Utilization of Lime−Silica Solids for Flue Gas Desulfurization

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Enhancement in the utilization of lime−silica solids for flue gas desulfurization has been experimentally investigated on the basis of their physical and chemical properties. Along the pozzolanic reaction, the utilization of $Ca(OH)_2$ in the solids increased because of the increase in their BET specific surface area resulting from formation of a calcium silicate phase. Continued hydration of the excess SiO_2 after the reaction had been completed, however, reduced the utilization of the sorbent particles because of undesirable precipitation of Si on the silicate. Increases in the initial $SiO_2/Ca(OH)_2$ ratio and the reaction temperature drastically reduced the period of preparation for solids having the same utilization and increased the maximum utilization. It is proposed that the changes in morphology and effective distribution of Si and Ca in the silicate phase were responsible for the latter utilization enhancement.

Introduction

Flue gas desulfurization (FGD) with $Ca(OH)_2$ in the dry phase has been in limited use because of its low utilization (10−40%) caused by pore plugging.[1,2] Improvement in the utilization of $Ca(OH)_2$ has been achieved through the formation of various types of calcium silicate hydrates, $(CaO)_x(SiO_2)_y(H_2O)_z$, from the pozzolanic reaction between $Ca(OH)_2$ and siliceous materials such as fly ash,[3−10] diatomaceous earth,[3,4,6] and recycled glass.[11] The conversion of $Ca(OH)_2$ increased with the weight ratio of fly ash to lime, the time, and the temperature of hydration because of the increased BET surface area of a new phase produced.[3,4,6,8,9] However, fly ash is mainly composed of SiO_2, Al_2O_3, Fe_2O_3, and CaO, and its composition varies widely.[5,6,8] Although the formation of calcium silicate from $Ca(OH)_2$ and SiO_2 in fly ash was believed to be responsible for the increase in the utilization, there have been few published studies investigating the effect of SiO_2 alone, instead of fly ash, on the pozzolanic product and thus its utilization for SO_2 removal. Furthermore, most studies had not paid attention to the systematic correlation between the Ca utilization and the chemical and physical properties of the lime−silica sorbent prepared under a wide range of reaction variables. In our previous study,[12] the lime−silica particles were prepared from reagent-grade $Ca(OH)_2$ and SiO_2 under widely ranging variations in conditions such as the temperature, the time of hydration, and the initial $SiO_2/Ca(OH)_2$ mole ratio. Jung et al.[12] reported that the silica-enhanced lime had a BET surface area of 170 m^2/g, about 6 times greater than was found for those prepared from fly ash for SiO_2.[3,5,10,11] They showed[12] that the change in the morphology of the product was much clearer with SiO_2 than in with fly ash[3,6,8,9] but that the excess hydration of SiO_2 had an adverse effect on the enhancement of the utilization. According to them,[12] the mole ratio of Ca/Si in the calcium silicate hydrate gradually decreased and then converged to ~1.5−0.9 depending on the temperature of hydration, independently of the initial mole ratio of $SiO_2/Ca(OH)_2$. They also reported[12] that hydration at elevated temperature and pressure was accelerated to reduce the size of primary particles but make a less compact structure, thereby yielding the maximum surface area similar to that obtained at lower temperature and pressure. This had not been clear with the hydration using fly ash.

In the present study, we continued to investigate the utilization for SO_2 removal of lime−silica sorbents prepared under various conditions. We, therefore, tried systematically to correlate the utilization of these sorbents with their physical and chemical properties determined in our previous study.[12]

Experimental Section

Sorbent Preparation. The sorbents were prepared from reagent-grade $Ca(OH)_2$, SiO_2, and water by the same procedures described in our previous study.[12] In brief, the mass ratio of water to solid reactants [$SiO_2 + Ca(OH)_2$] in the slurry was fixed at 20,[7,8] with the total amount of slurry fixed at 250 g. The initial mole ratio of $SiO_2/Ca(OH)_2$ varied from 0 to 6 with 1.5 as a reference. The hydration temperatures varied from 90 to 150 °C. The atmospheric hydration at 90 °C was performed in a 500-cm^3 flask witha reflux condenser in a thermostated water bath. The slurry was stirred vigorously throughout the extended hydration period, which varied from 1 to 86 h, much longer than previously investigated,[3,6,7,9−11] while the reference hydration time was selected as 48 h. The pressure hydration was performed in a stainless steel autoclave at 120 and 150 °C, the boiling temperatures corresponding to 200 and 480 kPa, respectively. After the completion of the hydration, the slurry was dried in two steps. It was first vacuum-dried for 1 day at a temperature of 35 °C, because in the preliminary experiment, the pozzolanic reactivity was found to be sufficiently low below 40 °C. After milling of the partially cracked cake from vacuum-drying, the powder was further dried in the oven at 85 °C for 2−3 days, for complete removal of remaining moisture, which was verified by thermogravimetry-(TGA-50H, Shimazu). No further hydration was found to occur during the entire drying period.

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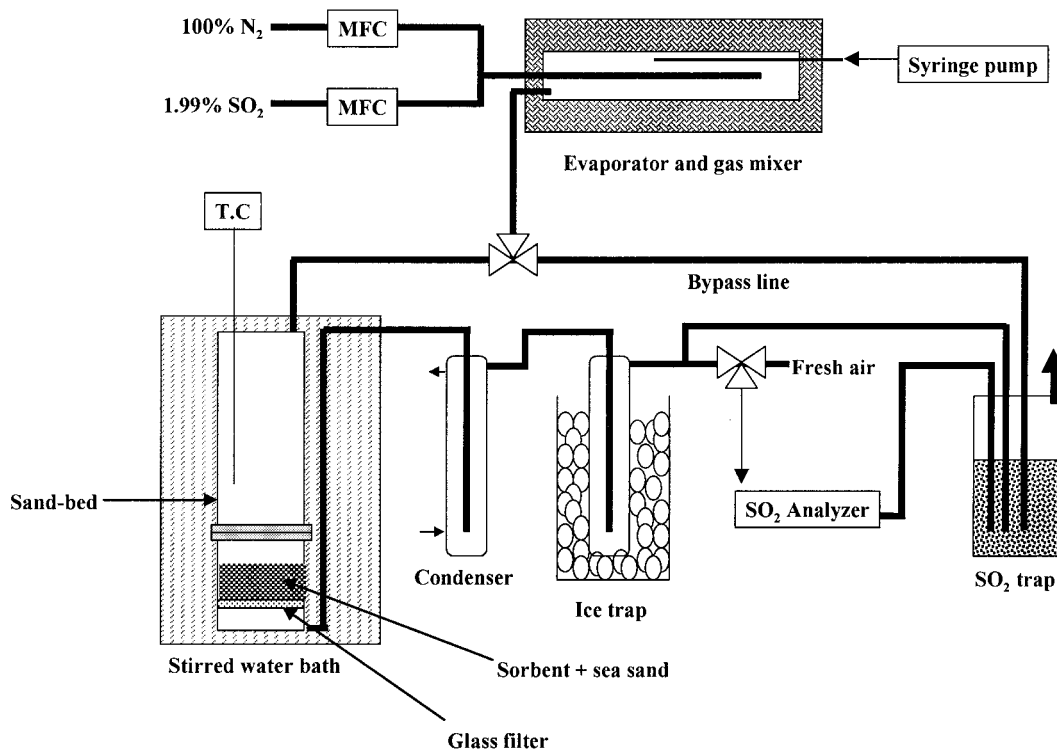
Figure 1. Schematic diagram of sand-bed reactor for evaluating sorbent reactivity with SO_2.

The methods of characterization were well described in our previous study.[8]

Desulfurization. The reactivity of the various sorbents was evaluated in a sand-bed reactor as shown in Figure 1. One gram of silica-enhanced lime sorbent was well dispersed in 40 g of sea sand (30–50 mesh) in a cylindrical mixer whose body was rotating at 100 rpm for 1 h, and the mixture was then poured into the sand-bed reactor. The sand-bed reactor (46 mm o.d. and 150 mm height) was equipped with a glass filter and immersed in a thermostated water bath. The sea sand prevented channeling of simulated flue gas as well as agglomeration of sorbent particles. To investigate the effect of only the sorbents, all process variables concerned with the desulfurization experiment were fixed at the typical bag-house condition.[3,4] The flow rate of the simulated flue gas containing 500 ppm of SO_2 and the balance nitrogen was controlled at 4.7 L/min by mass flow controllers (MFCs). The gas then entered a humidifier with a volume of 600 mL at 180 °C, where the water from the syringe pump was evaporated and well mixed with the gas. The relative humidity of the simulated flue gas was maintained at 60%. The tubing from the humidifier to the sand-bed reactor was heated at the reactor temperature of 65 °C with a heating band to keep water vapor from condensing. Downstream of the reactor, the water vapor in the desulfurized gas was completely condensed by both a condenser and an ice trap, and then the SO_2 concentration was measured with an SO_2 analyzer (model CE-22ASM-P, Jung Eng.) every 1 min. Prior to each desulfurization run, the samples were preconditioned in the reactor for 20 min by flowing N_2 with a relative humidity of 60% without SO_2.[8] The effect of the sea sand on the desulfurization was assumed to be negligible as the percent desulfurization with sea sand remained within the error bounds of the SO_2 analyzer ($\pm 1\%$).

The reactivity of the sorbents toward SO_2 was expressed as the Ca utilization of the lime–silica sorbent,
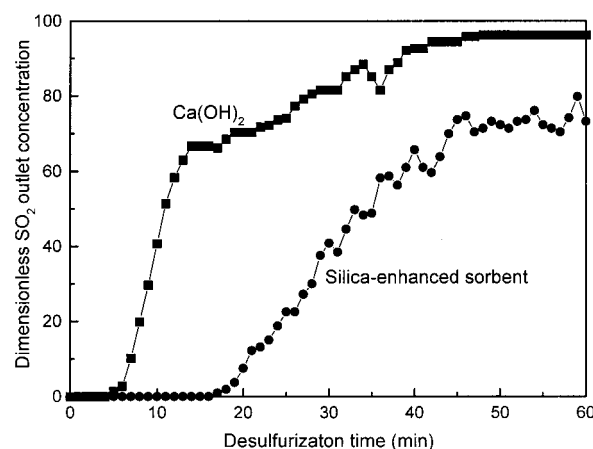

Figure 2. Dimensionless SO_2 outlet concentration vs time for pure $Ca(OH)_2$ and sorbent hydrated with an initial $SiO_2/Ca(OH)_2$ mole ratio of 1.5 at 90 °C for 48 h.

defined as the fraction or percentage of the number of moles of CaO in the silicate reacted with SO_2.

Results and Discussion

Sorbent Utilization and SO_2 Removal Efficiency vs Hydration Time. Figure 2 shows the SO_2 concentration at the outlet of the reactor with respect to time for pure $Ca(OH)_2$ and for silica-enhanced lime prepared with an initial molar ratio of $SiO_2/Ca(OH)_2 = 1.5$ at 90 °C for 48 h. The SO_2 removal efficiency was obtained by dividing the area above the corresponding curve by the desulfurization time (60 min), and the Ca utilization was found by dividing the efficiency by the stoichiometric ratio. Thus, by hydration, the removal efficiency of SO_2 increased from 29.2% to 63.8%, while the utilization dramatically increased from 13.0% to 61.7%. The break times, which were defined as the times at which the
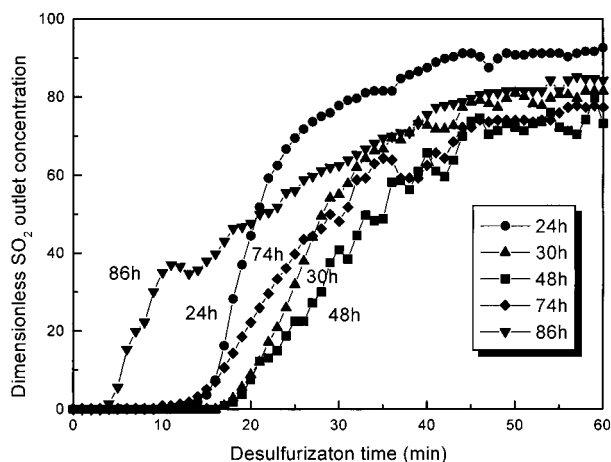
Figure 3. Dimensionless SO_2 outlet concentration vs time for sorbents prepared with various hydration times with an initial $SiO_2/Ca(OH)_2$ mole ratio of 1.5:1 at 90 °C.
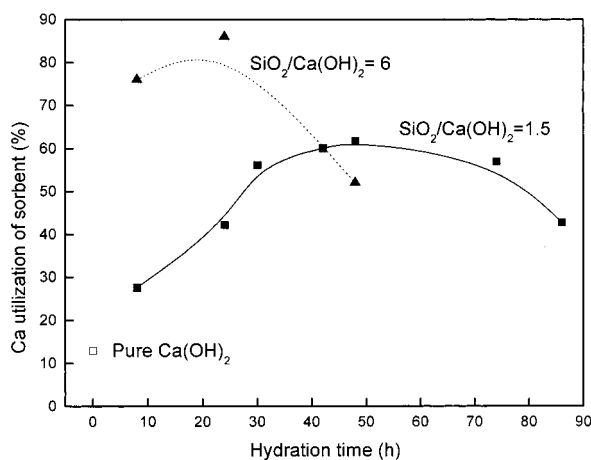

Figure 4. Effect of hydration time on Ca utilization of sorbents hydrated at 90 °C with $SiO_2/Ca(OH)_2$ mole ratios of 1.5 and 6.

outlet SO_2 concentration reached 0.05 times its inlet concentration, were 6 and 20 min for pure $Ca(OH)_2$ and silica-enhanced sorbent, respectively. The increase in the utilization was caused by the increase in the break time as well as the subsequent slower increase in the outlet concentration. Therefore, even after 60 min of exposure to SO_2, the silica-enhanced lime sorbent was not saturated, still having potential for more SO_2 capture. This implied that the pore plugging[1,3] in the case of pure $Ca(OH)_2$ might be less active in the new sorbent.

To determine the effect of the hydration time on the Ca utilization of the sorbent, the breakthrough curves, similar to Figure 2, were drawn in Figure 3 as a function of hydration time, for the sorbents hydrated with an initial $SiO_2/Ca(OH)_2$ mole ratio of 1.5 at 90 °C. In Figure 3, with a hydration time of up to 48 h, the break time increased, the breakthrough curve moved down, and consequently, the Ca utilization increased. However, hydration for more than 48 h had an adverse effect on the Ca utilization. The breakthrough curve moved up, and the break time decreased with the time of hydration.

The Ca utilization of the sorbent, obtained from the breakthrough curves, thus varied with the hydration time as shown in Figure 4. The hollow square at the hydration time of 0 h indicates the utilization of pure $Ca(OH)_2$. For the initial $SiO_2/Ca(OH)_2$ ratio of 1.5, the

maximum Ca utilization of the hydrated sorbents, which is about 5 times that of pure $Ca(OH)_2$, occurred at a hydration time of around 50 h. Figure 4 also showed that the Ca utilization at the initial $SiO_2/Ca(OH)_2$ ratio of 6 varied in a fashion similar to that at the ratio of 1.5.

Correlation of Utilization of Hydrated Sorbents with Their Characteristics. The morphology, BET specific surface area, conversion to calcium silicate, and Ca/Si ratio in the new silicate phase with respect to the period of hydration were well discussed in our previous paper,[12] the result of which was partially shown in the introduction of this paper. According to Jung et al.,[12] the pozzolanic reaction between $Ca(OH)_2$ and less soluble SiO_2 proceeded until the product silicate contained a certain ratio of Ca/Si, and then excess SiO_2 continued to dissolve out to the surface and change the surface morphology of the product particles without changing the Ca/Si ratio in the silicate. For the hydration batch with the initial mole ratio of $SiO_2/Ca(OH)_2$ = 1.5 at 90 °C, the ultimate Ca/Si ratio of 1.5 was obtained at 48 h, and afterward therefore, the product particles consisted of the calcium silicate and self-hydrated SiO_2.[12]

It was clear that the enhancement of calcium utilization, as shown in Figure 4, resulted from the increase in the surface area of the calcium silicate phase produced during the pozzolanic reaction, as shown in our previous paper.[12] However, further dissolution of excess SiO_2 following silicate formation, no longer participating the formation of calcium silicate, merely led to its precipitation on the silicate sorbent to modify its surface[12] and decrease its Ca utilization. As shown in Figure 3, up to 48 h, the three breakthrough curves are similar for the first 20 min, while they are quite different for the last 20 min. However, after 48 h, the curves are different for first 20 min while they ultimately converge to the same concentration. It is confirmed that the participation of SiO_2 in silicate formation assisted in the effective use of Ca, probably because of the reduction of pore plugging, but the precipitation of excess SiO_2 resulted in a reduction of surface reactivity, as described above.

An increase in the initial $SiO_2/Ca(OH)_2$ ratio generally enhanced the Ca utilization for the sorbents prepared at short hydration times and shortened the time required for the maximum utilization to occur, as shown in Figure 4. The latter again coincides with the time for the pozzolanic reaction to stop, and this supports the close correlation between Ca utilization and conversion to silicate in the sorbent. The enhancement of the Ca utilization with the initial $SiO_2/Ca(OH)_2$ ratio seems peculiar as the ultimate Ca/Si ratio in the product silicate depended only on the hydration temperature, not on the reactant ratio.[12] Therefore, it is supposed that an increase in $SiO_2/Ca(OH)_2$ ratio accelerates the rate of SiO_2 dissolution and promotes the early inclusion of Si in the silicate, thereby resulting in a more uniform distribution of Ca and Si and thus an enhancement of the Ca utilization of the sorbent. Figure 5 shows the effect of the initial $SiO_2/Ca(OH)_2$ mole ratio on the Ca utilization of the sorbents hydrated at 90 °C for 8 and 48 h. The figure shows that the Ca utilization of the sorbent prepared by the 8-h hydration increased with the initial $SiO_2/Ca(OH)_2$ ratio, whereas the utilization of the sorbent prepared by the 48-h hydration increased up to a reactant ratio of 1.5 and had a plateau for higher
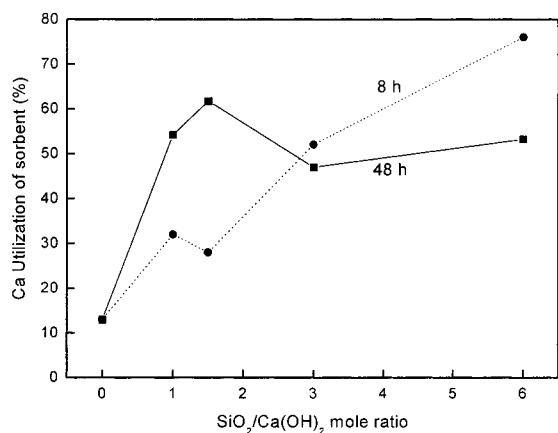
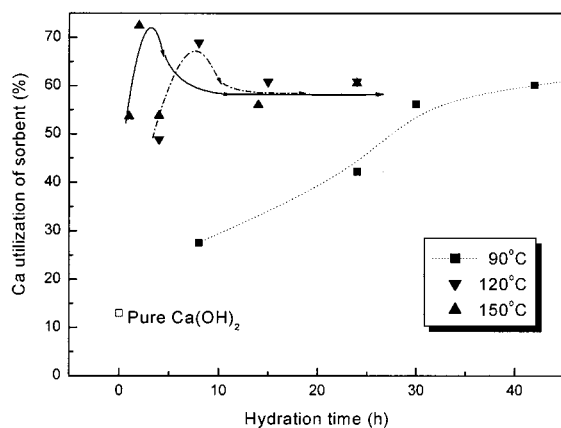**Figure 5.** Effect of $SiO_2/Ca(OH)_2$ mole ratio on utilization of sorbents hydrated at 90 °C for 8 h and 48 h.

Figure 6. Effect of hydration time on Ca utilization of sorbents hydrated with an initial $SiO_2/Ca(OH)_2$ mole ratio of 1.5 at 90, 120, and 150 °C.

ratios. The formation of the plateau implies that, at the higher ratio, the negative effect on the utilization attributable to the precipitation of excess SiO_2 was balanced by the positive effect of the effective dispersion of Ca, as described above.

Pressure Hydration. In general, pressure hydration, which naturally proceeds at higher temperatures, could promote the solubility and rate of dissolution of SiO_2, which is the rate-limiting step of the pozzolanic reaction, but slightly demote the solubility of $Ca(OH)_2$. The time for sorbent preparation was significantly reduced, as shown by Jozewicz et al.,[9] Jozewicz et al.,[3] and Jung et al.[12]

Jung et al.[12] also reported that the ultimate conversion of the mixed reactant to silicate increased from 65% at 90 °C to 78% at 150 °C, and more Si was included at 150 °C (the ultimate Ca/Si ratio = 1.0), resulting in more open structures with smaller primary particles agglomerated to thinner and longer chains.

Figure 6 shows the effect of the hydration time on the utilization of the sorbents prepared by pressure hydration at temperatures of 120 and 150 °C with that at 90 °C as a reference. The Ca utilization varied with the hydration time similarly, regardless of the temperature. However, the maximum utilization increased and occurred at a much shorter preparation time with increasing hydration temperature. Thus, at a temperature of 150 °C, the maximum utilization of 72% was obtained at 2 h, and at 120 °C, the maximum of 69% was obtained

at 10 h, whereas a maximum utilization of63% was obtained at 55 h at 90 °C.

Despite the almost constant BET area and reduced Ca/Si ratio,[12] the enhancement of Ca utilization with temperature is proposed to result from increased inclusion of Si in the silicate phase, corresponding to a more open structure, which would be necessary to keep the pores from plugging. Because the situation is similar to that for a high $SiO_2/Ca(OH)_2$ ratio at 90 °C, this strongly supports our earlier assumption of the uniform distribution of Si and Ca in that case.

Conclusions

Silica-enhanced lime particles were prepared from reagent-grade SiO_2 and $Ca(OH)_2$ under variations in conditions such as the temperature, the time of hydration, and the initial $SiO_2/Ca(OH)_2$ mole ratio. We obtained more clear-cut effects of the reactants by using reagent-grade reactants and more profound effects by extending the hydration time than had ever before been found for the desulfurization ability of the product.[3−11] The atmospheric pozzlanic reaction at 90 °C increased the utilization of the silica-enhanced sorbents based on $Ca(OH)_2$ up to 61.7% from 13.5% based on mixed mass of the sorbent. These increases were closely related to increases in the BET surface area and the conversion to calcium silicate hydrate, which were both highly correlated with each other. The hydration of excess SiO_2 reduced the sorbent utilization because the exposed area of the calcium silicate produced was reduced by the redeposition of SiO_2 on it. Increases in the initial $SiO_2/Ca(OH)_2$ ratio and hydration temperature accelerated the silicate formation, resulting in an increase in the maximum Ca utilization and a decrease in the time required for the maximum to occur. The utilization increased from 61.7% to 73% as the temperature increased from 90 to 150 °C, whereas the maximum BET specific area remained constant, and the ultimate Ca/Si ratio even decreased.

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