{OH})_2$ may also have some effect on reactivity.

2.3 COMPARISON OF MODEL AND EXPERIMENTAL RESULTS

2.3.1 Enhancement Predicted by Slurry Absorption Model

A first step in predicting enhancement in slurries with the slurry absorption model was to validate that reducing the D_{OH} by 40 percent improved the ability of the model to predict the experimental results obtained in the stirred-tank. Figure 2-1 shows enhancement measured in the stirred-tank for a 35mM $\text{Ca}(\text{OH})_2$ slurry compared with enhancement predicted by the slurry absorption model for the same solution under 3 conditions. First, the model was run without adjusting the D_{OH} to 40 percent of the referenced value. As found in the case of the 17mM saturated $\text{Ca}(\text{OH})_2$ solution, the model overpredicted enhancement by a factor of 2. The model was then run with D_{OH} reduced by 40 percent at 2 different particle sizes.

Reducing D_{OH} by 40 percent enabled the slurry absorption model to predict the enhancement measured in the stirred-tank experiments for the 35mM slurry solution. This procedure improved the model's agreement with all the slurry solutions studied. All remaining model results for slurry solutions presented in this report were generated using the reduced D_{OH} .

Figure 2-1. Enhancement Predicted by Slurry Absorption Model for 35mM Ca(OH)₂ Slurry.

Increasing the particle size from 1 to 5 μm did not have a large effect on the predicted enhancement. The larger particle size did result in a slightly lower enhancement factor, which was expected. The effect of particle size was studied in more detail for a 0.1M $\text{Ca}(\text{OH})_2$ slurry, because experiments with different sources of $\text{Ca}(\text{OH})_2$ were performed at this slurry concentration. Figure 2-2 shows the model's predicted enhancement at 4 different particle sizes, compared to experimental results from tests in reagent grade 0.1M $\text{Ca}(\text{OH})_2$ slurry.

Also, a comparison was made among the enhancements predicted at different contact times. All model results presented in this report were evaluated at a contact time of 0.9 s. Figure 2-2 shows model results generated at a particle size of 1.0 μm at a 2.5 s contact time. The range of contact times simulated in the stirred-tank was 0.9 to 2.5 s. It has been assumed that the enhancement factor in slurry solutions is not a function of contact time over the range studied in the experiments. The model verifies that this is a good assumption.

The model predicts that relatively no change in enhancement results from reducing the particle size from 1.0 μm to 0.5 μm . However, increasing the particle size to 5 μm and further to 10 μm results in measurably lower enhancement. The experimental results appear to be best described by a slurry with a particle size between 5 and 10 μm .

The model was also run at 3 different particle sizes for a slurry concentration of 0.4M $\text{Ca}(\text{OH})_2$. Figure 2-3 shows that little difference in enhancement was predicted for increasing the particle size from 1-5 μm . A larger difference in enhancement was predicted for increasing the particle size to 10 μm . The few model runs at a particle size of 10 μm indicate that the experimental measurements of enhancement are best predicted by a particle size of at least 10 μm .

The particle sizes required by the slurry absorption model for agreement with the enhancement measured in the stirred-tank experiments increased as solids concentration increased. In other words, the model predicts a greater increase in enhancement owing to the addition of solids to the slurry.

This conclusion is further supported by the few measurable results obtained from the stirred-tank using 1.0M $\text{Ca}(\text{OH})_2$ slurry. Most of the measurements were too gas-film controlled to report accurate enhancement factors. However, 3 test runs indicated less than 100 percent gas-film controlled absorption. The slurry absorption model was run with 1.0M $\text{Ca}(\text{OH})_2$ slurry concentration, specified at 2 particle sizes to predict the degree of gas-film control expected in this solution. Table 2-1

Figure 2-2. Effect of Particle Size on Enhancement Predicted by Slurry Absorption Model for 0.1M $\text{Ca}(\text{OH})_2$ Slurry.

Figure 2-3. Enhancement Predicted by Slurry Absorption Model for 0.4M Ca(OH)₂ Slurry.

Table 2-1. PREDICTED GAS-FILM RESISTANCE IN 1.0M Ca(OH)₂ SLURRY AT VARIOUS SO₂ CONCENTRATIONS

	SO ₂ Concentration				
	1000 ppm	2000 ppm	3000 ppm	4000 ppm	5000 ppm
Model 1.0 μm	100%	100%	100%	100%	100%
Model 10 μm	100%	100%	100%	90%	75%
Stirred-Tank	100%	85%	80%	-	-

compared the gas-film resistance predicted by the model with the resistance measured in the stirred-tank.

The absorption model predicts that this 1.0M Ca(OH)₂ slurry should be more reactive than the results of the stirred-tank experiments indicate. The model predicted that the absorption should have been completely gas-film controlled for all SO₂ concentrations less than 4000 ppm.

2.3.2 Effect of Solids Concentration on Enhancement and Gas-Film Resistance

Stirred-tank experiments showed that the addition of solids greatly enhanced the absorption of SO₂. However, the additional amount of enhancement appeared to diminish as the slurry solids concentration was increased. A 50 percent increase in enhancement was observed when the Ca(OH)₂ concentration was doubled from 17mM to 35mM. When Ca(OH)₂ solids content was nearly tripled from 35mM to 0.1M, a 25-30 percent increase in enhancement was measured. Quadrupling Ca(OH)₂ solids content from 0.1M to 0.4M enhanced absorption by only 20-25 percent. Eventually, a limit would be reached where adding solids would cause virtually no increase in SO₂ absorption.

Figure 2-4 summarizes the enhancement factors the model predicted for absorption in each of the slurry solutions studied. These factors are presented as a function of SO₂ concentration. The data was taken from the model runs that best represented the stirred-tank results. In absorption that was gas-film controlled, the enhancement in the liquid phase becomes infinite and could not be measured in the stirred-tank.

The effectiveness of increasing solids concentration to improve SO₂ absorption is limited when the absorption reaches a gas-film controlled state. Results of clear solution experiments presented in

Figure 2-4. Effect of Ca(OH)_2 Concentration in Slurry on Enhancement Predicted by Slurry Absorption Model.

previous progress reports pointed out that enhancement measurements in slurry solutions would not be possible with bulk gas SO_2 concentrations less than 2,000 ppm because these conditions would yield a gas-film controlled absorption. Initial slurry tests were limited to the range of 2,000-5,000 ppm SO_2 , and tests with higher slurry solids content required over 3,000 ppm SO_2 to remain under 80 percent gas-film controlled. Finally, the tests at 1.0M $\text{Ca}(\text{OH})_2$ required over 4,000 ppm SO_2 to make accurate measurements of enhancement. The stirred-tank was not able to produce meaningful enhancement factors under these conditions because the absorption was too gas-film controlled.

These limitations are shown in Figure 2-5. The gas-film resistance was determined from the same data generated by the slurry absorption model that was plotted in Figure 2-4. The model accurately predicted where the gas-film resistance became great enough to make measurement in the stirred-tank difficult.

The degree of error associated with determining the enhancement factor increased dramatically as gas-film resistance became dominant. In tests where the conditions resulted in gas-film resistances greater than 80 percent, the enhancement factor could not be determined with accuracy. As Figure 2-5 indicates, this lack of accuracy limited the range of measurements that could be taken in the stirred-tank, especially when solids concentration was increased to 0.4 and 1.0M $\text{Ca}(\text{OH})_2$. Inaccuracy was found to be inherent in the calculation of ϕ and could not be improved much by enhancing the accuracy of individual measurements.

The stirred-tank reactor operates at a gas-film mass transfer coefficient that is an order of magnitude smaller than might be expected for a slurry droplet. Therefore, it should be remembered that the enhancement factors and gas-film resistances measured in the slurry absorption experiments may not be of the same magnitude as found in a slurry droplet. The trends identified in the stirred-tank reactor should, however, be similar to behavior within a slurry droplet.

2.4 FUTURE WORK

Work for the upcoming quarter will focus on running the slurry absorption model with inputs that simulate SO_2 absorption in a slurry droplet. The procedure will involve increasing the gas-film coefficient by an order of magnitude. No stirred-tank reactor tests are planned for the next quarter.

Figure 2-5. Effect of Ca(OH)_2 Concentration in Slurry on Gas-Film Resistance Predicted by Slurry Absorption Model.

SECTION 3

TASK 4.2 — ENHANCEMENT OF DRY INJECTION: MOIST SOLIDS

3.1 SHORT TIME DIFFERENTIAL REACTOR (STDR)

3.1.1 Reactor and Solids Preparation

The modified STDR that allows solids with an increased amount of initial free moisture to be tested has been used throughout experiments described in this subsection. The reactor and solids preparation were described in detail in Quarterly Report No. 8. No changes have been made to the system or to preparations procedures.

3.1.2 Sorbents

Several sorbents produced by reacting fly ash with Ca(OH)_2 were used. Clinch River and Meredosia were the 2 fly ashes used throughout this study, both of which result from combustion of eastern bituminous coal. For some sorbents, the fly ash was ground prior to reacting it with Ca(OH)_2 . The weight ratio of fly ash to Ca(OH)_2 was varied to produce sorbents with varying surface area. Table 3-1 shows the structural properties of fly ashes used to produce sorbents.

TABLE 3-1. STRUCTURAL PROPERTIES OF FLY ASHES USED TO PRODUCE FLY ASH/ Ca(OH)_2 SORBENTS.

Fly ash Source	Fly ash Type	Surface Area [m^2/g]	Porosity [cm^3/g]	Median Pore Size [$\text{\AA}$]
Meredosia	U ^a	1.2	0.003	91
Meredosia	G ^b	6.8	0.027	159
Clinch River	U	2.2	0.005	92
Clinch River	G	5.6	0.020	145

^aU = Unground fly ash

^bG = Ground fly ash

As can be seen in Table 3-1, the structural properties of Meredosia and Clinch River fly ashes were similar before grinding. Grinding resulted in a significant increase in surface area and porosity for both, although their structural similarities remained the same.

Both ground and unground fly ashes were used to produce sorbents. These sorbents' slurring conditions and structural properties are presented in Table 3-2. Sorbents with similar structural properties were produced by slurring ground Meredosia or ground Clinch River fly ash for 3 h at 90 °C, using a 3:1 weight ratio of fly ash to Ca(OH)_2 . The surface area and porosity for Meredosia and Clinch River-based sorbents produced at the above conditions were 27 m²/g and 0.122 cm³/g, and 30 m²/g and 0.132 cm³/g, respectively. All sorbents produced by slurring ground fly ash and Ca(OH)_2 had higher surface area and porosity than the sorbent produced with unground fly ash. For a given source and type of fly ash, increasing the weight ratio of fly ash to Ca(OH)_2 resulted in a sorbent with greater surface area and porosity.

Scanning Electron Microscope (SEM) photomicrographs of "as received" and ground Clinch River fly ash are shown in Figures 3-1 and 3-2, respectively. The typical microscope field of "as

TABLE 3-2. STRUCTURAL PROPERTIES OF FLY ASH/ Ca(OH)_2 SORBENTS.

Fly ash Source	Fly ash Type	Slurring		Fly ash/ Ca(OH)_2 Weight ratio [g/g]	Sorbent		
		Time [h]	Temperature [°C]		Surface Area [m ² /g]	Porosity [cm ³ /g]	Median Pore Size [Å]
Meredosia	U ^a	8	90	3:1	6.9	0.039	225
Meredosia	G ^b	3	90	3:1	27.4	0.122	178
Meredosia	G	3	90	2:1	17.5	0.100	229
Meredosia	G	3	90	1:1	16.6	0.099	239
Clinch River	G	3	90	3:1	30.2	0.132	174

U = Unground fly ash
G = Ground fly ash

Figure 3-1. SEM photomicrograph of "as received" Clinch River fly ash sample, x 2,000.

Figure 3-2. SEM photomicrograph of ground Clinch River fly ash sample, x 5,000.

received" Clinch River fly ash in Figure 3-1 shows spherical particles with smooth surfaces. The median particle size of this sample measured by X-ray sedimentation (Sedigraph) was found to be 12.05 μm .

As Figure 3-2 shows; grinding changed significantly the morphology of Clinch River fly ash. All particles visible in the SEM field are smaller than 10 μm , with most of them having an irregular shape. The Sedigraph method yielded a median particle size of 4.96 μm .

3.1.3 Effect of Fly Ash Source

Two sorbents were produced using different fly ashes to compare the effect of fly ash source on their reactivity. Both fly ashes (Clinch River and Meredosia) were ground prior to reacting them with $\text{Ca}(\text{OH})_2$ at the same time/temperature conditions (3 h at 90 $^{\circ}\text{C}$) and at the same fly ash-to- $\text{Ca}(\text{OH})_2$ weight ratio of 3:1. The resulting sorbents developed similar specific surface areas of 30 and 27 m^2/g for the one produced with Clinch River and Meredosia fly ash, respectively. Both sorbents were loaded with moisture to yield 30 weight percent of initial free moisture content. The sorbents were then exposed to SO_2 in the STDR operated at 11 $^{\circ}\text{C}$ approach to saturation and with 2,000 ppm SO_2 . Figure 3-3 presents results for STDR contact time from 0.5 to 5 s. Generally, for a given contact time, there was no significant difference in reactivity with SO_2 for the sorbents produced with the two fly ashes.

In the next step, both sorbents, with initial free moisture content varying from 10-60 weight percent, were reacted with SO_2 . STDR results for 5 s contact time at 11 $^{\circ}\text{C}$ approach to saturation and 2,000 ppm SO_2 are shown in Figure 3-4. This finding is similar to the results presented in Figure 3-3. Fly ash source had no significant effect on sorbent reactivity with SO_2 . The datapoints at approximately 5 weight percent initial free moisture represent conditions for "dry" sorbents at equilibrium with the gas. The slightly higher reactivity of sorbent produced with ground Clinch River fly ash in comparison with ground Meredosia fly ash may be a consequence of the slightly higher specific surface area of the former sorbent (for equilibrium sorbents, conversion increases with increasing surface area).

For both sorbents, there was an optimum initial free moisture content for maximum conversion with SO_2 at conditions tested in the STDR. Solids produced with ground Clinch River fly ash had the

Figure 3-3. The effect of fly ash source on reactivity of sorbent with SO_2 (ground fly ash-to- $\text{Ca}(\text{OH})_2$ weight ratio of 3:1, 30 weight percent initial free moisture, 2,000 ppm SO_2 , 11 °C approach to saturation).

Figure 3-4. Combined effect of fly ash source and initial free moisture content on sorbent's reactivity with SO_2 (ground fly ash-to- $\text{Ca}(\text{OH})_2$ weight ratio of 3:1, 2,000 ppm SO_2 , 11 °C approach to saturation, 5 s contact time).

maximum conversion occur with initial free moisture content of 30 and 40 weight percent. For solids produced with Meredosia fly ash, the maximum conversion occurred at 30 weight percent initial free moisture content. This maximum conversion was approximately 15 percent for both sorbents after 5 s contact time in the STDR operated at 11 °C approach to saturation and with 2,000 ppm SO₂.

3.1.4 Effect of the Amount of Initial Free Moisture

Previous results (Quarterly Report No. 8) indicated that increasing the amount of initial free moisture up to approximately 40 weight percent resulted in increased calcium conversion. Because solids produced by chemically reacting fly ash and Ca(OH)₂ can contain up to 60 weight percent of initial free moisture and be flowable, the amount of initial free moisture was increased up to 60 weight percent. Solids produced by chemically reacting ground Clinch River fly ash and Ca(OH)₂ at the weight ratio of 3:1 and at 90 °C for 3 h were used for these experiments. Results for STDR operated at 11 °C approach to saturation and with 2,000 ppm SO₂ are presented in Figure 3-5. For short contact time (0.5 and 1 s) the effect of an increased amount of initial free moisture (up to 60 weight percent) was weak, and the maximum conversion was approximately 5 percent only. Significantly increased conversion as a result of increased levels of initial free moisture took place for 3 and 5 s contact times. The rate of reaction of sorbent with SO₂ was highest for 30 and 40 weight percent of initial free moisture. When tested at conditions in the STDR, conversion decreased as the amount of initial free moisture increased from 40 to 60 percent.

3.1.5 Effect of the Approach to Saturation

Previous experiments with equilibrium moisture solids indicated the strong effect of approach to saturation on conversion of the sorbent with SO₂. Conversion of equilibrium solids increased as approach to saturation decreased. To study the effect of the approach to saturation on conversion with increased initial free moisture, the sorbent was prepared by chemically reacting ground Clinch River fly ash with Ca(OH)₂ at the weight ratio of 3:1 at 90 °C for 3 h. A sorbent with 30 percent initial free moisture was exposed to 2,000 ppm SO₂ in the STDR as the approach to saturation varied from 2.8 to 22 °C. As a baseline test, sorbent with 30 percent initial free moisture was first exposed to 2,000 ppm SO₂ in the STDR operated with dry gas. Conversion was measured after 0.5, 1, 3, and 5 s to be 3.9, 5.2, 7.1, and 10.8 percent, respectively. Following baseline tests, experiments with moist flue gas

Figure 3-5. Conversion as a function of initial free moisture content (ground Clinch River fly ash-to- $\text{Ca}(\text{OH})_2$ weight ratio of 3:1, 2,000 ppm SO_2 , 11 °C approach to saturation).

were performed. Results are presented in Figure 3-6. As can be seen, exposing sorbent with 30 percent initial free moisture to the moist gas at short contact times (0.5 and 1 s) did not affect its conversion significantly, compared with that attained as a result of exposure to the dry gas. An increase of conversion was observed for contact times longer than 1 s. For example, 5 s exposure to SO_2 of solids with an initial 30 weight percent free moisture to dry gas and to moist gas at 11 °C approach to saturation resulted in 10.8 and 15.6 percent conversion, respectively. However, for 1 s exposure of the above solids to SO_2 , conversion was 5.2 and 5.5 percent, respectively.

For short contact times with moist gas, there was no detectable effect of the approach to saturation (between 2.8 and 22 °C) on conversion of a sorbent with SO_2 . For 5 s contact time, sorbent conversion increased as the approach to saturation decreased. Sorbent conversion following 5 s contact time increased by only 2.5 percent when decreasing the approach to saturation from 22 to 2.8 °C.

3.1.6 Combined Effect of Initial Free Moisture and Approach to Saturation.

The sorbent's initial free moisture content was varied from 5 to 60 weight percent. A previously described sorbent produced by chemically reacting ground Clinch River fly ash and $\text{Ca}(\text{OH})_2$ was used in this series of experiments. SO_2 concentration in the STDR was 2,000 ppm. Solids were exposed for 5 s to dry gas and moist gas at 11 or 22 °C approach to saturation. The results are given in Figure 3-7. For sorbents prepared with initial free moisture content up to 30 weight percent the conversion was highest for 11 °C approach to saturation. No significant conversion difference could be measured between 22 °C approach and dry gas. Results for the 40-60 percent initial moisture range are less clear.

3.1.7 Effect of the Sorbent's Surface Area

Two sorbents were prepared by chemically reacting Meredosia fly ash with $\text{Ca}(\text{OH})_2$ at the weight ratio of 3:1. By using ground and unground fly ash, it was possible to produce sorbents with surface area of 27.4 and 6.9 m^2/g , respectively, while keeping the fly ash-to- $\text{Ca}(\text{OH})_2$ weight ratio constant. These sorbents were loaded with moisture to yield initial free moisture levels from 5-60 weight percent. Figure 3-8 presents results in terms of sorbent conversion with SO_2 resulting from 5 s exposure to 2,000 ppm SO_2 in the STDR operated at 11 °C approach to saturation. The highest

Figure 3-6. The effect of approach to saturation on the conversion of sorbent with an initial free moisture content of 30 weight percent (ground Clinch River fly ash-to- $\text{Ca}(\text{OH})_2$ weight ratio of 3:1, 2,000 ppm SO_2).

Figure 3-7. Combined effect of the approach to saturation and initial free moisture on 5 s conversion of sorbent with SO_2 (ground Clinch River fly ash-to- $\text{Ca}(\text{OH})_2$ weight ratio of 3:1, 2,000 ppm SO_2).

Figure 3-8. The effect of sorbent surface area on 5 s conversion of Meredosia fly ash/ $\text{Ca}(\text{OH})_2$ sorbent (weight ratio of 3:1, 11 °C approach to saturation, 2,000 ppm SO_2 , 5 s contact time).

conversion of 15 percent was obtained in this series of experiments for 27.4 m²/g sorbent with 30 weight percent of initial free moisture. The highest conversion for 6.9 m²/g was 11 percent and it occurred for sorbent with 20 weight percent of initial free moisture. More experiments are needed for these results to be fully conclusive.

3.1.8 Conclusions

Based on the results discussed, several conclusions may be drawn.

- For sorbents with comparable surface area, fly ash source (2 fly ashes tested) did not have a significant effect on reactivity of solids with excess initial free moisture.
- When compared with equilibrium (or dry) solids, conversion with SO₂ in the STDR was greatly enhanced by increasing the initial free moisture to about 30 weight percent.
- Maximum conversion for 5 s contact time and 11 °C approach to saturation was measured for solids with 30 to 40 weight percent initial free moisture.
- The conversion decreased when the initial free moisture increased beyond 30-40 percent.
- Conversion of solids with excess initial free moisture was not affected by the approach to saturation in the STDR for short contact times of 0.5 and 1 s. With longer contact time of 5 s, conversion in the STDR increased with decreasing approach to saturation.
- The initial free moisture content and corresponding level of maximum sorbent conversion with SO₂ varied with the surface area of the sorbent.

3.2 GRINDING FOR RECYCLE REACTIVATION

Once-through contact of dry hydrated lime with SO₂ under typical 50 cfm pilot-plant conditions (2 s residence time, Ca/S = 2, Δt_s = 11 °C, [SO₂] = 2,000 ppm) results in approximately 30 percent removal of SO₂ in the duct. Previous experiments with recycling of spent lime downstream of the humidification point indicated that there was no significant increase in the removal of SO₂. This finding implies the need to reactivate recycled solids prior to their reinjection into the duct, in order to accomplish additional calcium utilization.

Grinding of recycled solids is considered for the reactivation of a recycled material. The batch of spent solids was generated by injecting Mississippi Ca(OH)₂ into the pilot-plant duct. The duct

was operated at 11 °C approach to saturation with 2,000 ppm SO₂ and at Ca/S = 2. The pilot-plant run was made with the cyclone in-line between the duct and the fabric filter. Solids intended for grinding were taken from the cyclone catch. These solids from the cyclone catch were ground in a bench-scale attrition grinder for 15 min and for 1 h. Following grinding, the increase in specific surface area and porosity was measured. Significant decrease of a median particle size was measured by the Sedigraph method. Table 3-3 presents structural properties of "as received" and ground pilot-plant solids.

Future plans include testing of "as received" and ground solids in the STDR for their reactivity with SO₂. The effect of fly ash presence on the effectiveness of grinding recycled materials will also be evaluated.

TABLE 3-3. STRUCTURAL PROPERTIES OF PILOT-PLANT SOLIDS

Solids	Specific Surface Area [m ² /g]	Porosity [cm ³ /g]	Median Pore Size [Å]	Median Particle Size [μm]
"As received" ^a	14.2	0.0698	196	4.18
Ground for 15 m ^b	22.3	0.0991	178	1.20
Ground for 1 h ^b	27.8	0.1406	202	0.90
^a from the pilot plant				
^b in the bench scale attrition grinder				

SECTION 4

TASK 4.2 — ENHANCEMENT OF DRY INJECTION: SOLIDS MOISTURE CAPACITY

4.1 INTRODUCTION

This report documents progress on a study to investigate the moisture capacity of solids used for duct injection. The objectives of the study include: 1) developing an experimental method to quantify the moisture capacity of SO₂ sorbents; 2) correlating moisture capacity with solid surface area; and 3) determining the effects of source materials and slurry conditions on moisture capacity of solids produced by slurry reaction. The first objective has been achieved, and work continues on the latter.

Sieve tests were used to quantify a solid's moisture capacity. Less material passes through a sieve as the moisture content of the material is increased. The moisture content that results in 50 percent of a material being retained by an 80 mesh sieve (180 µm) was identified as the critical moisture content. The materials tested to date have been solids produced by slurrying fly ash with calcium hydroxide, and their critical moisture content correlates well with their surface area. Work with a variety of fly ash types and slurry additives continues in order to broaden the correlation and to identify conditions that enhance moisture capacity.

4.2 EXPERIMENTAL PROCEDURE

4.2.1 Sieve Tests

The procedure described below requires a shorter sieving time than the procedure described in the previous quarterly report. The change was necessary to make the data obtained from new sieves match the data obtained from sieves previously used.

Materials to be sieved were dried in an atmospheric oven at 110 °C for 8-12 h. They were allowed to cool in a desiccator and were then sieved by hand through an 80 mesh (180 µm) sieve. Any material that did not pass was ground with a pestle in a mortar so that it would pass. This initial sieving of all solids with no moisture added was to ensure that aggregates were reduced in size and

that the material was homogeneous, thereby promoting uniform distribution of added moisture. The material was stored in plastic containers for sieve tests and surface area determination.

Five gram samples were used for each sieve test. Water was added dropwise and mixed with a metal spatula. All visible agglomerates formed around water drops were crushed. The sample was weighed after the water was mixed to determine the moisture content. The damp sample was then sieved through an 80 mesh (180 μm) sieve followed by a 115 mesh (125 μm) sieve; a pan was placed at the bottom, and a lid was placed on the 80 mesh (180 μm) sieve. The sieves were shaken for 10 min on a mechanical sieve shaker; the shaker did not have a tapping device. After shaking, the weight of material retained by each sieve and collected by the pan was determined. The amount of material passing through each sieve was expressed as a weight percentage.

4.2.2 Critical Moisture

The results of sieve tests on one material at different moisture contents were used to identify the critical moisture content of that material. Critical moisture is defined in this study as the moisture content level in the initial solid that results in 50 percent of the material being retained by an 80 mesh (180 μm) sieve after 10 min of sieving. The distinction of initial moisture content is made because some water evaporates from the sample during sieving.

During testing, the amount of water added to a sample is rarely the critical amount; therefore linear interpolation between data points was used. Figure 4-1 illustrates the method of determining critical moisture. A line was drawn through the 2 80-mesh datapoints that are closest to 50 percent passing. The point of intersection with 50 percent passing identifies the critical moisture.

Figure 4-1 is illustrative of the data typically obtained. There is a range of moisture where the amount of material passing through a sieve decreases sharply with increasing moisture. At moisture contents below and above the range, almost all of the material either passes through the 80 mesh (180 μm) sieve or is retained. The critical moisture content lies within this range, which separates moisture contents that do not significantly cause solids agglomeration from those that cause a material to clump together.

Figure 4-1. Sieve test data for solids produced by slurring Clinch River fly ash with hydrated lime at the weight ratio of 3:1 for 8 h. Critical moisture content is 17 percent.

4.2.3 Solids Preparation

Solids for testing were prepared by slurring the reactants in water at constant temperature. A 500 mL stainless-steel vessel was used. The reactants were added to 400 mL of water and were stirred continuously. The temperature was maintained at 92 °C. At various times, samples were drawn and filtered, and the solids were placed in a 110 °C oven for 8-12 h to dry. In addition, a physical mixture of the reactants was made without slurring, but in the same weight proportions as the solids added to the slurry.

4.2.4 Materials Tested

Most of the materials tested were products of lime/fly ash slurries. Other materials were pure reagent chemicals, and some were products from slurries of silica fume. Two types of fly ash were used: Clinch River (low calcium) and Harrington (high calcium). The Clinch River fly ash was slurried with lime hydrate and with both lime hydrate and calcium sulfite, at slurry times of up to 16 h. The Harrington fly ash was slurried only once alone, for up to 24 h. An additional material tested was the Clinch River fly ash/calcium hydroxide slurry product prepared by Acurex in 1987 (8-12 h hydration). The pure reagents tested were lime hydrate, calcium hydroxide, and calcium sulfite hemihydrate. Finally, products from slurry mixtures of silica fume and calcium hydroxide, and silica fume with both calcium hydroxide and calcium sulfite, were tested. Table 4-1 lists all these materials.

4.3 RESULTS AND DISCUSSION

The surface area and critical moisture content of all materials tested is listed in Table 4-1. A range of values is given for slurry products that were sampled at various times; both surface area and critical moisture increase with slurry time. When the lime hydrate was sieved, less than 50 percent passed through an 80 mesh (180 μ m) sieve; therefore the critical moisture is reported as less than zero. Two separate sources of calcium sulfite hemihydrate were tested. Although the surface area of each was significantly different; the critical moisture, however, was not. The high surface area hemihydrate was used in the lime/fly ash slurry, and the low area hemihydrate was used in the silica fume slurry. The low values of area and critical moisture for the silica fume materials come from a non-slurried physical mixture of reactants; all the slurry products had values at the high end.

Table 4-1. MATERIALS TESTED AND RANGE OF VALUES FOR CRITICAL MOISTURE AND SURFACE AREAS

Material	Mass ratio	Surface Area (m ² /g)	Critical H ₂ O (percent)
Mississippi Lime Hydrate	-	17	<0
Ca(OH) ₂	-	9*	4
CaSO ₃ •0.5 H ₂ O	-	6, 21	5, 6
Lime/ Fly Ash Materials			
Clinch River/ Lime Hydrate	3/1	9 - 25	4 - 17
Clinch River/ Ca(OH) ₂ (1987)	3/1	16	10
Clinch River/ Hydrate/ CaSO ₃	4/1/4	10 - 26	7 - 15
Harrington Fly Ash	-	7 - 19	2 - 7
Silica Fume Materials			
Silica Fume/ Ca(OH) ₂	1/1	20 - 104	4 - 44
Silica Fume/ Ca(OH) ₂ /CaSO ₃	1/1/1	24 - 85	5 - 37

* Surface area reported in Ruiz-Alsop, R. N., "Effect of Relative Humidity and Additives on the Reaction of Sulfur Dioxide with Calcium Hydroxide," PhD Dissertation, The University of Texas at Austin (1986).

The critical moisture of each sample is plotted against the sample's surface area in Figure 4-2. A line representing the best fit of all the data is included. The critical moisture of the lime/fly ash materials correlates well with their surface area. Both Clinch River and Harrington slurry products fall on the same line. Also, the addition of calcium sulfite to the slurry did not affect the correlation of critical moisture with surface area. The reagent calcium sulfite samples lie on the correlation, but the lime hydrate, even with a surface area of 17 m²/g, has a poor critical moisture content and does not follow the correlation. The high surface area silica fume materials fall on the same correlation, and again the addition of calcium sulfite had no effect.

4.4 FUTURE WORK

4.4.1 Slurry Reactants

Additional solids will be prepared for testing the effect of the presence of calcium sulfite and/or gypsum in slurries of both Clinch River and Harrington fly ash. Solids prepared with ground Clinch River fly ash will also be tested in an identical manner. A variety of existing materials were previously prepared to study the effects of silica and alumina on the production of lime/fly ash

Figure 4-2. Correlation of critical moisture content with solid surface area. Data are for slurry products and pure reagents.

absorbents. These will be tested to fill in areas of the correlation where data are absent and to add critical moisture data to existing reactivity and solids characterization data.

4.4.2 Other Slurry and Solid Conditions

The effect of slurry temperature and solids loading on critical moisture and surface area may be studied by producing solids and subsequently testing them. Temperature would be both raised and lowered from 92 °C, and solids loading would be increased. To study an extreme case, the slurry solids loading could be increased until effective mixing is no longer possible, which suggests measuring some slurry property such as viscosity. In this way, slurry solids loading content of slurries could be identified, below which the mixture is no longer a slurry. It is expected that there will be a gap between the values of critical moisture for damp solids and the critical moisture of slurries.

Another factor to study is the direction of approach to moisture content. All sieve tests to date have been conducted on damp solids that started as dry solids. A series of sieve tests will be conducted on damp solids that are dried to the moisture content of interest. The critical moisture will be identified and compared to the value obtained by adding moisture to dry solids.

SECTION 5
SPECIAL STUDY

5.1 BENCH-SCALE EVALUATION

Four Ca(OH)_2 sorbents from Illinois State Geological Survey (ISGS) were evaluated for their reactivity with SO_2 in the STDR. The conditions in the STDR were as follows: 2,000 ppm SO_2 , 11 °C approach to saturation (corresponding to ~60 percent relative humidity), and contact time varying from 0.5-5 s. The properties of sorbents (as given by ISGS) are presented in Table 5-1.

TABLE 5-1. PROPERTIES OF ISGS SORBENTS

Sorbent Type	Surface Area [m ² /g]	MMD [μm]
ISGS Control	20	3.5
BH-161	40	1.5
BH-101	50	0.6
BH-130	65	1.0

The ISGS Control was a commercial hydrate and the remaining 3 Ca(OH)_2 were produced by ISGS. The results of a bench scale testing in the STDR are presented in Figure 5-1 giving calcium conversion as a function of contact time for 4 ISGS sorbents. Previously tested commercial Mississippi Ca(OH)_2 is shown in Figure 5-1 for comparison. The reactivity difference between commercial Mississippi Ca(OH)_2 and a commercial Ca(OH)_2 , as measured in the STDR, was insignificant. Compared with commercial Ca(OH)_2 , a significant increase in calcium conversion was measured for BH-101 and BH-130. A comparison of the structural data from Table 5-1 and reactivity data presented in Figure 5-1 revealed increasing conversion with increasing surface area for ISGS sorbents. It was impossible to detect any clear effect of the sorbent's median particle size on conversion with SO_2 .

Figure 5-1. Bench-scale testing of ISGS Sorbents (STDR, 11 °C approach to saturation, 2,000 ppm SO_2).

5.2 Pilot-Plant Testing

Pilot-plant testing of ISGS sorbents during this period involved using the 50 cfm unit to evaluate the ISGS high surface area hydrated lime (air classified BH-101 with surface area of 55 m²/g). The material was compared to commercially available Mississippi Ca(OH)₂. Conditions in the pilot plant were as follows: spray dryer inlet temperature = 140 °C, approach to saturation (DT_{AS}) = 11 °C throughout the system, inlet SO₂ concentration = 2,000 ppmv, and calcium-to-sulfur ratio (Ca/S) = 2.0. Tests were conducted with the lime only and lime dry mixed with fly ash from the Meredosia power plant.

Test results are presented in Figure 5-2. The plot shows SO₂ removal as a function of run number. The data were plotted to show reproducibility and to facilitate the comparison with Mississippi Ca(OH)₂. Figure 5-2 shows that, at the pilot-plant conditions given above, ISGS lime produced an average of 44 percent SO₂ removal in-duct and 58 percent throughout the system (duct plus baghouse). The Mississippi Ca(OH)₂ removed 28 and 46 percent, respectively. It should be noted that only run number 1, with the ISGS lime, was conducted without the cyclone in-line before the baghouse; all other tests were conducted with the cyclone in-line. Tests using the ISGS lime dry mixed with Meredosia ash showed essentially the same removal in-duct and only slight enhancement through the system, compared with ISGS lime. When testing the Meredosia ash alone with 2,000 ppm SO₂, the results showed only 1.5 percent SO₂ removal through the system, which is within the experiment's margin of error.

Figure 5-2. Pilot-plant testing of air classified BH-101 sorbent from ISGS.

END

DATE FILMED

12 / 12 / 90