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**GLOBAL APPROACH FOR ENHANCED MASS TRANSFER EFFECTS:
IN-DUCT INJECTION FGD PROCESSES**

Topical Report No. 1 Experimental Studies

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**By
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GLOBAL APPROACH FOR ENHANCED MASS TRANSFER
EFFECTS: IN-DUCT INJECTION FGD PROCESSES

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TOPICAL REPORT NO. 1
EXPERIMENTAL STUDIES

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INTRODUCTION

This topical report describes the experimental results from a global investigation of in-duct SO_2 capture by lime-slurry sprays. The purpose of this investigation was twofold. To a large extent the experiments were guided by a parallel model-development effort. The data were used to test and refine various assumptions made by the model about internal vs. external mass transfer, temperature, humidity, SO_2 concentration and slurry concentration. Also, the experiments performed a scoping function for the overall DOE duct injection program. By testing lime slurry sprays for SO_2 capture over a range of conditions, this program has identified limits and variabilities of sorbent performance which may be encountered in future pilot - and demonstration - scale tests.

A significant fraction of the experimental effort was applied to a continual evolution of the system design. This evolution of design was a response to the changing needs of the program. These were defined both by the modeling effort and the understanding of the important process parameters which developed as the experimental database increased. Aspects which were especially critical were the slurry atomizer design, the sampling system, and control of the complete reactor environment, including temperature, humidity, and gas composition.

Key findings of this study are as follows:

- 1.) The experiments support the model's contention that the maximum rate of SO_2 capture by line slurry is controlled by gas-phase diffusion of SO_2 .
- 2.) Handling of the lime after calcination can be a key factor in determining slurry reactivity. Sorption of atmospheric CO_2 either before or after slaking can severely reduce the slurry utilization. This effect is strong enough to mask most other experimental variables.

3.) Line utilization is increased at lower slurry solids concentrations.

4.) Increasing hydrate surface area above 15 m₂/g does not itself increase lime slurry utilization.

Figure 1. Diagram of the slurry droplet reactor (SDR) configuration with the settling chamber and heated extractive sampling probe.

2.0 DESCRIPTION OF THE EXPERIMENT

Slurry reactivity experiments were conducted in EER's Slurry Droplet Reactor Facility (SDR). The SDR consists of a rotary disk atomizer placed on top of a laminar flow reactor. Gas flow to the reactor is provided by a flame burner with methane fuel. The baseline SO_2 concentration is 1500 ppm and the dew point is 60°C . The atomizer delivers a slurry spray to the reactor where it mixes with the burner gas and reacts with SO_2 . Dried slurry samples are collected on a Gelman A/E filter at the base of an oil-heated sampling probe. The oil-heated probe heats the entrained gas stream to 180°C in 30 ms. This effectively flash evaporates the slurry droplets, rendering them unreactive toward SO_2 .

During the course of the program, the experimental system design was continually evolving. This was in response to the experimental demands, and in order to accommodate the level of control required to test model assumptions. The oil-heated sampling probe is an example of such a change. The previous sampling system consisted of passive collection of slurry spray in a heated cup. The need for greater analytical accuracy, hence, longer samples, demanded a longer volume sampling system with the capability to flash evaporate the slurry droplets. At the start of this phase of experimental activity the SDR was modified by the addition of a settling chamber placed between the disk atomizer and the reactor. The settling chamber permits the slurry droplets, which have an initial velocity of 130 m/s, to relax to their terminal velocities before entering the reaction zone. As the droplets settle into the reactor they are entrained into the flue gas by mixing vanes which provide a temporary turbulent zone near the reactor entrance. Toward the end of the experimental program modifications were made to provide better positive control over reactor temperature and the temperature and humidity of the flue gas. This was accomplished by water jacketing the reactor and passing the flue gas through tube-and-shell heat exchanges. These two systems were linked through a controlled - temperature water reservoir providing $\pm 1^\circ\text{F}$ process control.

An important experimental parameter is the size distribution of the slurry droplets. This is affected mainly by the rotation speed of the atomizer. Drop size characterization results are shown in Figure 2. The data were obtained for

Figure 2. Drop size distribution for water and 20 percent slurry droplets generated by the rotary disk atomizer.

3.0 DISCUSSION OF DATA

3.1 Baseline Test Results

The data in Figure 3 show the slurry utilization vs. time for the baseline reactor operating condition. Sorbent utilization is over 60 percent. Reactivity testing up to this point used bags 2 and 3 from the second 500 lb. shipment from Marblehead Lime Company. Bag 1 from that shipment was used during spray characterization tests with the new SDR design. Variables tested using bags 2 and 3 included slurry concentration and SO_2 concentration.

Figure 4 shows the data obtained at the baseline operating condition using bags 2 through 7 from the second 500 lb. shipment of the Marblehead hydrated lime. These data show that utilizations measured for hydrate from bags 4-7 are significantly lower than the 60-65 percent utilizations obtained with bags 2 and 3. Bag 5 had the lowest utilization, about 20 percent. Bags 4 and 6 consistently showed about 23-27 percent utilization, while bag 7 attained 37 percent.

These data are at once striking and revealing. Not only was a wide variation found in reactivity between different bags, but within a single bag of sorbent, measured utilizations were relatively constant, within experimental error, even for tests performed over a month apart. Thus, although the experimental procedure was found capable of producing reliable data, the sorbent supply was highly variable. This point must be kept firmly in mind while reviewing the data in the following sections. Variation must be considered relative to the baseline data for the bag of sorbent employed.

3.2 Sorbent Variability Studies

One of the most significant variables found to impact slurry utilization during this program was the bag of sorbent chosen. Therefore, considerable effort was devoted to discovering the critical factor responsible for this variability. Particle size and surface area analyses were conducted early on for bags 2 through 5. The results, shown in Table I, provide no insight.

Figure 3. Baseline sorbent utilization measured using Bag 3 of the second shipment of Marblehead calcium hydroxide.

Figure 4. Measured calcium utilizations for different bags taken from a single 500 lb shipment of Marblehead hydrated lime.

TABLE I. PHYSICAL AND CHEMICAL ANALYSES OF SORBENTS FROM
THE SECOND SHIPMENT OF MARBLEHEAD HYDRATED LIME

Bag No.	mm Microns	SSA m ² /g	mol-percent	
			CaCO ₃	Ca(OH) ₂
2	4.0	16.2	-	-
3	4.5	16.6	7.8	92.2
4	2.6	15.6	15.3	84.7
5	3.6	16.6	16.4	83.6
5 (bottom)	-	-	16.9	83.1
6	-	-	25.8	74.2

Subsequently, hydrates from bags 3 through 6 were analyzed gravimetrically to determine their hydroxide and carbonate contents (sufficient sample remaining from bag 2 was not available for this analysis). These data (Table I) show that bag 3 had significantly less carbonate than did the others. The utilizations measured for these sorbents at the baseline reactor condition are plotted in Figure 5 as a function of their carbonate contents. The correlation shown in Figure 5 is by itself weak because the data cover a very narrow range of carbonate contents. However, a hypothesis proposed to explain these results was shown to be consistent with certain assumptions of the droplet reactivity model.

The hypothesis is that the carbonate occupies the reactive, external surface of the hydrate particles. The carbonate formation need not even have occurred after hydration, although that seems most likely. When the slurry is prepared, the carbonate "blinds" the particles, preventing diffusion of calcium species away from the particle surface. This would shift the dominant resistance to reaction from external to internal diffusion.

An attempt was made to predict this effect using the droplet reactivity model. The approach used was first order approximation based upon the limited data. The available surface area of the particles was assumed to correlate linearly with carbonate content, and no carbonate implied about $16 \text{ m}^2/\text{g}$. The result of the model predictions that a reasonable prediction of the experimental results can be achieved by making a very simple assumption about the effect of carbonation on the sorbent.

Two further tests were done to test the carbonate blinding hypothesis. The first test involved freshly slaking quicklime to make the slurry. The quicklime was provided by Marblehead Lime Co. and was the same material used by Marblehead to prepare their commercial hydrate - the baseline test sorbent. A test of the quicklime showed that approximately 10-15 percent of the calcium was tied up as carbonate, approximately the same amount as in bags 4-6 of the baseline hydrate. Thus, this provided a means of determining whether the hydration process would mitigate the deleterious effects of carbonate contamination.

Figure 5. Correlation between measured utilization and carbonate content of calcium hydroxides. The curve through the data is a model prediction made assuming that carbonate content correlates with availability of carbonate surface area.

The second test involved recalcining a batch of hydrate from bag 7. The calcination was carried out at 950°C for 6 1/2 hours in an atmosphere of commercial dry nitrogen. Under these conditions all of the CO₂ and hydrate should have been effectively eliminated leaving essentially all calcium oxide. This "carefully calcined" material was then handled and stored in dry nitrogen up to and during the slaking process in order to minimize any possible contact with atmospheric CO₂.

Both of these lime slurries were tested in the SDR at the baseline operating condition. The results of these tests are shown in Figure 6 along with the baseline test results for bag 7. The data show that the freshly slaked Marblehead lime achieved utilization comparable with the bag 7 hydrate. This indicates that fresh slaking may provide some advantage in reactivity but does not eliminate the blinding effect of carbonate contamination. Otherwise, utilization in excess of 60 percent would have been expected.

The carefully calcined lime, on the other hand achieved 52 percent utilization. This lends considerable support to the hypothesis that carbonate contamination is largely or wholly responsible for the variation in reactivity between the different bags of sorbent.

Although the carefully calcined material did not achieve the 62 percent utilization of bags 2 and 3, or the 77 percent predicted by the droplet reactivity model it should be noted that the calcination conditions employed were rather extreme. The reactivity of hydrated lime in furnace dry injection tests has been correlated with both calcination and hydration conditions. The extended time at temperature used here to ensure complete calcination may have sintered, or "dead-burned" some of the lime, reducing its availability for SO₂ sorption, though to a lesser extent than carbonate blinding.

3.3 Alternate Sorbents

The three sorbents selected by Gilbert/Commonwealth for demonstration testing under this program were also procured. Two of these -- Mississippi hydrate and mid-Ohio Valley quicklime -- arrived in time for testing in the SDR. Results of these tests are shown in Figure 7. Both sorbents reactivities lay

Figure 6. Utilization of a lime slurry prepared from a "carefully calcined" lime. The carefully calcined lime was prepared at 950°C under a dry nitrogen atmosphere. Data for the baseline Marblehead hydrate and a freshly slaked Marblehead quicklime are shown also.

Figure 7. Comparison of alternative sorbents reactivity under baseline test conditions.

in the range of data for bags 4 - 6 of the baseline Marblehead hydrate. The Mississippi hydrate was the most reactive of the two, achieving nearly 34 percent utilization.

3.4 Slurry Concentration Effects

The effect of slurry concentration on sorbent utilization is shown in Figures 8 and 9. These data were obtained using bag 3 of the Marblehead hydrate. Figure 8 shows that the difference in reactivity, from 1 wt - percent to 30 wt - percent slurry is greatest for short sampling distances. At longer distances differences in reactivity diminish, except for the 1 percent slurry which quickly achieves nearly 100 percent utilization. Figure 9 shows the same data set, but this time represented as utilization vs. slurry concentration. In Figure 9 it is more apparent that slurry concentration has a dramatic effect on utilization only for concentrations below 5 wt - percent.

3.5 Droplet Diameter

Droplet mean diameter was increased by reducing the atomizer speed to 10,000 rpm. Referring back to Figure 2, this gives a mean diameter of 69 μm with 80 percent of the mass between 10 and 90 μm . Figure 10 shows the measured sorbent utilization under this condition. Overall, the data lie within the range of the baseline test results using bag 5 of the Marblehead hydrate. However, the data trend is flatter than generally observed. Model predictions concur that under non-evaporating conditions drop size should have a small effect in the range examined here.

3.6 SO₂ Concentration

The data in Figure 11 show the increase in slurry utilization with increasing sampling distance (from the reactor entrance) at 100, 500, and 1500 ppm SO₂. These data were obtained using bag 2. No increase in utilization is observed beyond 17 cm regardless of SO₂ concentration. The same data are plotted in Figure 12 to show the impact of SO₂ concentration on slurry utilization. For these test conditions SO₂ concentration has an effect on utilization for concentrations as high as 1500 ppm.

Figure 8. Effect of slurry concentrations on sorbent utilization.

Figure 9. Slurry concentration dependence of sorbent utilization.

Figure 10. Impact of drop size on slurry reactivity.
Triangles are data for 70µm and droplets.

Figure 11. Sorbent utilization measured at 100, 500, and 1500 ppm SO₂.

Figure 12. Impact of SO₂ concentration on measured sorbent utilization at different sampling distances.

Figure 13 shows the effect of higher (than the baseline) SO_2 concentration on measured slurry utilization. The results shown were obtained with bag 4. These data imply that higher SO_2 concentrations give a faster sulfation rate only at short times. This is consistent with a model which assumes external mass transfer control at longer times. However, the measured increase in utilization is not proportional to the increase in SO_2 concentration. The data shown in Figures 11 and 12 suggested that at SO_2 concentrations below 1500 ppm, a roughly proportional effect was obtained.

3.7 Impact of Sorbent Surface Area

In addition to the baseline calcium hydroxide sorbent, which has an average surface area of $15 \text{ m}^2/\text{g}$, a high surface area material ($50 \text{ m}^2/\text{g}$) was prepared in-house and tested. The high surface area hydrate was prepared using an alcohol hydration procedure. In this procedure methanol is added to the hydration water. It also moderates the reaction temperature by boiling off and carrying away excess heat.

Figure 14 shows that the high surface area material actually achieves a moderate utilization which is higher than all but bags 2 and 3 of the Marblehead hydrate. This suggests that the surface area of the starting material is not the most critical factor in determining reactivity. It also implies that other differences between materials can greatly affect sorbent utilizations. The mean particle diameter of the alcohol hydrate was $1.2 \mu\text{m}$, somewhat smaller than the Marblehead hydrate (see Table I). More work is required to fully understand this behavior.

In an attempt to understand this result a "cation scan" was performed on representative samples of the two sorbents. These results are shown in Table II. Unfortunately, these results indicate nothing of particular significance. Most of the cations detected are present at only trace quantities and never differ by more than a factor-of-three between the two sorbents. Only the calcium concentrations are significantly different between the two materials.

Figure 13. Impact of high SO₂ concentrations on slurry utilization with Bag 4 of the Marblehead AH.

TABLE II. CHEMICAL ANALYSIS OF MARBLEHEAD AH (COMMERCIAL) AND ALCOHOL HYDRATE (PREPARED IN-HOUSE)

Element	Concentration (mg/g)		Ratio
	Marblehead AH	Alcohol Hydrate	Normalized to Calcium
Al	1.3989	1.2248	1.1247
Sb	-----	-----	-----
As	-----	-----	-----
Ba	0.0152	0.0296	2.5014
Be	-----	-----	-----
B	-----	0.0119	-----
Cd	-----	-----	-----
Ca	532.9	414.9	*0.7786
Cr	0.0019	0.0040	2.7039
Co	-----	-----	-----
Cu	0.0057	0.0059	1.3294
Au	-----	-----	-----
Fe	2.2840	1.9755	1.1109
Pb	-----	-----	-----
Mg	5.5196	9.6800	2.2524
Mn	0.1427	0.3161	2.8450
Hg	-----	-----	-----
Mo	-----	-----	-----
Ni	-----	-----	-----
K	-----	0.3951	-----
Se	-----	-----	-----
Si	3.8066	3.5559	1.1998
Ag	-----	-----	-----
Na	0.2665	0.2173	1.0472
Sr	0.2474	0.0869	0.4511
Tl	-----	-----	-----
Sn	0.0295	0.0573	2.4947
Ti	0.0466	0.0395	1.0887
V	0.0038	0.0079	2.6701
Zn	0.0086	0.0099	1.4785
insolubles	27.56	26.23	1.2226

*This value represents the actual ratio of the calcium concentrations in the two sorbents

One hypothesis which was tested in an attempt to explain these data is that residual methanol from the hydration process may have in some way reduced the calcium availability. In order to test this slurries were prepared containing 1.25% v/v and 4.75% v/v methanol. Results of these tests (using bag #4) are shown along with the baseline test results in Figure 14.

The results in Figure 15 lie within the range of data for the baseline condition (broken curve). Interestingly, the utilizations measured for the lower methanol concentration were the lower. The appearance of the data, however, suggests that this is most likely due to a systematic bias in the chemical analysis.

3.8 Effect of CO₂ on Slurry Reactivity

Figure 16 shows that eliminating CO₂ from the reactor atmosphere had no noticeable effect on the slurry reactivity. The tests were done by generating a hydrogen flame with 100 percent excess theoretical air. This provided the necessary 60°C dewpoint. All other experimental conditions were the same as the baseline. Although the data in Figure 16 tend to lie above the baseline curve, they are well within the normal data spread.

3.9 Droplet Evaporation

Figure 17 illustrates the results of tests performed in an evaporating mode, where the relative humidity of the reactor was near zero percent. Model predictions (curves) are also shown. The data show that the short time reactivity is similar for evaporating and non-evaporating conditions, but the reaction is halted under evaporating conditions when the slurry droplet becomes dry.

The model predicts that the rate of SO₂ uptake by an evaporating droplet should be greater than that of a non-evaporating droplet. This results from the accumulation of sorbent at the droplet surface during evaporation. When this occurs an excess of calcium is present at the droplet surface and the minimal diffusional distances for both the calcium and sulfur species results in a rate of SO₂ absorption approaching the limit of external mass transfer. A non-

Figure 14. Difference in reactivity between a commercial hydrated lime (Marblehead, 15 m²/g) and an in-house prepared high surface area hydrated lime (50 m²/g).

Figure 15. Utilization of Marblehead AH slurries containing 1.25% and 4.75% v/v methanol.

Figure 16. Impact of CO₂ on baseline sorbent utilization.

Figure 17. Data and model predictions for evaporating and non-evaporating cases.

evaporating droplet, by contrast, has relatively long diffusional distances which increase with time as the sorbent near the surface is consumed. The rate of SO_2 uptake is then limited by liquid phase mass transfer (short times only). In contrast to the above discussion, the data shows utilization to be lower for the evaporating case. This is likely a result of the high approach to saturation used during the evaporating case (90°C throughout the length of the reactor) which caused an evaporation rate greater than that which would normally be encountered in a duct.

4.0 QUALITY ASSURANCE ISSUES

Data quality remained a critical issue throughout this experimental program. Especially key in this area are the incumbent problems of sampling a reactive solid from a gas mixture. This was addressed by minimizing the sample collection time and by flash drying the slurry, rendering it relatively unreactive, during sample collection. In order to continuously monitor the efficacy of these precautions "background" and "probe capture" tests were run at each test condition.

Sample collection times were limited to 5 minutes, except for the 1- and 2- percent slurry concentrations, for which 15 minute samples were obtained. Probe capture tests, however, all ran for 15 minutes. In the probe capture test a sample of slurry was collected, SO_2 was then introduced to the reactor and drawn through the sampling system to expose the fresh dried sorbent.

Probe capture utilizations varied from 0.1% to 9% over the course of the program. Some results from bag 2 are shown in Table III. The measured probe capture utilizations are considered to represent upper limits for two reasons. First of all, the sample exposure time in the filter holder is six times the average exposure time of a sorbent particle during sampling. Secondly, sorbent reactivity is much greater for fresh sorbent than it is for already reacted material.

In support of the model development task two special probe capture tests were run. In the first, SO_2 was introduced to the reactor by a tube placed adjacent to the sampling probe entrance. This restricted the slurry reaction to the hot, evaporating environment inside of the probe. The second test involved measuring in-probe SO_2 capture while a water spray was introduced to the reactor. The objective was to determine the effect of "wetting" the probe filter by the occasional unevaporated droplet.

Results of these tests are shown in Figure 18 alongside the baseline SO_2 capture at 17 cm and the average measured probe capture. Results of the first test indicate that even fresh unreacted slurry will not capture very much SO_2 in the brief (<30 ms) evaporating zone inside the probe. The total measured

TABLE III. MEASURED IN-PROBE SO₂ CAPTURE (15 MINUTE EXPOSURE,
1500 ppm SO₂) USING THE OIL-HEATED SAMPLING PROBE.

<u>Sample No.</u>	<u>Sample Temperature</u>	<u>Utilization Percent</u>
127712	135	3.3
127704	127	4.8
127680	157	0.75

utilization is roughly twice that of a normal probe capture test. The second special test shows that water spray has little impact on measured "on-filter" probe capture. Visual inspection of the sample revealed a smooth, glassy surface, demonstrating that unevaporated droplets did reach the filter. However, the measured utilization is merely on the high side of the range of normal probe capture results.

5.0 SUMMARY OF FINDINGS

Data collected in this program indicate that lime slurry utilization is most sensitive to the gas-phase SO_2 concentration and to the slurry concentration. The effects of initial sorbent surface area and slurry droplet diameter were unclear. Gas-phase CO_2 had no effect on slurry utilization in these experiments. Slurry utilization was not improved at short times by allowing the droplets to evaporate. Further, overall utilization was best under saturated conditions.

A key parameter found in these tests is the material used to prepare the slurry. Some variation was found between hydrates from different sources, and it was shown that fresh-slaked lime can be more reactive than slurry prepared from hydrate. However, the most significant discovery was the range of utilizations obtained from different bags of material from the same source. At the baseline test condition slurry utilizations for Marblehead AH were found to vary from about 19% to about 65%. The only explanation found to consistently account for this is carbonation of the sorbent, resulting in reduced calcium availability, and a shift from external to internal mass transfer control of the reaction rate.

Baseline SO₂ Capture:

- Normal test. Sample Collection at 17 cm

"Normal" Probe Capture:

- Sample collected in absence of SO₂. Then exposed to SO₂, on filter, for 15 minutes.

In-Probe-Only SO₂ Capture:

- SO₂ is introduced at probe entrance while sample is collected

Probe Capture w/H₂O:

- Same as "Normal" probe capture, but water spray is added to reactor during SO₂ exposure

Figure 18. In-probe SO₂ capture test results compared with baseline.

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