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# Heated Fly Ash/Hydrated Lime Slurries for SO<sub>2</sub> Removal in Spray Dryer Absorbers

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Coal fly ashes have been slurried with quicklime at elevated temperatures to determine their reactivity with  $SO_2$  in a minipilot spray dryer. Bench-scale experimental results indicate that this hydration process greatly increases the total surface area of the solids. Minipilot-scale spray dryer tests reveal that the slurry reaction step can significantly increase calcium utilization and  $SO_2$  removal of these fly ash/quicklime sorbents, depending on the type of fly ash used. One type of fly ash showed considerably better reactivity in the spray dryer tests. This enhancement is considered due to the presence of calcium silica hydrate material formed from the reaction between calcium and the alumina silicate found in the fly ashes and the difference in reactivity due to the type of calcium silica hydrate material formed. The benefit, however, decreases with the calcium feed rate. Pozzolanic strength tests were performed on the fly ashes used, and the measured unconfined compressive strengths followed the reactivity results in the spray dryer; the most reactive fly ash possessed the highest pozzolanic activity.

#### Introduction

Spray dryer flue gas desulfurization with bag filter particulate collection provides a viable alternative to wet limestone scrubbing in boilers burning low-sulfur coals (less than 2% sulfur by weight) and also shows promise in medium- to high-sulfur coal (2-3.2% sulfur) applications. The advantages of spray drying include creation of a dry waste product not requiring sludge handling equipment, smaller space requirements, and the use of mild steel in materials of construction (Keener and Keener, 1986).

As of 1989, 17 full-scale utility spray drying units were in operation in the United States treating over 6000 MW of coal fire derived flue gas. These units burn primarily low-sulfur western subbituminous coals and have demonstrated the ability to remove 90% SO<sub>2</sub> (Keener and Keener, 1986). Pilot tests conducted at the Electric Power Research Institute's High Sulfur Test Center have also shown the ability to achieve 90% or greater removal with a variety of different limes when burning high-sulfur coals (2500 ppm SO<sub>2</sub> inlet) (Blythe et al., 1988).

During the spray drying process the flue gas makes contact with a fine spray of alkaline slurry in a reaction chamber providing a droplet residence time of 10-15 s. The slurry droplets simultaneously evaporate and react with SO<sub>2</sub> in the flue gas. Parameters that are considered important for determining spray dryer efficiency include the approach to saturation temperature, the size and type of hydrated lime, the drop residence time, and the slurry solids concentration. Not all the moisture in the droplets is evaporated in the spray chamber, which allows further reaction of the slurry particles with SO<sub>2</sub> in the following ductwork and particulate control device. Fabric filters are normally favored over electrostatic precipitators (ESPs) for particulate control because they allow better SO<sub>2</sub> removal, 12-16% as opposed to 10-12% for the latter in mediumto high-sulfur applications (Blythe et al., 1988).

Most spray drying systems today recycle a portion of their waste solids back into the feed slurry. Recycling has been shown to increase sorbent utilization by allowing partially reacted sorbent to react further with the flue gas. In addition, recycling of fly ash together with Ca(OH)<sub>2</sub> has been shown to be more beneficial toward SO<sub>2</sub> removal than recycling of Ca(OH)<sub>2</sub> alone (Felsvang et al., 1981). The reason for the above phenomenon was postulated to be the pozzolanic reaction between the recycled fly ash and the calcium hydroxide in the feed slurry to form hydrated calcium silicates and/or calcium aluminates (Jocewicz and Rochelle, 1986).

Although the SO<sub>2</sub> removing potential of fly ash/lime sorbents has been established in bench-scale sandbed reactors (Jocewicz and Rochelle, 1986; Peterson and Rochelle, 1988; Martinez et al., 1991; Ho and Shi, 1992) and in dry sorbent injection (Jozewicz et al., 1988a; Hall et al., 1992), their usefulness in spray drying applications has not been thoroughly studied. Jozewicz et al. (1988a) attempted to spray dry these solids in a pilotscale unit and found significant wet solid deposits on the wall at approaches to saturation lower than 75 °C. Petersen et al. (1988) attempted the same in a benchscale spray dryer and did not experience a wall deposit problem. They did not, however, see any significant improvement in calcium utilization or SO<sub>2</sub> removal over Ca(OH)<sub>2</sub> alone. Nakamura et al. (1991) attempted a bench-scale spray drying study with heated slurries of fly ash, Ca(OH)2, and gypsum and reported removals of up to 30% over Ca(OH)2 alone. This study examined the surface area development and subsequent reactivity of two different types of fly ashes used to produce mixtures of fly ash and hydrated lime and then used as sorbent material in minipilot spray dryer tests. Pozzolanic strength tests were performed on the fly ashes. the unreacted mixtures, and the products produced in the spray dryer after reaction.

# Calcium Silicates and the Pozzolanic Reactions

Several different types of calcium silicates and calcium aluminates have been shown to be, in dry or hydrated form, very reactive toward SO<sub>2</sub> (Yang and Shen, 1979; Martinez et al., 1991; Ho and Shi, 1992). Some, including  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> and CaAl<sub>2</sub>O<sub>4</sub>, are components of cement. Another, CaSiO<sub>3</sub>, is found in a commercial insulation powder (Yang and Shen, 1979).

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One hydrated form, CaSiO<sub>3</sub>·H<sub>2</sub>O, can be formed by hydrating Ca<sub>3</sub>SiO<sub>5</sub>, another component of cement, or by mixing hydrated lime and amorphous silica in a water slurry (Barret et al., 1977). The above reaction between Ca(OH)2 and amorphous SiO2 in a water slurry to form CaSiO<sub>3</sub>·H<sub>2</sub>O is an example of a pozzolanic reaction. A pozzolan is defined as "a siliceous or aluminosiliceous material that in itself possesses little or no cementitious value but that in finely divided form and in the presence of moisture will chemically react with alkali and alkaline earth hydroxides at ordinary temperatures to form or assist in forming compounds possessing cementitious properties" ASTM, 1992). Examples of natural pozzolans include diatomaceous earth and some volcanic ashes. Fly ash, containing on average 28-52% SiO<sub>2</sub> and 15-34% Al<sub>2</sub>O<sub>3</sub>, is an example of a man-made pozzolan (Transportation Research Board, 1976).

The major pozzolanic reactions are (Pollard et al., 1989)

$$\begin{array}{ccc} {\rm Ca(OH)_2 + SiO_2 + H_2O \rightarrow & (CaO)_x(SiO_2)_y(H_2O)_z} \\ & {\rm calcium \ silicate \ hydrates} \end{array}$$

$$\begin{aligned} \text{Ca(OH)}_2 + \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \\ & (\text{CaO)}_x(\text{Al}_2\text{O}_3)_y(\text{H}_2\text{O})_z \\ & \text{calcium aluminate hydrates} \end{aligned}$$

$$\begin{aligned} \text{Ca(OH)}_2 + \text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{H}_2\text{O} \rightarrow \\ & (\text{CaO})_x(\text{Al}_2\text{O}_3)_y(\text{SiO}_2)_z(\text{H}_2\text{O})_w \\ & \text{calcium aluminate silicate hydrates} \end{aligned}$$

$${
m Ca(OH)_2 + Al_2O_3 + SO_3 + H_2O} \rightarrow$$
 ${
m (CaO)_x(Al_2O_3)_y(CaSO_3)_z(H_2O)_w}$ 
calcium aluminate calcium sulfate hydrates

in which the coefficients w, x, y, and z can assume a large number of values. These products in general are poorly crystallized and have very high surface areas which can enhance  $SO_2$  removal capability (Taylor, 1950; Jozewicz and Rochelle, 1986).

The products of pozzolanic reactions are quite similar to those formed in the hardening process of portland cement. In this process, the hydration of tricalcium silicate is the dominant mechanism (Pollard et al., 1989):

$$(CaO)_3SiO_2 + (1.3 + x)H_2O \rightarrow (CaO)_{1.7}(SiO_2)(H_2O)_x + 1.3Ca(OH)_2$$

Thus, hydrated calcium silicates and/or calcium aluminates are mainly responsible for strength development in both cement-hardening reactions and pozzolanic reactions. Some of these silicates and aluminates also have potential as SO<sub>2</sub> sorbents.

# Fly Ash Hydration

The pozzolanic reaction between fly ash and hydrated lime in water slurry at elevated temperatures has been studied extensively. Several researchers have shown in bench-scale sandbed reactors that the dried product of the above reaction is more reactive toward SO<sub>2</sub> than Ca(OH)<sub>2</sub> alone (Jozewicz and Rochelle, 1986; Peterson and Rochelle, 1988; Martinez et al., 1991; Ho and Shi, 1992). Similar results were obtained in a pilot-scale dry duct injection system with these reacted fly ash/lime

Table 1. Mineral Analysis of Ashes on a Percent Ignited Basis $^{\sigma}$ 

fly ash	MF7	MF8	fly ash	MF7	MF8
SiO <sub>2</sub>	49.77	56.51	K <sub>2</sub> O	2.21	2.39
$Al_2O_3$	23.76	28.53	$TiO_2$	1.65	2.08
$Fe_2O_3$	17.86	4.62	CaO	1.59	1.49

<sup>a</sup> From Standard Laboratories, Inc., South Charleston, WV.

solids (Jozewicz et al., 1988a; Hall et al., 1992). The surface area and SO<sub>2</sub> reactivity of fly ash/lime sorbents increased with temperature and time of hydration (Jozewicz and Rochelle, 1986; Ho and Shi, 1992). Hydration at elevated pressures also proved beneficial in producing a reactive sorbent (Jozewicz et al., 1988b). Other factors that increased the reactivity of the sorbent include grinding the fly ash (Petersen et al., 1988), adding NaOH to the slurry (Peterson and Rochelle, 1988), and substituting a more reactive form of silica for the fly ash (Jozewicz et al., 1988a). Two compounds positively identified in reacted fly ash/lime mixtures as being highly reactive to SO<sub>2</sub> were CaO·SiO<sub>2</sub>·H<sub>2</sub>O (calcium silicate monohydrate, C-S-H) and (CaO)4-Al<sub>2</sub>O<sub>3</sub>·13H<sub>2</sub>O (hydrated tetracalcium aluminate) (Martinez et al., 1991; Ho and Shi, 1992). The main objective of this study, however, was not to identify specific pozzolanic products, but to determine whether these products enhance SO2 removal in a minipilot spray dryer. A secondary objective was to determine whether the SO<sub>2</sub> removal enhancement provided by the addition of a certain fly ash could be related to the pozzolanic strength developed by the fly ash in the ASTM C311 test (Pozzolanic Activity Index With Lime) (ASTM, 1992).

#### **Experimental Section**

The fly ashes used were obtained from the No. 7 and No. 8 boilers of the Miami Fort Station of the Cincinnati Gas and Electric Co. The MF7 ash was from a 2.1% sulfur coal, and the MF8 ash was from a 0.7% sulfur coal. An analysis of the ashes can be found in Table 1. The surface areas of the MF7 and MF8 ashes were measured to be 0.5 and 1.2 m²/g, respectively. Reagent grade Ca(OH)<sub>2</sub> from Fisher Scientific with a surface area of 13.9 m²/g was used in forming fly ash/lime sorbents for surface area determination. Commercial grade quicklime from Dravo Lime Co. was used to prepare sorbents that were tested in the spray dryer.

Bench-scale sorbent samples consisted mostly of 4 parts fly ash by weight to 1 part hydrated lime. The water to solids ratio was kept at 15:1. The samples were heated in a Fisher Scientific water bath at 80 or 95 °C for varying periods of time. After heating, the samples were filtered and a portion of the solids vacuum desiccated over night. The solids were then measured for surface area with a Quantachrome Monosorb single-point BET machine.

Scanning electron micrographs (SEMs) of the MF8 ash, Ca(OH)<sub>2</sub>, and reacted mixture product after two different reaction periods are shown in Figures 1-4. Figure 1 shows the typical spherical nature of coalderived fly ash, and the presence of large spheres of alumina silicate glass particles is readily apparent. Figure 2 shows the reagent grade Ca(OH)<sub>2</sub> used in the initial surface area experiments. The crystalline structure of this material is also readily apparent. The product produced from a 4:1 MF8 ash/calcium hydroxide mixture slurried with a water to solids ratio of 15:1 at 95 °C for 3 h is shown in Figure 3. The presence of

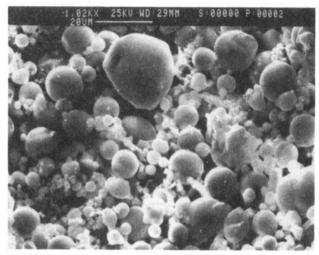


Figure 1. SEM micrograph of the MF8 ash.

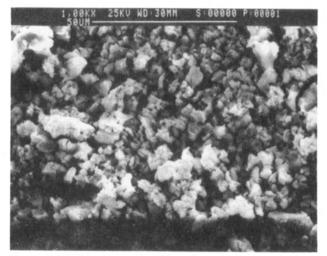


Figure 2. SEM micrograph of the calcium hydroxide.

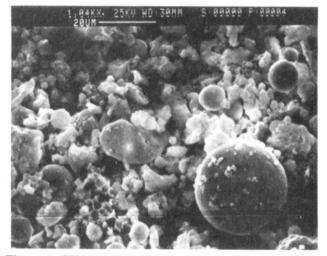


Figure 3. SEM micrograph of the reacted mixture after 3 h.

calcium silicate hydrates (C-S-H) can been seen as a "weblike" material forming in the lower right-hand portion of the micrograph. Also, the overall spherical nature of the predominant fly ash material is no longer apparent. Figure 4 shows the same product mixture after 15 h of reaction. The individual nature of the fly ash particles is now completely lost as the growth of the calcium aluminum silicate material has completely encased the parent solids.

Sorbents to be spray dried were made with varying

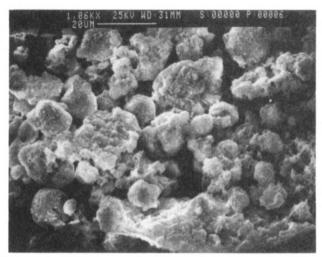


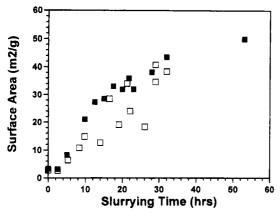
Figure 4. SEM micrograph of the reacted mixture after 15 h.

ratios of fly ash and quicklime, but mostly 4:1 and 1:1 (corresponding to fly ash to calcium hydroxide ratios of 4:1.32 and 1:1.32). The solids loading of the slurries was kept at 10%, which was the maximum that the twofluid atomizer could handle without clogging. In addition, the fly ashes were sieved through a 250  $\mu$ m sieve to prevent large carbon black particles in the fly ashes from plugging the atomizer. Samples were heated in an insulated 150 L stainless steel drum by allowing steam to flow through the outer jacket. A steam solenoid and temperature controller kept the slurry temperature constant at 95 °C.

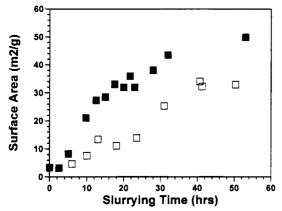
The UC minipilot spray dryer has an air flow capacity of 250 m<sup>3</sup>/h. The residence time of the simulated flue gas is about 11 s. The atomizer is a two-fluid external mixing nozzle. The inlet heater has a 10 kW capacity and heats the flue gas to 150 °C. The bag house is a single-compartment self-cleaning cloth pulse jet dust collector with 42 individual bags and a total surface area of 9.1 m<sup>2</sup>. Inlet and outlet SO<sub>2</sub> concentrations were measured continuously with two infrared analyzers (Horiba Model 2000 NDIR). The simulated flue gas was prepared by doping heated ambient air with SO<sub>2</sub> from compressed cylinders of liquified SO2. The inlet SO2 concentration was maintained at a level between 2200 and 2600 ppm. After each test, the solid product was taken from the fabric filter, dried overnight in a heated vacuum desiccator, and measured for sulfur content in a Leco total sulfur analyzer (Model 571-052). This pilot system has been shown to give results similar to those obtained on a pilot-scale system of industrial size (the Electric Power Research Institute High Sulfur Test Facility), and additional details concerning the spray dryer description and operation may be found elsewhere (Wang and Keener, 1993).

Additional sulfur uptake tests with MF7 and MF8 slurries were performed after the spray dryer tests to help verify the results obtained in bench-scale and minipilot-scale tests. Both ashes were slurried with Ca-(OH)<sub>2</sub> at a 4:1.32 fly ash/Ca(OH)<sub>2</sub> ratio. The solids content of the slurry was 10% in each case. Samples were heated at 100 °C for 2 h, cooled to room temperature and then sparged with 2800 ppm SO<sub>2</sub> for 0, 5, or 30 min. After sparging the samples were filtered, dried overnight in a heated vacuum desiccator, and measured for sulfur content in a Leco sulfur analyzer.

Pozzolanic strength tests were performed on both fly ashes, heated and unheated 1:1.32 MF8/Ca(OH)<sub>2</sub> mixes, and the sulfated 1:1.32 MF8/Ca(OH)2 sorbent obtained



**Figure 5.** Surface area development in MF7 sorbents  $(\Box)$  and MF8 sorbents  $(\blacksquare)$ .



**Figure 6.** Surface area development in MF8 sorbents heated at  $80~(\square)$  and  $95~^{\circ}C~(\blacksquare)$ .

from the baghouse of the spray dryer. Each test followed the format given in ASTM Specification C311 (ASTM, 1992). Each admixture listed above was mixed with a specified amount of hydrated lime, sand, and enough water so that the mixture possessed a flow of 110%. The mixtures were then poured into 2 in.  $\times$  2 in. cube molds, aged for 24 h in a 100% humidity room, sealed, aged at 131 °F for 7 days, and finally tested for unconfined compressive strength on a Tinius and Olsen machine.

# Results and Discussion

Figure 5 displays the surface areas obtained from slurrying the MF7 and MF8 ashes with Ca(OH)<sub>2</sub> at a 4:1.32 ash/Ca(OH)<sub>2</sub> ratio at 95 °C for varying amounts of time. The surface areas of both sorbents increased markedly with time, most likely due to the formation of high surface area hydrated calcium silicates and aluminates. The MF8 ash sorbents, however, developed on average slightly higher surface areas than the MF7 ash sorbents. The reason for this may be because MF8 ash has more total silica and alumina than the MF7 ash. From Table 1, the total percentages of silica and alumina are 85.04 for the MF8 ash and 73.53 for the MF7 ash.

Figure 6 displays the surface area results from heating 4:1 MF8/Ca(OH)<sub>2</sub> sorbents at two different temperatures, 80 and 95 °C. The surface areas developed at 95 °C were significantly greater than those developed at 80 °C. Hence, the rate of the pozzolanic reaction increases with increasing temperature.

The results of the spray dryer tests with the fly ash sorbents are in Figures 7-9. The SO<sub>2</sub> removal was

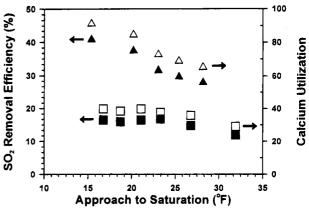


Figure 7.  $SO_2$  removal in spray dryer from MF7 sorbent ( $\blacksquare$ ) and MF8 sorbent ( $\triangle$ ); calcium utilization with MF7 ( $\square$ ) and MF8 sorbent ( $\triangle$ ).

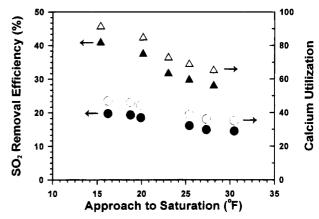


Figure 8.  $SO_2$  removal in spray dryer from heated MF8 sorbent ( $\triangle$ ) and unheated MF8 sorbent ( $\bigcirc$ ); calcium utilization with heated MF8 sorbent ( $\bigcirc$ ) and unheated MF8 sorbent ( $\bigcirc$ ).

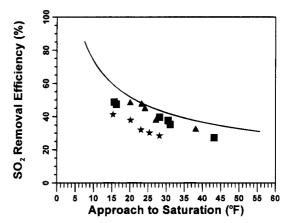


Figure 9. SO<sub>2</sub> removal in spray dryer from baseline CaO slurry (—), 1:4 MF8/CaO sorbent (▲), 1:1 MF8/CaO sorbent (■), and 4:1 MF8/CaO sorbent (★).

measured across the spray dryer alone. Figure 7 compares the spray dryer performance of the MF7 and MF8 ash sorbents, as well as the calcium utilization for these tests. The average inlet  $\mathrm{SO}_2$  concentration was 2500 ppm. Both sorbents consisted of 4 parts ash to 1.32 parts calcium hydroxide and were slurried at 95 °C for 15 h prior to testing. The MF8 sorbent proved to be more effective at removing  $\mathrm{SO}_2$ . We could not analyze the chemical structure of the sorbents with our experimental capabilities. But other researchers (Yang and Shen, 1979; Kenney et al. 1993) have found that  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub> showed higher overall rates and higher capacities for sulfation as compared with calcium oxide on a molar basis while the  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub> and Ca<sub>3</sub>SiO<sub>5</sub>

Table 2. Removal Efficiency and Ca Utilization of Various Heated MF8/Ca(OH)<sub>2</sub> Slurries with Different Fly Ash/Quicklime Mass Ratios at the 11 °C Approach

fly ash/ CaO	removal efficiency (%)	Ca/S ratio	Ca utilization (%)
0:1	52	1.75	30
1:4	49.5	1.65	30
1:1	44	1.0	45
4:1	38	0.4	95

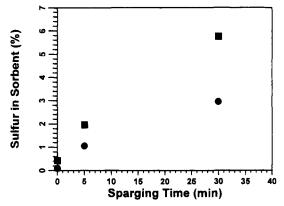


Figure 10. Sulfur capture in solution from heated MF7 sorbent (●) and heated MF8 sorbent (■).

sulfation rates were not higher than that of calcium oxide. It was found that the bound water in the silicates, the morphology, and the crystallinity were important factors which affected the sulfation rates. Because of these results, the MF8 ash was used for additional tests.

Figure 8 displays the effect that heating of a 4:1.32 MF8/Ca(OH)<sub>2</sub> slurry for 15 h at 95 °C has upon SO<sub>2</sub> removal in the spray dryer. The removal increased 20 percentage points at 11 °C (20 °F) approach to saturation, which translates to an increase in calcium utilization from 45% to 95%. As a result of heating the mixtures of quicklime and fly ash, the calcium utilization is increased for this particular ash.

Figure 9 compares the SO<sub>2</sub> removal of a 12.8% Ca-(OH)<sub>2</sub> solution (10% CaO prior to hydration) to three heated slurries, each with a different amount of MF8 ash substituted for CaO. The objective of this set of experiments was to determine whether the increase in calcium utilization noted above would lead to the existence of a fly ash/Ca(OH)2 slurry that removed more SO<sub>2</sub> than the pure Ca(OH)<sub>2</sub> slurry. The fly ash mass fractions in the solid content of the slurries were 20%, 50%, and 80%, the heating time was once again 15 h, and the temperature was 95 °C. None of the slurries removed as much SO2 as the pure CaO slurry, although the 80% and 50% fly ash slurries were within 10 percentage points at the 11 °C (20 °F) approach. Table 2 summarizes the SO<sub>2</sub> removal efficiencies and calcium utilizations of each slurry. The Ca utilization in the 0% and 20% fly ash slurries was only 30%, but rose dramatically as more fly ash was substituted. The 50% fly ash slurry had a Ca utilization of 45%, and the 80% fly ash slurry had a 95% Ca utilization. However, the presence of a large percentage of inert material in the fly ash plus the limit of 10% solids loading in the slurries imposed by the two-fluid atomizer prevented the testing of a 4:1.32 fly ash/Ca(OH)<sub>2</sub> slurry with heavier solids loading.

The results of the bench-scale SO<sub>2</sub> sparging tests are given in Figure 10, where the sulfur content at sparging time zero corresponds to the sulfur content in the fly

Table 3. Unconfined Compressive Strengths of Various Pozzolanic Admixtures Prepared per ASTM Standard

admixture	Ca(OH) <sub>2</sub> (%)	admixture (%)	water (%)	sand (%)	UCS (psi)
MF7 fly ash	7	14	16	63	716
MF8 fly ash	7	13	17	63	879
$mix 1^a$	7	13	20	60	313
$\min 2^b$	6	12	<b>27</b>	55	27
mix 3c	6	12	23	58	92
$\min 4^d$	6	13	25	56	193
sand (control)	7	0	18	75	13

<sup>a</sup> Mix 1, 1:1.32 MF8 ash/hydrated lime mixture. <sup>b</sup> Mix 2, 1:1.32 MF8 ash/hydrated lime mixture slurried for 15 h at 95 °C and 10% solids loading, dewatered, and oven-dried. c Mix 3, Waste product obtained from reacting mix 2 with SO2-laden flue gas in the spray dryer. d Mix 4, Acurex scrubber sludge; consists of a heated 3:1 fly ash/hydrated lime sorbent reacted with SO2 laden flue gas in a pilot wet scrubber.

ashes as received. The MF8 sorbent proved to be more reactive than the MF7 sorbent when reacted with SO<sub>2</sub> in solution for 5 min or 30 min. The unreacted MF8 sorbent contained approximately 0.3% more sulfur than the unreacted MF7 sorbent. However, the amount of additional sulfur picked up by the MF8 sorbent during the reaction was significantly greater. The MF8 sorbent had 0.9% more sulfur than the MF7 sorbent when reacted for 5 min and 2.8% more sulfur when reacted for 30 min. These results verify the greater reactivity of the MF8 sorbent observed in the spray dryer and show that this increase in reactivity is also present when the SO<sub>2</sub> reaction occurs in solution.

Pozzolanic strength tests were performed on a variety of samples. These tests were performed to determine whether pozzolanic activity would correlate with mixture reactivity in the spray dryer and to provide preliminary information concerning the potential of using the solid spray dryer product for uses such as admixtures for roadway construction.

Mixes 1-4 in Table 3 were created in order to determine what effects mixture preparation and sulfation have on the pozzolanic strength of the MF8 fly ash/ quicklime sorbents tested in the spray dryer. The admixture tested in mix 1 was a 1:1.32 mixture of MF8 ash and hydrated lime. The compressive strength of mix 1 was 64% less than that of the MF8 ash. The admixture in mix 2 was a 1:1.32 MF8/hydrated lime mixture slurried for 15 h at 95 °C, dewatered, and ovendried for 24 h. Therefore, mix 2 was equivalent to mix 1, except for the mixture preparation step. The mixture preparation, however, caused the strength to plummet from 313 psi in mix 1 to 27 psi in mix 2. This drop in strength can most likely be attributed to the chemical change in the sorbent. Heating causes the surface area and total pore volume of the mixture to increase significantly (Kenney, et al. 1993). Hence, mix 2 required more water (27% vs 20%) to achieve the correct flow prescribed by the standard. This extra water tends to remain in the pores of the sample and may have a deleterious effect upon compressive strength. Mix 3 was similar to mix 2, but had been reacted with SO2 in the spray dryer. It is of interest to note that the presence of sulfur in the mixture increases the unconfined compressive strength of the sample produced from the fly ash/hydrated lime mixture and subsequently reacted in the spray dryer as compared to that of the mixture alone (i.e., mix 3 compared to mix 2 in Table 3). The presence of sulfur in the form of gypsum is used in the production of portland cement to control flash setting

of the clinker from the tricalcium aluminate (Mindess and Young, 1981). Sulfation affected a small increase in strength compared to mix 2, although much less than the value obtained for mix 1. The admixture in mix 4 was a wet scrubber sludge obtained from Acurex Corp., Research Triangle Park, NC. The sludge contained approximately 6% sulfur and was formulated from a mixture preparation process including 3 parts fly ash to 1 part hydrated lime. The strength of mix 4 was significantly higher than that of mix 3 because mix 4 had a higher ratio of fly ash and, therefore, more available silica. Finally, a control sample was run to see if the sand was contributing to the sample strength. The results (13 psi) showed that not to be the case. These results appear to indicate that pozzolanic strength may be suitable for ranking different fly ashes in terms of their potential reactivity in spray dryers. The results do not indicate, however, that the spray dryer products may be suitable for road use. These results should be confirmed with a greater variety of fly ashes in order to better correlate reactivity with ash physical and chemical properties.

# Conclusions

The pozzolanic reaction between mixtures of certain fly ashes and hydrated lime at elevated temperatures can affect significant increases in calcium utilization over Ca(OH)<sub>2</sub> alone when the mixtures are reacted with SO<sub>2</sub>-laden flue gas in a spray dryer absorber. These results depend, however, on the type of fly ash used. The fly ash that showed greater reactivity in spray dryer tests here also had higher total silica and alumina content, gave slightly higher levels of surface area when reacted with hydrated lime under controlled conditions, had higher pozzolanic activity, and had higher levels of total sulfur uptake in simple sparging experiments. This improvement in utilization may make certain fly ashes an effective sorbent additive in spray dryer flue gas desulfurization. The level of the effectiveness of the fly ash could possibly be evaluated by its pozzolanic strength and through simple sparging experiments of the type performed here, although more tests need to be performed to confirm this.

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