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## MATERIALS AND INTERFACES

# Structural Properties and Reactivities of $\text{Ca}(\text{OH})_2$ /Fly Ash Sorbents for Flue Gas Desulfurization

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$\text{Ca}(\text{OH})_2$ /fly ash sorbents were characterized and tested for reactivity toward  $\text{SO}_2$  at conditions similar to those in the bag filters in the dry and semidry flue gas desulfurization processes. The sorbents were mesoporous, and their specific surface areas linearly correlated with their specific total pore (1.7–300 nm) or mesopore (2–50 nm) volumes. The 1 h utilization of Ca in a sorbent increased, in general, with increasing fly ash content. Sorbents with  $\text{Ca}(\text{OH})_2$  contents larger than 33 wt % had higher weights of  $\text{SO}_2$  captured per unit weight of sorbent than  $\text{Ca}(\text{OH})_2$  had alone, and the sorbent with 70 wt %  $\text{Ca}(\text{OH})_2$  had the maximum capture. The 1 h utilizations of Ca for the sorbents and  $\text{Ca}(\text{OH})_2$  increased almost linearly with increasing specific surface area or pore volumes of the sorbent. The  $\text{SO}_2$  captured per unit surface area or pore volume of the sorbent decreased almost linearly with smaller  $\text{Ca}(\text{OH})_2$  content. The reactivities of the sorbents were enhanced mainly by their large specific surface areas and to a lesser degree by the reactive constituents in fly ash.

### Introduction

The reduction of  $\text{SO}_2$  emission from coal-fired power plants is a major issue for environmental protection. Many flue gas desulfurization (FGD) processes are available for the reduction of  $\text{SO}_2$  emission.<sup>1</sup> The dry and semidry FGD processes have the advantages of lower capital cost and easier waste treatment in comparison with the wet processes commonly adopted in power plants; however, the utilization of the sorbent, which is mostly hydrated lime [ $\text{Ca}(\text{OH})_2$ ], in the operation of these processes is not high. Through an increase of the sorbent reactivity and utilization, economics of the dry or semidry processes can be improved significantly.

Recently, many researchers have shown that sorbents prepared from fly ash and hydrated lime have higher  $\text{SO}_2$  capture and degree of Ca utilization than hydrated lime has.<sup>2–17</sup> Fly ash is the solid waste produced by coal-fired power plants. Its use to activate hydrated lime not only improves the economics of FGD but also has the merit of waste recycling. Fly ash contains plenty of amorphous silica and alumina, which would react with hydrated lime to form calcium silicate hydrates ( $x\text{CaO}\cdot\text{SiO}_2\cdot y\text{H}_2\text{O}$ ) and other products in the presence of water.<sup>18</sup> The reaction between hydrated lime and fly ash taking place in the slurry has been considered to be the reason leading to sorbents having higher reactivities toward  $\text{SO}_2$ .<sup>2,5,8–10,13</sup>

Because of the formation of products,  $\text{Ca}(\text{OH})_2$ /fly ash sorbents have different structural properties from those of the starting  $\text{Ca}(\text{OH})_2$  and fly ash. The structural properties, such as specific surface area and pore-

volume distribution, are determined by the sorbent preparation conditions, such as the type of fly ash,  $\text{Ca}(\text{OH})_2$ /fly ash ratio, water/solid ratio, type of additive, hydration temperature, and hydration time. The influences of the structural properties on the  $\text{SO}_2$  captures by the sorbents have been widely reported in the literature; however, the conclusions are not in agreement.<sup>3,4,6,7,13–15,19–21</sup> Jozewicz et al.<sup>4</sup> found a good correlation between  $\text{SO}_2$  capture and the logarithm of the specific surface area. Martinez et al.<sup>6</sup> reported that  $\text{SO}_2$  removal correlated well with the relative surface area increment for their sorbents. Diffenbach et al.<sup>7</sup> observed a linear correlation between the specific surface area and  $\text{SO}_2$  uptake per unit weight of sorbent. Garea et al.<sup>19</sup> and Fernández et al.<sup>20</sup> prepared sorbents of different specific surface areas by varying the slurring time, and they found that a constant maximum desulfurization yield was obtained for the sorbents despite their different surface areas. Tsuchiai et al.<sup>14</sup> found that the sorbent showed the maximum desulfurization activity when the mean pore diameter reached the maximum, but the specific surface area did not reach the maximum at that time. Most recently, Renedo et al.<sup>21</sup> prepared sorbents at a 5/3 fly ash/hydrated lime ratio and 90 °C with slurring times from 3 to 30 h and performed sulfation experiments on their sorbents at 57 °C for 1 h. They found that there was an optimal slurring time (15 h) for the sorbents to obtain the maximum conversion of  $\text{Ca}(\text{OH})_2$  in the sorbents. They pointed out that the pore-size distribution and small-macro- and mesopore volumes were the main structural variables related to the maximum utilization of the  $\text{Ca}(\text{OH})_2$ /fly ash sorbent and that the specific surface area seemed to be related to the desulfurization rate, but the micropore showed no influence on the utilization of the sorbent. They also noted that there was a near-to-constant value

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of the SO<sub>2</sub> capture per unit volume of mesopore and that value depended only on the relative humidity of the gas mixture for their sorbents with various mesopore volumes.

Because the SO<sub>2</sub> capture capacity of a Ca(OH)<sub>2</sub>/fly ash sorbent is affected by its composition and structural properties, a better understanding of these effects will help the preparation of sorbents with higher reactivity. Accordingly, the present work aims to elucidate the influences of the structural properties and composition of a Ca(OH)<sub>2</sub>/fly ash sorbent on its reactivity toward SO<sub>2</sub>. The Ca(OH)<sub>2</sub>/fly ash sorbents were prepared by varying the Ca(OH)<sub>2</sub>/fly ash weight ratio and slurring time. They were characterized and subjected to sulfation tests. The relations between the structural properties, composition, and sorbent reactivity were analyzed.

## Experimental Section

**Preparation of Sorbents.** The hydrated lime used was reagent grade Ca(OH)<sub>2</sub> (purity >95%; Hayashi Pure Chemical Industries, Ltd.). Fly ash was from boiler 3 of the Shin-Da pulverized-coal power plant of Taiwan Power Co. The chemical composition of the fly ash was 59.0% SiO<sub>2</sub>, 26.7% Al<sub>2</sub>O<sub>3</sub>, 5.5% Fe<sub>2</sub>O<sub>3</sub>, 2.5% K<sub>2</sub>O, 1.6% CaO, 1.3% TiO<sub>2</sub>, 1.2% Na<sub>2</sub>O, 0.9% MgO, 0.47% SO<sub>3</sub>, 0.05% V<sub>2</sub>O<sub>5</sub>, and 2.7% ignition loss.<sup>8</sup> The fly ash was ground for 16 h using a ball mill.

Ca(OH)<sub>2</sub>, fly ash, and 80 g of deionized water were placed into a 250 mL polypropylene flask at a water/solid weight ratio (L/S) of 10. The Ca(OH)<sub>2</sub>/fly ash weight ratios tested were 0/100, 10/90, 30/70, 50/50, 70/30, 90/10, and 100/0. The flask was then sealed with a rubber stopper at the mouth and inserted into a water bath at 65 °C. The slurry was stirred with a magnetic stirrer. The samples with a ratio of 70/30 were prepared using different stirring times ranging from 25 min to 16 h; the samples with other ratios were stirred for 16 h. After slurring, the slurry was placed into a vacuum oven to evaporate the water; the solid phase left was further vacuum-dried at 110 °C. The dried cake obtained was crushed into powder and sealed in a bottle before subjecting it to characterization and sulfation tests.

**Sulfation Test.** Experiments for the reaction of the Ca(OH)<sub>2</sub>/fly ash sorbents with SO<sub>2</sub> were carried out under the conditions of 60 °C, 70% RH, and 1000 ppm SO<sub>2</sub>, which are the typical bag filter conditions in the dry and semidry FGD processes, for 1 h using a differential fixed-bed reactor. The bulk of the test gas was N<sub>2</sub>. CO<sub>2</sub> and O<sub>2</sub> were not added to make the synthetic flue gas because they had not been found to have a significant effect on the SO<sub>2</sub> uptake of the sorbent.<sup>16</sup> The total gas flow rate was 4 L/min(STP). About 30 mg of sample was used for each run. The experimental setup and procedure were described in detail in refs 8 and 23. At least two replicate measurements were made for each kind of sorbent.

The reactivity of a sorbent toward SO<sub>2</sub> was expressed as the utilization of Ca and the SO<sub>2</sub> capture. The utilization of Ca or the conversion of Ca(OH)<sub>2</sub> for a reacted sample was determined by its SO<sub>3</sub><sup>2-</sup>/Ca<sup>2+</sup> molar ratio. The SO<sub>3</sub><sup>2-</sup> content in a sample was determined by iodometric titration and the Ca<sup>2+</sup> content by EDTA titration. The SO<sub>2</sub> capture (SC) for a sample was defined as the ratio of the weight of the SO<sub>2</sub> captured to the initial weight of the sample. SC is related with the utilization of Ca by

$$SC = M_{\text{SO}_2} M^{-1} \quad (\text{utilization of Ca}) \quad (1)$$

where  $M_{\text{SO}_2}$  is the molecular weight of SO<sub>2</sub> and  $M$  is the initial sorbent weight per mole of Ca.  $M$  was determined from the EDTA titration of Ca<sup>2+</sup> for the unreacted sample or calculated from its Ca(OH)<sub>2</sub>/fly ash weight ratio; the relative difference between these two  $M$  values was less than 9%.

**Chemical and Physical Analyses.** The sorbent particle-size distribution was measured by laser diffraction using a Coulter LS-230 analyzer. The specific surface area of a sorbent was determined by nitrogen adsorption using the BET method and the pore-size distribution was determined from the nitrogen desorption data using the BJH method (cylindrical pore model) on a Micromeritics ASAP 2010 analyzer. The sorbents were subjected to X-ray diffraction (XRD) analysis using a Mac Science M03XHF X-ray diffractometer. A scanning electron microscope (SEM), Hitachi S-2400, was used to observe the sorbent morphology. The further experimental details of the sorbent characterization were described elsewhere.<sup>22</sup>

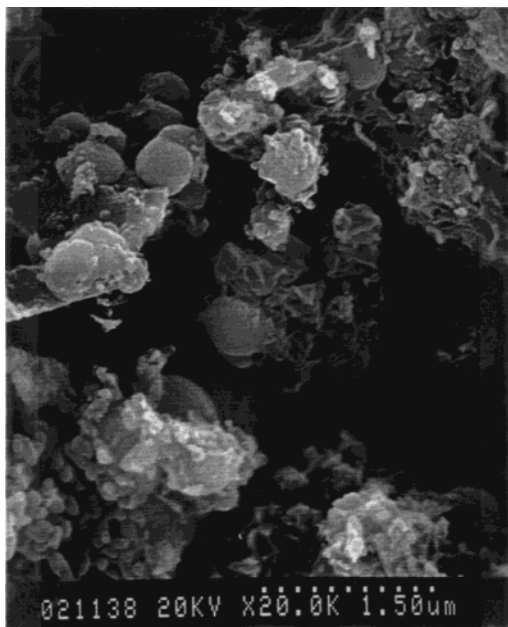
## Results and Discussion

**Characterization of Sorbents.** XRD patterns of the Ca(OH)<sub>2</sub>/fly ash sorbents showed the products of hydration to be mainly C-S-H(I), which is one kind of calcium silicate hydrate (CSH).<sup>8,18</sup> More CSHs were formed in the sorbents with ratios of 70/30, 50/50, and 30/70 than in those with ratios of 90/10 and 10/90. Besides, the amounts of fly ash and Ca(OH)<sub>2</sub> left in the latter two sorbents, respectively, were very small. CSH contents in the Ca(OH)<sub>2</sub>/fly ash (weight ratio 70/30) sorbents prepared with 1–16 h slurring times were about the same and were more than that in the sorbent with 25 min slurring time. The shutoff of the reaction to form CSHs within 1 h may be due to the high K and Na contents in the fly ash. Kind et al.<sup>10</sup> found that the accumulation of K<sup>+</sup> and Na<sup>+</sup> in the slurry would lower the concentration of dissolved Ca and shut off silicate formation.

XRD analyses of the sulfated samples showed the product to be CaSO<sub>3</sub>·1/2H<sub>2</sub>O.

According to SEM observations, CSHs were mainly foil-like, but some were platelike and spherelike, and they tended to cause particles to cohere to form a porous structure. Figure 1 is a typical SEM micrograph of the sorbent with a 70/30 ratio. The highly porous particles compose of foils of CSHs. The large spheres are fly ash particles, and the small ones may be particles of spherelike CSHs. On the bottom-left side of the graph, one can observe the fine Ca(OH)<sub>2</sub> particles which were formed by recrystallization. The sorbents with ratios of 50/50 and 30/70 showed particle morphology similar to that in Figure 1. The sorbent with a ratio of 90/10 appeared like the slurried Ca(OH)<sub>2</sub>. The sorbent with a ratio of 10/90 contained mainly fly ash particles covered with the precipitates of CSHs. The sulfated sorbent appeared to be almost the same as the unreacted one, but the foil-like substances seemed to be thicker.<sup>25</sup>

Table 1 summarizes the mean-volume particle diameters and specific surface areas of sorbents. The mean particle diameters of the Ca(OH)<sub>2</sub>/fly ash sorbents, except the one with a ratio of 90/10, were larger than that of Ca(OH)<sub>2</sub> or fly ash alone because of the coherence of particles caused by the formation of CSHs in the

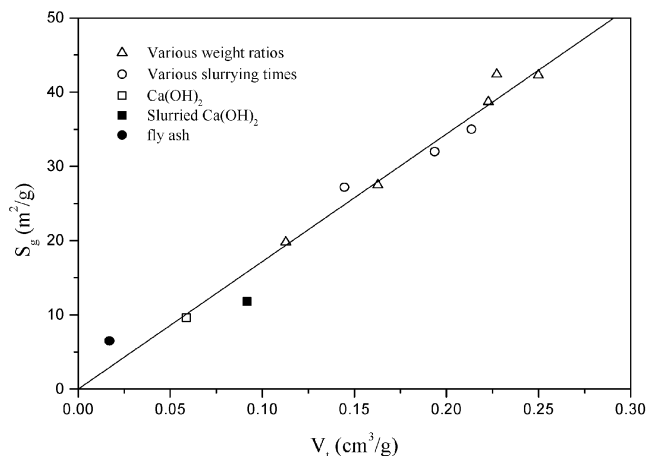


**Figure 1.** SEM micrograph of a Ca(OH)<sub>2</sub>/fly ash (weight ratio 70/30) sorbent. Slurrying conditions: 65 °C, L/S = 10/1, and 16 h.

sorbents. All of the Ca(OH)<sub>2</sub>/fly ash sorbents had much larger surface areas than the starting Ca(OH)<sub>2</sub> (9.6 m<sup>2</sup>/g) and fly ash (6.5 m<sup>2</sup>/g) had because of the formation of CSHs with large surface area. There were two local maxima in the sorbent specific surface areas, 42.4 and 42.3 m<sup>2</sup>/g, at ratios of 70/30 and 10/90, respectively. In addition, the specific surface area increased with longer slurrying time; the increase rate was rapid during the first 1 h and became slower and nearly constant thereafter.

The nitrogen adsorption and desorption isotherms for the Ca(OH)<sub>2</sub>/fly ash sorbents, and the starting Ca(OH)<sub>2</sub> and fly ash indicated that they were materials with porosity in the mesopore range and had slit-shaped pores or space between platelike particles, according to the classification of IUPAC.<sup>24</sup>

The volumes of the micropore (pore diameter < 2 nm), mesopore (2 nm ≤ pore diameter ≤ 50 nm), and total pores smaller than 300 nm for sorbents are listed in Table 1. The Ca(OH)<sub>2</sub>/fly ash sorbents had much larger total pore and mesopore volumes than Ca(OH)<sub>2</sub> or fly ash alone had, indicating that the CSHs formed had created a more porous sorbent structure. The mesopores occupied a large portion of the total pore volume, and



**Figure 2.** Relationship between specific surface area and specific total pore volume for Ca(OH)<sub>2</sub>/fly ash sorbents and Ca(OH)<sub>2</sub>. Slurrying conditions: 65 °C and L/S = 10/1.

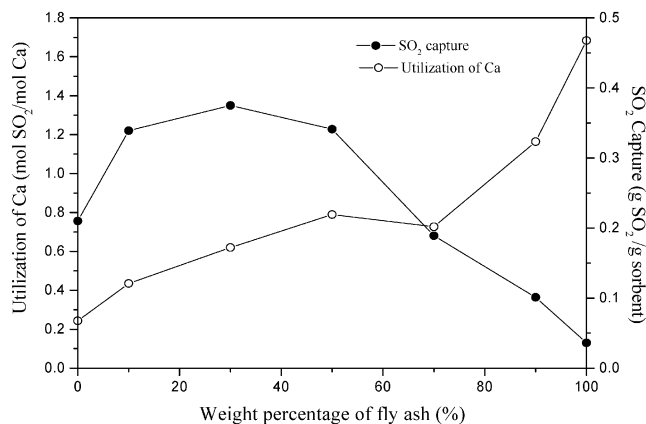
the micropore volume was very small. The three pore volumes varied with the weight ratio in a similar manner as the specific surface area did; there were two local maxima at 70/30 and 10/90 ratios for each pore-size range. However, on the whole, the sorbent with a ratio of 10/90 had the largest total pore volume, and that with a ratio of 70/30 had the largest meso- and micropore volumes. Furthermore, as indicated by the sorbents with a 70/30 ratio, the pore volumes increased with increasing slurrying time. The XRD results, however, showed little difference in the content of CSHs in the sorbents prepared using 1–16 h slurrying times. Thus, the increase in the specific surface area and pore volumes with increasing slurrying time may indicate that the structure of the already formed CSHs continued to change into a more porous form as the slurrying time increased.

It is interesting to note that there was a linear correlation between the specific surface areas ( $S_g$ ) of the sorbents and Ca(OH)<sub>2</sub> and their specific total pore volumes ( $V_t$ ) or mesopore volumes ( $V_m$ ). As shown in Figure 2 for the case of the total pore volume, the linear least-squares-fitting line has a slope of  $171.9 \pm 2.1$  m<sup>2</sup>/cm<sup>3</sup> with a correlation coefficient of 0.986. For the case of mesopore volume, the correlation coefficient was 0.955. Figure 2 indicates that these sorbents and Ca(OH)<sub>2</sub> had about the same mean pore diameter, the value of which was calculated to be 23.3 nm, assuming

**Table 1. Structural Properties and Sulfation Results for Ca(OH)<sub>2</sub>/Fly Ash Sorbents (Slurrying Conditions: 65 °C and L/S = 10/1. Sulfation Conditions: 60 °C, 70% RH, 1000 ppm SO<sub>2</sub>, and 1 h)**

Ca(OH) <sub>2</sub> /fly ash weight ratio	slurrying time (h)	mean diameter (μm)	surface area (m <sup>2</sup> /g)	pore volume (cm <sup>3</sup> /g)			utilization of Ca (mol of SO <sub>2</sub> /mol of Ca)	SO <sub>2</sub> capture (g of SO <sub>2</sub> /g of sorbent)
				micropore (< 2 nm)	mesopore (2–50 nm)	total pore (1.7–300 nm)		
100/0	0	7.4	9.6	0.0005	0.0439	0.0587	0.197	0.170
100/0	16	4.9	11.8	0.0000	0.0578	0.0917	0.243	0.210
0/100	0	3.6	6.5	0.0006	0.0101	0.0170	1.684	0.036
0/100	16	3.9					1.511	0.033
70/30	0.42	10.3	27.2	0.0018	0.1219	0.1446	0.479	0.289
70/30	1	15.2	29.8				0.518	0.314
70/30	4	15.1	32.0	0.0022	0.1582	0.1936	0.575	0.348
70/30	8	13.5	35.0	0.0024	0.1708	0.2136	0.592	0.359
70/30	16	9.1	42.4	0.0037	0.1801	0.2273	0.620	0.375
90/10	16	4.4	19.8	0.0002	0.0786	0.1127	0.435	0.339
50/50	16	23.6	38.7	0.0015	0.1490	0.2227	0.789	0.341
30/70	16	35.1	27.5	0.0012	0.1020	0.1627	0.727	0.189
10/90	16	13.2	42.3	0.0016	0.1591	0.2499	1.164	0.101





**Figure 3.** Effect of the weight percentage of fly ash on the utilization of Ca and the SO<sub>2</sub> capture for Ca(OH)<sub>2</sub>/fly ash sorbents. Slurring conditions: 65 °C, 16 h, and L/S = 10/1; fly ash was as received. Sulfation conditions: 60 °C, 70% RH, 1000 ppm SO<sub>2</sub>, and 1 h.

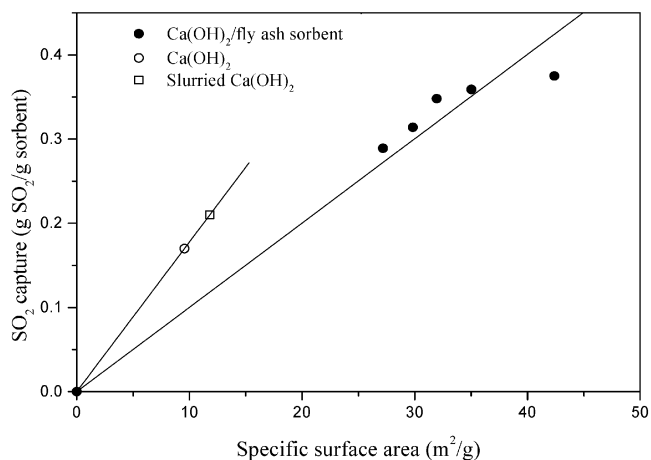
cylindrical pores. This result shows that these solids were mesoporous materials.

**Reactivities of Sorbents.** Like that reported by Liu et al.<sup>25</sup> on the sulfation of sorbents with a ratio of 70/30, the reaction of each sorbent was fast before 10 min and the utilization of Ca for a sorbent at a 20 min reaction time had already been equal to or very close to its maximum value. Results of the 1 h sulfation tests are summarized in Table 1.

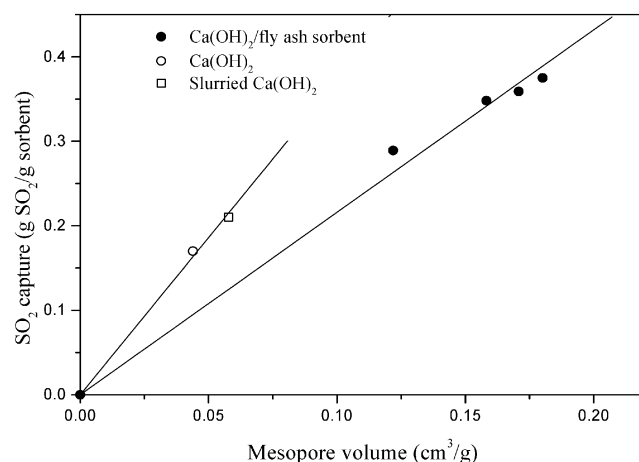
Figure 3 presents both the utilization of Ca and the SO<sub>2</sub> capture for sorbents prepared with a 16 h slurring time as functions of the fly ash content in the starting solid mixture. The utilizations of Ca for all of the sorbents were higher than that for hydrated lime alone. The utilization of Ca first increased with increasing fly ash content until 50 wt % fly ash; it then dropped slightly at 70 wt % fly ash and increased markedly thereafter. The utilizations of Ca for the sorbent with a ratio of 10/90 and the fly ash as received were higher than 1.0 because of the presence of compounds of Na, K, and Mg, which are also reactive toward SO<sub>2</sub>, in fly ash particles. In terms of the SO<sub>2</sub> capture of sorbent, the SO<sub>2</sub> capture increased as the fly ash content increased, reaching a maximum (0.375 g of SO<sub>2</sub>/g of sorbent) when the content was 30 wt %; a further increase in the content resulted in a gradual decrease in the SO<sub>2</sub> capture. In addition, as estimated from Figure 3, a sorbent prepared with a Ca(OH)<sub>2</sub> content of less than 100 wt % and larger than 33 wt % would have a SO<sub>2</sub> capture higher than that of Ca(OH)<sub>2</sub> alone. The difference in the trends of the utilization of Ca and the SO<sub>2</sub> capture can be explained by referring to eq 1.  $M^{-1}$  in the equation is the moles of Ca per unit weight of sorbent, the value of which decreases as the content of fly ash increases.

For the sorbents prepared with a ratio of 70/30 and different slurring times, the utilization of Ca and the SO<sub>2</sub> capture increased with increasing slurring time. In this case, because  $M^{-1}$  in eq 1 is constant, the SO<sub>2</sub> capture varies only with the utilization of Ca.

**Correlations between Reactivities and Structural Properties.** For the sorbents prepared using different slurring times, the SO<sub>2</sub> capture of sorbent was found to increase linearly with the specific surface area of sorbent, as shown in Figure 4. Also, the SO<sub>2</sub> capture was found to be linearly correlated with the specific total pore volume or mesopore volume of the sorbent, as can



**Figure 4.** Effect of specific surface area on the SO<sub>2</sub> capture for Ca(OH)<sub>2</sub>/fly ash (weight ratio 70/30) sorbents and Ca(OH)<sub>2</sub>. Slurring conditions: 65 °C, L/S = 10/1, and 0.42–16 h. Sulfation conditions: 60 °C, 70% RH, 1000 ppm SO<sub>2</sub>, and 1 h.

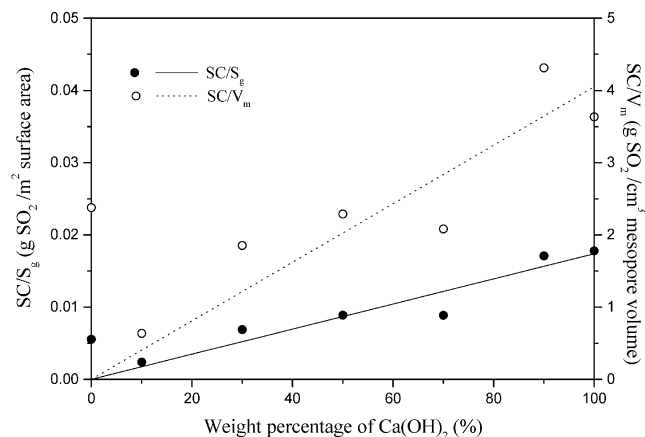


**Figure 5.** Effect of specific mesopore volume on the SO<sub>2</sub> capture for Ca(OH)<sub>2</sub>/fly ash (weight ratio 70/30) sorbents and Ca(OH)<sub>2</sub>. Slurring conditions: 65 °C, L/S = 10/1, and 0.42–16 h. Sulfation conditions: 60 °C, 70% RH, 1000 ppm SO<sub>2</sub>, and 1 h.

be seen from Figure 5 for the case of mesopore volume. This finding is not unexpected in view of the linear relationship between the specific surface area and the specific total pore or mesopore volume as discussed previously. A linear relationship between the SO<sub>2</sub> capture and the specific mesopore volume was also reported by Renedo et al.<sup>21</sup> for their sorbents with a ratio of 3/5, but they did not find a good correlation between the SO<sub>2</sub> capture and the specific surface area or total pore volume.

A linear regression of the data in Figure 4 gave the slope of the straight line as  $0.0100 \pm 0.0004$  g of SO<sub>2</sub>/m<sup>2</sup> with a correlation coefficient of 0.982. This slope is the average value of the ratio  $SC/S_g$ , which is the weight of SO<sub>2</sub> captured per unit initial surface area of the sorbent, for the sorbents with a ratio of 70/30. The SO<sub>2</sub> captures of the slurried and raw Ca(OH)<sub>2</sub> samples are also shown in Figure 4. It is evident that the SC and  $S_g$  of Ca(OH)<sub>2</sub> also followed a linear relationship, but with a larger slope, 0.0178 g of SO<sub>2</sub>/m<sup>2</sup>.

The slope of the straight line in Figure 5 was determined to be  $2.16 \pm 0.06$  g of SO<sub>2</sub>/cm<sup>3</sup> with a correlation coefficient of 0.995. This slope represents the average value of the ratio  $SC/V_m$ , which is the weight of SO<sub>2</sub> captured per unit initial mesopore volume of the sorbent, for the sorbents with a ratio of 70/30. The

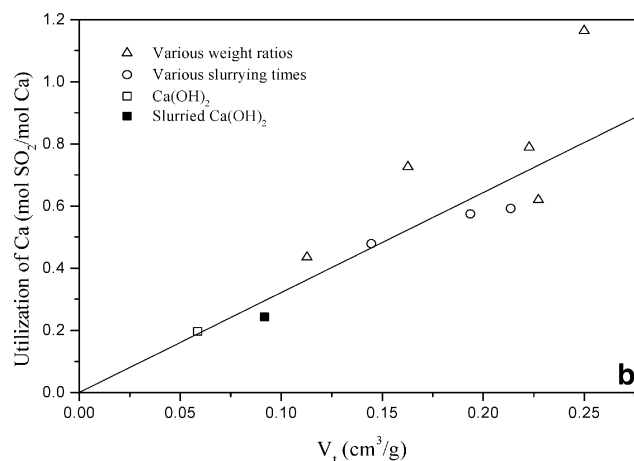
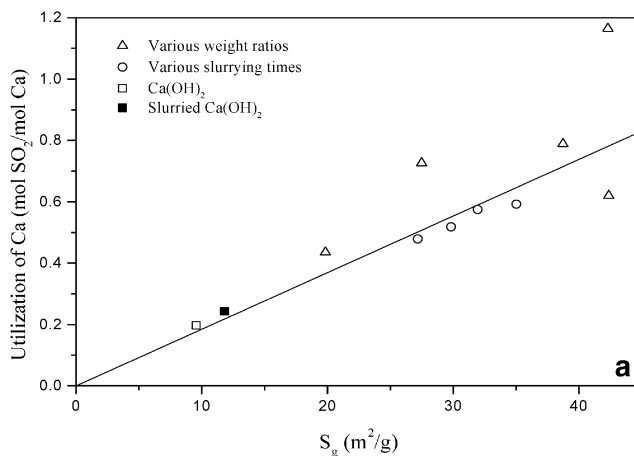


**Figure 6.** Effect of the weight percentage of  $\text{Ca(OH)}_2$  on the weight of  $\text{SO}_2$  captured per unit surface area and per unit mesopore volume for  $\text{Ca(OH)}_2$ /fly ash sorbents. Slurring conditions:  $65^\circ\text{C}$ , 16 h, and  $L/S = 10/1$ ; fly ash was as received. Sulfation conditions:  $60^\circ\text{C}$ , 70% RH, 1000 ppm  $\text{SO}_2$ , and 1 h.

correlation between  $SC$  and  $V_t$ , not shown here, had a slightly smaller correlation coefficient, 0.990. As seen in Figure 5, a linear relationship between the  $\text{SO}_2$  capture and the mesopore volume is also valid for  $\text{Ca(OH)}_2$ , and the slope of the fitting line,  $3.72 \text{ g of SO}_2/\text{cm}^3$ , is larger.

For the sorbents discussed above, the utilization of  $\text{Ca}$ , like the  $\text{SO}_2$  capture, was linearly correlated with the specific surface area or total pore volume or mesopore volume, according to eq 1. The linear relationship between the utilization of  $\text{Ca}$  and the specific surface area had been reported before for some of the sorbents. For the sulfation of the sorbents with a 70/30 ratio, Liu et al.<sup>25</sup> found that both the initial rate and the maximum utilization of  $\text{Ca}$  increased linearly with increasing specific surface area. The same finding was reported by Ho and Shih<sup>26</sup> for the sulfation of  $\text{Ca(OH)}_2$  and by Shih et al.<sup>27</sup> for the carbonation of  $\text{Ca(OH)}_2$ .

The effect of the weight percentage of  $\text{Ca(OH)}_2$  used to prepare a sorbent on  $SC/S_g$  and  $SC/V_m$  is represented in Figure 6. The  $SC/S_g$  values ranged from 0.0024 to  $0.0178 \text{ g of SO}_2/\text{m}^2$  and the  $SC/V_m$  values from 0.64 to  $4.31 \text{ g of SO}_2/\text{cm}^3$ . Renedo et al.<sup>21</sup> reported the values of  $SC/V_m$  to be 0.0353 and  $0.0514 \text{ mol}/\text{cm}^3$  (their original values should be corrected by dividing 100) at 50% RH and 80% RH, respectively, for their sorbents with a  $\text{Ca(OH)}_2$ /fly ash ratio of 3/5. Our value (70% RH) at the same  $\text{Ca(OH)}_2$ /fly ash ratio estimated from Figure 6 was about the same as their value at 50% RH. The data shown in Figure 6 are somewhat scattering; however, the general trend indicates that  $SC/S_g$  or  $SC/V_m$  decreased linearly with smaller weight percentage of  $\text{Ca(OH)}_2$ . The correlation coefficients of the straight lines for  $SC/S_g$  and  $SC/V_m$  were 0.951 and 0.914, respectively. The correlation of  $SC/V_t$  with  $\text{Ca(OH)}_2$  weight percentage (correlation coefficient = 0.921), not shown here, was slightly better than that of  $SC/V_m$ . Fly ash itself did not follow this pattern because of the presence of reactive constituents other than  $\text{Ca(OH)}_2$  and CSHs. These results indicate that the  $\text{SO}_2$  capture capacities of the surfaces or pores of the  $\text{Ca(OH)}_2$ /fly ash sorbents were lower than that of  $\text{Ca(OH)}_2$  and decreased almost linearly with decreasing  $\text{Ca(OH)}_2$  content. In reference to eq 1, because  $M^{-1}$  in the equation is proportional to the  $\text{Ca(OH)}_2$  weight percentage, the above results thus imply that the utilizations of  $\text{Ca}$  per



**Figure 7.** (a) Effect of specific surface area and (b) effect of specific total pore volume on the utilization of  $\text{Ca}$  for  $\text{Ca(OH)}_2$ /fly ash sorbents and  $\text{Ca(OH)}_2$ . Slurring conditions:  $65^\circ\text{C}$ ,  $L/S = 10/1$ , and 0.42–16 h. Sulfation conditions:  $60^\circ\text{C}$ , 70% RH, 1000 ppm  $\text{SO}_2$ , and 1 h.

unit surface area or per unit pore volume for the sorbents and  $\text{Ca(OH)}_2$  were about the same. This inference can be confirmed by parts a and b of Figure 7, which show that the utilizations of  $\text{Ca}$  of  $\text{Ca(OH)}_2$  and the sorbents increased almost linearly with increasing  $S_g$  or  $V_t$  in the same manner. The data of the sorbent with a ratio of 10/90 is higher than the general trend because of the excess of fly ash content. Linear regression of the other data gave the slope of the regression line as  $0.0185 \pm 0.0012 \text{ g}/\text{m}^2$  with a correlation coefficient of 0.871 for Figure 7a and  $3.22 \pm 0.20 \text{ g}/\text{cm}^3$  with a correlation coefficient of 0.877 for Figure 7b. The correlation of the utilization of  $\text{Ca}$  with  $V_m$  (correlation coefficient = 0.756) was not as good as that with  $V_t$ .

The linear correlation between the 1 h utilization of  $\text{Ca}$  and  $S_g$  has the physical meaning that the reaction of  $\text{SO}_2$  with a sorbent took place on the surface of the sorbent and about the same weight per unit surface area was reacted for each sorbent. The correlation between the utilization of  $\text{Ca}$  and  $V_t$  or  $V_m$  may just result from the linear relationship between  $S_g$  and  $V_t$  or  $V_m$  as discussed previously. Liu et al.<sup>25</sup> and Ho et al.<sup>28</sup> pointed out that the reaction of a sorbent with  $\text{SO}_2$  stopped and the sorbent reached the maximum utilization of  $\text{Ca}$  when the reactive surface was completely covered by the product; the pore volume of sorbent was reduced because of reaction, but it did not vanish at the maximum utilization of  $\text{Ca}$ .

From the above analyses, we may conclude that the reactivities of the Ca(OH)<sub>2</sub>/fly ash sorbents were enhanced mainly by their large specific surface areas and to a lesser degree by the reactive constituents in fly ash.

**Optimum Sorbent Formulation.** Figure 3 shows that the utilization of Ca for a Ca(OH)<sub>2</sub>/fly ash sorbent increases, in general, as the Ca(OH)<sub>2</sub> content of the sorbent decreases and that the SO<sub>2</sub> captured per unit weight of sorbent first increases with decreasing Ca(OH)<sub>2</sub> content until about 70 wt % Ca(OH)<sub>2</sub> and then decreases thereafter, being equal to that of Ca(OH)<sub>2</sub> alone at about 33 wt % Ca(OH)<sub>2</sub>.

The results of Figure 3 indicate that, for a given requirement of SO<sub>2</sub> removal, the amount of Ca(OH)<sub>2</sub> required to prepare the sorbent decreases, in general, when the Ca(OH)<sub>2</sub> content of sorbent decreases and, in the meantime, the total amount of sorbent required also decreases if the Ca(OH)<sub>2</sub> content of sorbent is larger than 33 wt %. The results of Figure 3 also indicate that, for the same feed rate of sorbent, the use of the Ca(OH)<sub>2</sub>/fly ash sorbent to replace Ca(OH)<sub>2</sub> can reduce the amount of Ca(OH)<sub>2</sub> required and increase the utilization of Ca as well as the SO<sub>2</sub> removal efficiency if the sorbent is prepared with a Ca(OH)<sub>2</sub> content larger than 33 wt %.

The sorbent can be prepared by using an aqueous slurry of CaO (thereby slaking the lime) to react with the fly ash instead of starting out with dry Ca(OH)<sub>2</sub>. Because the fly ash required is available on the site of a coal-fired power plant without extra cost, the use of the Ca(OH)<sub>2</sub>/fly ash sorbent in the dry or semidry FGD process will substantially reduce the capital and operation costs of the FGD facility.

The optimum sorbent formulation depends on factors such as the costs of the CaO reagent, sorbent preparation and transport, and waste disposal. These costs relate to the amounts of CaO and sorbent required and may vary from one site to another. Thus, a detailed site-specific analysis of costs is required to determine the optimum sorbent formulation.

## Conclusions

The influences of the compositions and structural properties of the Ca(OH)<sub>2</sub>/fly ash sorbents on their reactivities toward SO<sub>2</sub> have been investigated.

The specific surface areas and pore volumes of the Ca(OH)<sub>2</sub>/fly ash sorbents were larger than those of the starting Ca(OH)<sub>2</sub> and fly ash because of the formation of calcium silicate hydrates. The sorbents, Ca(OH)<sub>2</sub>, and fly ash were mesoporous materials, and their specific surface areas linearly correlated with their specific total pore or mesopore volumes. The 1 h utilization of Ca for a sorbent to react with SO<sub>2</sub> increased, in general, when the fly ash content increased, and the increment was more pronounced when the fly ash content was greater than 70 wt %; however, the SO<sub>2</sub> capture of sorbent reached a maximum (0.375 g of SO<sub>2</sub>/g of sorbent) at 30 wt % and then decreased. Sorbents with a Ca(OH)<sub>2</sub> content of less than 100 wt % and larger than 33 wt % would have a SO<sub>2</sub> capture higher than that of Ca(OH)<sub>2</sub> alone. The SO<sub>2</sub> captured per unit surface area or pore volume of sorbent decreased almost linearly with decreasing Ca(OH)<sub>2</sub> content. The utilizations of Ca for the sorbents and Ca(OH)<sub>2</sub> were roughly proportional to their specific surface areas or total pore or mesopore volumes. The reactivities of the sorbents were enhanced mainly

by their large specific surface areas and to a lesser degree by the reactive constituents in fly ash.

The results of this study are useful to the preparation of Ca(OH)<sub>2</sub>/fly ash sorbents with high reactivity for use in the dry and semidry processes to remove SO<sub>2</sub> from the flue gas.

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## Nomenclature

- BET = Brunauer–Emmett–Teller method  
 BJH = Barrett–Johner–Halenda method  
 CSHs = calcium silicate hydrates  
 EDTA = ethylenediamine tetraacetate  
 FGD = flue gas desulfurization  
 IUPAC = International Union of Pure and Applied Chemistry  
 L/S = water/solid weight ratio  
 M = initial sorbent weight per mole of Ca, g of sorbent/mol of Ca  
 M<sub>SO<sub>2</sub></sub> = molecular weight of SO<sub>2</sub>, g/mol  
 RH = relative humidity, %  
 SC = SO<sub>2</sub> capture, g of SO<sub>2</sub>/g of sorbent  
 S<sub>g</sub> = initial specific surface area, m<sup>2</sup>/g  
 V<sub>m</sub> = initial specific mesopore volume, cm<sup>3</sup>/g  
 V<sub>t</sub> = initial specific total pore volume, cm<sup>3</sup>/g

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