Enhanced SO_2 Abatement with Water-Hydrated Dolomitic Particles

Ali Al-Shawabkeh, Hitoki Matsuda, and Masanobu Hasatani
Dept. of Energy Engineering and Science, Nagoya University, Nagoya, 464-01, Japan

A dolomitic calcine was hydrated with liquid water and then recalcined as an effective sorbent toward SO_2 *removal. The hydrated/recalcined sorbent was tested for* SO_2 *removal in a thermogravimetric analyzer under conditions applicable to an atmospheric fluidized-bed combustor: 1,123 K, 20 vol. % excess air, and 3,000 ppmv* SO_2*. Specific pore surface areas and volumes of hydrated/recalcined dolomites, hydrated at 80°C for 1 h, increased by four and five times, respectively, compared to unhydrated dolomitic calcines. Due to these improved pore characteristics, the* SO_2 *capture achieved by the hydrated/recalcined calcine, was* $1.3-1.6$ *times higher than that of the unhydrated one after a 1-h exposure to* SO_2 *concentrations of* $0.11-0.31$ *vol. % at* $1,073-1,173$ *K. In the hydrated/recalcined calcine CaO utilization was enhanced due to the absence of significant pore diffusional limitations, at least during the early reaction times, evidenced by the high apparent activation energy of 198 kJ/mol. On the contrary, the lower CaO utilization in the unhydrated calcine was presumably due to severe pore diffusional limitations, which dropped the apparent activation energy from 149 to 85 kJ/mol at* $> 1,123$ *K.*

Introduction

In the flue gases from combustors, sulfur dioxide is considered to be a major air pollutant because of its adverse impacts on the environment and human health. A great deal of attention should be paid to inexpensive methods of controlling sulfur dioxide emissions.

The numerous studies on the sulfation reaction, in particular under conditions applicable to a typical coal-based fluidized-bed combustor (FBC) include Borgwardt (1970); Borgwardt and Harvey (1972); Potter (1969); Pigford and Sliger (1973); Hartman and Coughlin (1974, 1976); Dogu (1981); Ciambelli et al. (1985). In most of these lab tests, moreover, limestones and dolomites were extensively utilized for curtailing SO_2 emissions because of their widespread availability at inexpensive costs. Nonetheless, the sorptive capacity of these sorbents for SO_2 removal in the FBC is normally limited due to their incomplete reactions with SO_2 even at relatively high Ca/S ratios. The incomplete conversion of CaO into $CaSO_4$ mainly arises from the volume increase as the reaction proceeds (by about 3 times) as reported in several previous articles (Al-Shawabkeh et al., 1994, 1995; Chang and Thodos, 1984).

Different methods of enhancing Ca-containing sorbent utilization, such as pyrolytic regeneration of the sorbent and conversion of the evolved SO_2 into elemental sulfur or sulfuric acid (Montagna et al., 1977; Yang and Shen, 1979), and modification by salt addition (such as NaCl or CaCl) to the sorbent (Yang, 1978), have been proposed. However, because of the chemical complexity of the regeneration process and the severe corrosive effect of the addition of salts, these methods are not currently regarded as commercially attractive. Instead, other reactivation methods, based on steam or liquid water hydration, have been shown to be more economical, simpler, and able to produce sorbents of higher SO_2 affinity, compared to natural sorbents (Couturier et al., 1994; Schmal, 1985). By hydration, Shearer et al. (1980) reactivated spent (partially sulfated) materials from a bubbling FBC. They reported that hydration occurs by water permeation through the partially sulfated layer and reaction with the inner (unreacted) CaO core to form $Ca(OH)_2$. Cole et al. (1986) attributed the enhanced reactivity of hydrated materials over limestone to the higher surface area and smaller particle size.

When the CaO particles are hydrated, the volume of grains is increased because of the relatively greater molar volume of the $Ca(OH)_2$ hydrate (33.1 cm^3/mol, Dean, 1979) than that

---

Correspondence concerning this article should be addressed to M. Hasatani.

of CaO (16.9 cm^3/mol). As this hydrate is subsequently calcined, the release of the H_2O molecule creates new pores in the swelled structure. Swelling during hydration is usually associated with a loss in the strength (or hardness) of the particles. However, depending on hydration conditions, the hydrated lime may be first strengthened by partial sulfation. Repeated hydration and recycling of spent sorbents can give high utilization of even unreactive limestone (Howard, 1983).

Inside the FBC, the injected dolomitic particles [$CaMg(CO_3)_2$] are first calcined into porous CaO·MgO oxides in accordance to Eq. 1

$$CaCO_3 \cdot MgCO_3 \Rightarrow CaO \cdot MgO + 2CO_2 \tag{1}$$

The developed porosity in the CaO·MgO calcines is most likely due to the CO_2 gas release from the interior of the sorbent particles during calcination. This porosity, however, will then be diminished during the sulfation reaction of CaO in the dolomite with SO_2 in excess air (ca. 5 kPa O_2) to form calcium sulfate ($CaSO_4$)

$$CaO \cdot MgO + SO_2 + \frac{1}{2}O_2 \Rightarrow CaSO_4 + MgO \tag{2}$$

The MgO content in the injected dolomite does not contribute to significant SO_2 capture due to the thermodynamic instability of magnesium sulfate ($MgSO_4$) above 1,048 K under atmospheric conditions (Dennis and Hayhurst, 1987). Nonetheless, MgO presence in the dolomitic sorbent plays a significant role in increasing the porosity during calcination (Münzner et al., 1985), as well as in offering more active sites for SO_2 fixation on the CaO grain surfaces.

The objective of the current study was to improve the reactivity of dolomitic particles towards SO_2 by liquid water hydration/recalcination. The effects of the hydration time and temperature on the pore characteristics of the hydrated/recalcined dolomitic calcine and its subsequent sulfation capacity were also investigated. Sulfation runs were carefully controlled in a thermogravimetric analyzer with the intent to closely simulate conditions encountered in a typical atmospheric fluidized-bed combustor (AFBC).

Experimental Studies

Materials

The sorbent used in all experiments was a dolomite obtained from Tochigi prefecture (Japan). The received dolomite sample was crushed, pulverized, and sieved into sizes of 90–106 μm. The chemical composition of an arbitrary sample is given in Table 1. The specific surface area and pore volume of the received dolomite were measured as 1.1 m^2/g and 0.006 cm^3/g, respectively. Measurements of the specific surface areas and pore volumes were done using an accelerated surface area and porosimetry system which utilized the low-temperature N_2 adsorption technique (ASAP2000, Norcross, GA, USA). The N_2 adsorption measurements were based on the Brunauer-Emmett-Teller (BET) method for the sample dried and degassed at 250°C.

Table 1. Chemical Composition (wt. %) of Tochigi Dolomite

CaO	MgO	SiO_2	Fe_2O_3	Ig. Loss
34.37	18.16	0.12	0.04	46.78

Calcination of dolomite

A Thermo-Gravimetric Analyzer (TGA-50, Shimadzu Corporation, Kyoto, Japan) was utilized to carry out the calcination and sulfation experiments. The dolomitic calcines (CaO·MgO) were prepared by heating the dolomite sample in pure N_2 (125 cm^3/min) at a heating rate of 50 K/min up to 1,123 K. Complete calcination was emphasized by monitoring the end of the weight loss which was fairly compared with the stoichiometry of the calcination reaction. Calcination increased the specific pore surface area up to 10.2 m^2/g as well as the pore volume up to 0.057 cm^3/g owing to the decrease in the particles molar volume and CO_2 escape from the particle interior during decomposition (Murthi et al., 1971).

Hydration of dolomitic calcine

Water hydration was performed by adding a preweighed calcine sample (about 1 g) to a freshly deionized water (30 mL), and the solution was then magnetically stirred at 1,000 rpm for different lengths of time ranging from 5 to 120 min. The flasks containing the calcine solutions were plugged with rubber stoppers to prevent water loss (through evaporation) and/or the interference of ambient water vapor or carbon dioxide. Hydration was conducted at three different temperatures (20, 40 and 80°C). After the predetermined hydration time had elapsed, the samples were placed in an oven set at 110 ± 1°C for 24 h to evaporate surface water.

Hydration/recalcination of dolomitic calcine

The dolomitic hydrates, prepared in the same hydration method mentioned above, were recalcined into calcines of more improved pore characteristics as will be shown later. In order to eliminate any expected effects of calcination on the pore properties of the resulting calcines, recalcination of the hydrates was carried out under similar calcination conditions, that is, 850°C, 125 cm^3 N_2/min, and 50 K/min heating rate.

Sulfation of dolomitic calcine

The sulfation gas mixture was simulated as 1,100–3,100 ppmv SO_2, 5 vol. % O_2 (which was maintained constant in all cases), and balance N_2 by adjusting each individual gas with an electronic mass-flow controller. The total gas rate was maintained at 141 cm^3/min and the retention time in the TGA reactor was estimated as 0.5 s. Sulfation tests were conducted with calcines drawn from dolomitic samples as small as 2.0–3.0 mg and the weight gained due to sulfation was continuously recorded and saved.

Results and Discussion

Hydration time and temperature

The specific surface areas *Sa* (m^2/g) measured by ASAP2000 of the dolomitic calcines hydrated at three different temperatures (20, 40 and 80°C) for time periods ranging from 5 to 120 min are illustrated in Figure 1. The loss in *Sa*

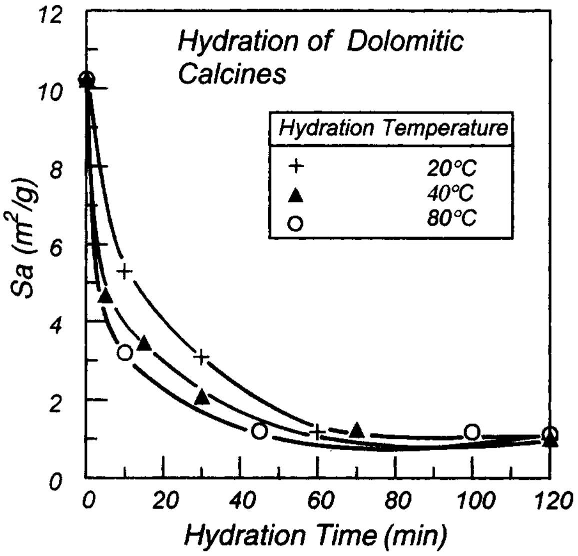

Figure 1. Hydration effect on the specific surface area of dolomitic calcines.

Dolomitic calcines were first hydrated at certain hydration time and temperature before measuring their specific surface areas

as hydration proceeds is principally due to the molar volume increase of the calcines reacting with water. The hydration rate, indicated by the loss in *Sa* with time, proceeded faster for calcines hydrated at higher temperature. After 1 h hydration, however, all the areas dropped to a certain value of ≈ 1 m^2/g independent of temperature indicating that a 1 h hydration period was sufficient for a complete hydration to be reached.

Now, the same hydrates were recalcined and then measurements of their new specific surface areas were performed. Figure 2 shows the measured areas of the hydrated/recalcined calcines plotted against the conditions in which the hydrates were prepared. As seen in this figure, recalcination led to a significant enhancement in the evolved areas as compared to the initial (unhydrated) dolomitic calcine ($Sa = 10.2$ m^2/g). It is further seen that the calcines hydrated at higher temperature were found to evolve larger areas upon recalcination. The areas of the hydrated/recalcined samples, which were hydrated for 1 h at 20, 40 and 80°C, were measured as 23, 29 and 41 m^2/g, respectively.

For a certain hydration temperature, the measured areas of the hydrated/recalcined samples were found to increase with increase in the hydration time for the first 1 h. After the first 1 h hydration, however, no enhancement in the areas was observed. This result with the one drawn from Figure 1 are not unexpected if a complete hydration was attained in the first 1 h, as will be confirmed later with XRD traces. Now, as the solid reactivity towards SO_2 increases with higher surface area of the solid, the calcines obtained from hydration (at 80°C for 1 h)/recalcination will be utilized for the coming sulfation tests.

Figure 3 shows the pore-size distribution curves drawn from the nitrogen porosimeter (ASAP2000, Norcross, GA, USA) for the dolomitic calcine prior to and after hydration (at 80°C)/recalcination. Hydration/recalcination led to larger pore volumes in the resulting calcine as compared to those in the unhydrated calcine. The hydrated/recalcined dolomitic calcines, hydrated for longer time periods, were found to possess larger pore volumes and their pore-size distribution shifted towards larger pore sizes. In particular, the recalcine which was hydrated for 60 min had a pore volume (0.291 cm^3/g) of about fivefold higher than the unhydrated one (0.057 cm^3/g).

The effect of hydration/recalcination as well as sulfation on the external morphology of the dolomitic calcines were examined with scanning electron microscopy (SEM). Representative photos of the unhydrated, hydrated/recalcined cal-

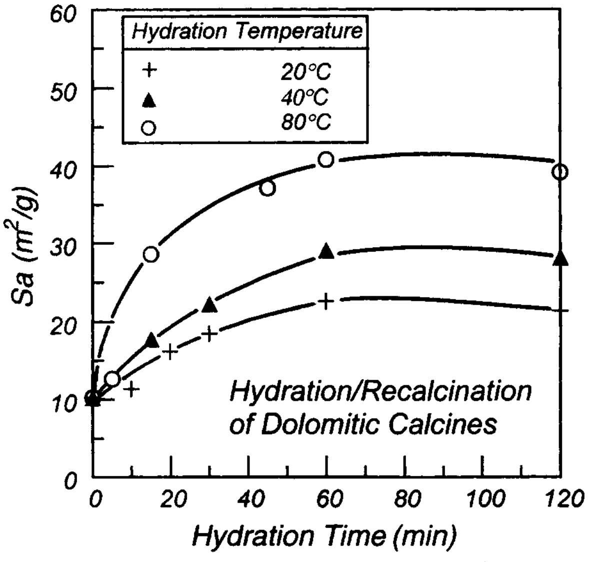

Figure 2. Specific surface areas of hydrated/recalcined dolomitic calcines.

Dolomitic calcines were first hydrated at certain hydration time and temperature and then recalcined before measuring their specific surface areas.

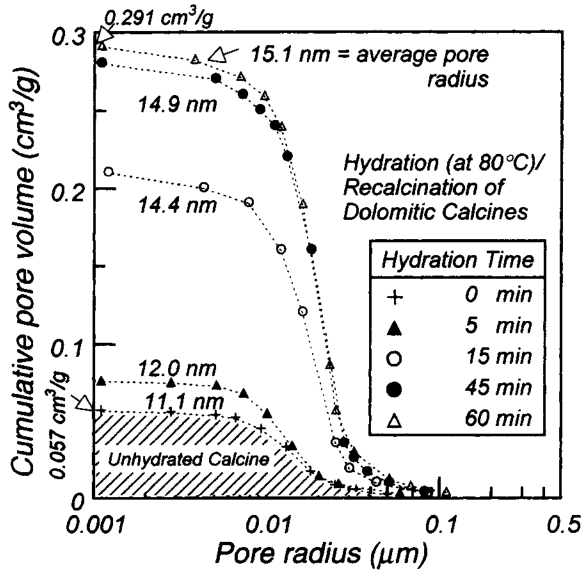

Figure 3. Cumulative pore volume of hydrated/recalcined dolomitic calcines.

Calcines were first hydrated, at 80°C for 5–60 min, and then recalcined before measuring their cumulative pore volumes.

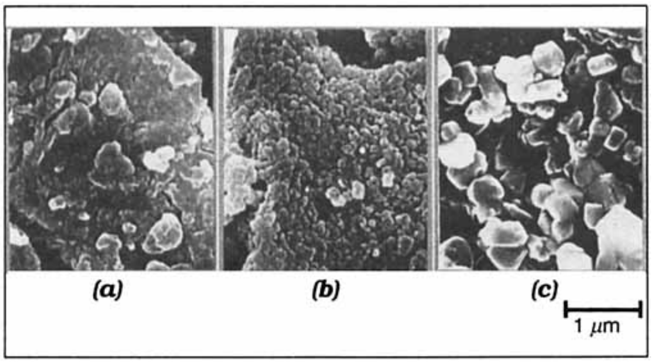

Figure 4. SEM photos of dolomitic calcines.

(a) Before hydration; (b) after hydration/recalcination; (c) after sulfation of the hydrated/recalcined calcine. Hydration = 80°C, 1 h; recalcination = 850°C, 125 cm^3/min N_2, 50 K/min heating rate; sulfation = 1,123 K, 0.31 vol. % SO_2, 141 cm^3/min total gas.

cines prior to and after sulfation are depicted in Figure 4. The hydrated/recalcined calcine was observed to have more developed structure in terms of smaller particles with rough external surfaces (Figure 4b) as compared to the smooth ones in the unhydrated calcine (Figure 4a). However, sulfation of the hydrated/recalcined sample (Figure 4c) resulted in larger particles of relatively smoother external surfaces than those prior to sulfation due to the fixation of SO_2 and O_2 over the particles.

The hydrated dolomitic calcine and the sulfated hydrated/recalcined dolomitic calcine were subjected to an X-ray powder diffractometer (Rigaku XRD) for examining the structural changes due to the hydration and sulfation reactions. The diffraction patterns shown in Figure 5 were compared to standard patterns from Hanawalt Search Manual (1993). In the hydrated dolomitic calcine (Pattern 5a), the CaO components seemed to be completely hydrated as confirmed by the relatively high-intensity peaks of $Ca(OH)_2$ at $2\theta = 18.1°$ ($d = 4.9$ Å), 34.1° ($d = 2.63$ Å), 47° ($d = 1.93$ Å), and 50.8° ($d = 1.796$ Å). On the other hand, only weak peaks of $Mg(OH)_2$ were detected ($2\theta = 18.6$ and 50.9°) suggesting that some of the MgO components slaked. The fact that the dolomitic CaO, rather than the dolomitic MgO, readily hydrates is, nevertheless, not unexpected since the MgO which exists in most types of dolomite is virtually insoluble (0.0086 g/g) and does not hydrate under atmospheric pressure. Moreover, during calcination of dolomite, the $MgCO_3$ is first decomposed at much lower temperatures in comparison to $CaCO_3$. As a result, the MgO components are usually hard-burned before the CaO is formed. It follows that when a dolomite is hydrated under atmospheric conditions, almost all its CaO components hydrate, but very little of MgO slakes (Yaverbaum, 1977). For more than two-thirds of the test samples hydrated at 80°C for more than 1 h, the calculated weight difference before and after hydration indicated reasonably that hydration was merely due to the complete conversion of CaO particles into $Ca(OH)_2$. Pattern 5a also exhibits the presence of magnesium carbonate ($MgCO_3$), which might be formed due to the interaction with ambient CO_2 during hydration.

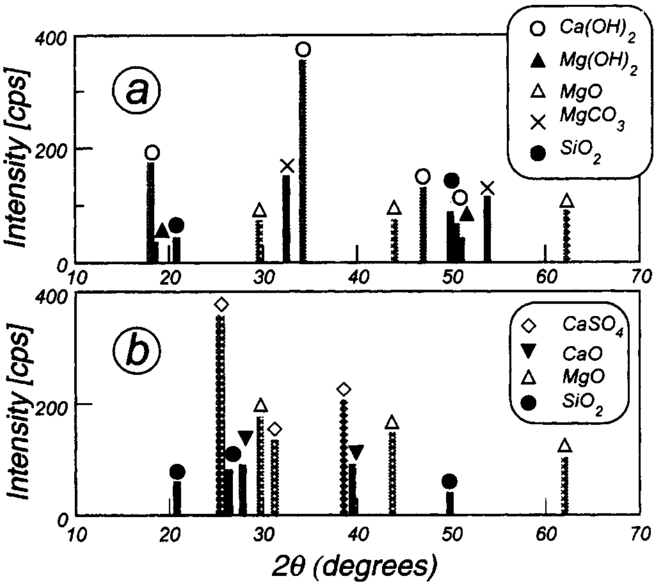

Figure 5. XRD patterns of dolomitic calcines.

(a) After hydration; (b) after sulfation of the hydrated/recalcined calcine. Hydration = 80°C, 1 h; recalcination = 850°C, 125 cm^3/min N_2, 50 K/min heating rate; sulfation = 1,123 K, 0.31 vol. % SO_3, 141 cm^3/min total gas.

After sulfation, XRD spectrum (pattern 5b) indicates that the SO_2 gas was trapped and fixed as $CaSO_4$. Compared to before sulfation, the higher diffraction peaks of MgO in the sulfated sample fairly indicate that $MgCO_3$ was completely decomposed during sulfation (notice that no $MgCO_3$ peaks were identified in the sulfated sample).

Sulfation of hydrated/recalcined dolomites

The sulfation curves of the unhydrated and hydrated/recalcined dolomitic calcines at 1,123 K and different SO_2 concentrations (0.11, 0.25, and 0.31 vol. %) are depicted in Figures 6 and 7, respectively. In both figures, the percentage of CaO conversion into $CaSO_4$ X (% mol-SO_2/mol-CaO) was

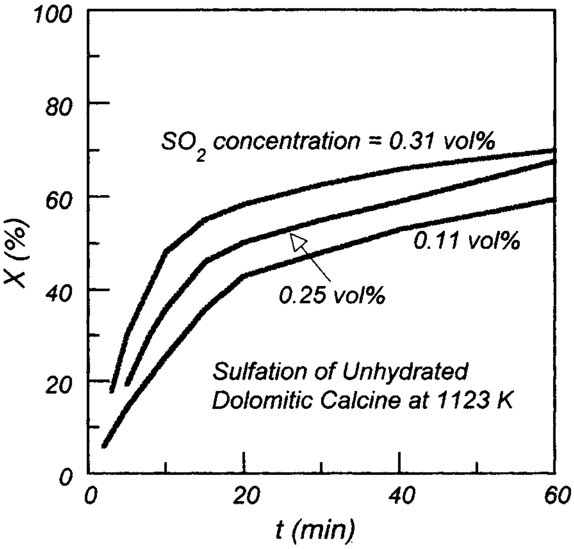

Figure 6. Effect of SO_2 concentration on CaO conversion in unhydrated dolomitic calcines sulfated at 1,123 K.

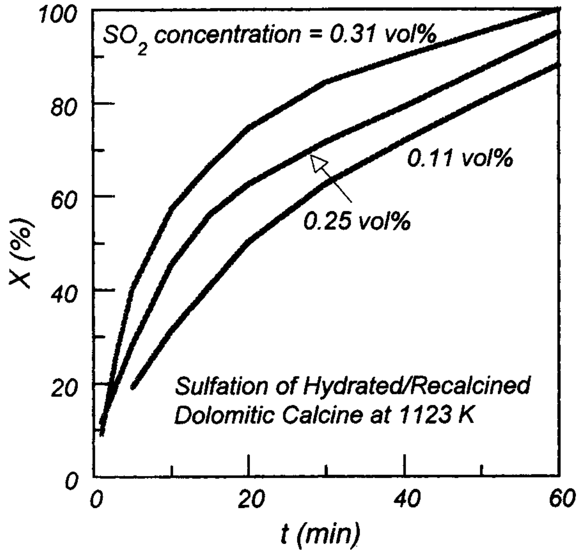

Figure 7. Effect of SO_2 concentration on CaO conversion in hydrated/recalcined dolomitic calcines sulfated at 1,123K.

found to increase with increasing the SO_2 partial pressure. Unlike the unhydrated calcine which exhibited a limited ultimate CaO utilization, the hydrated/recalcined one showed superior reactivity towards SO_2 in terms of the initial rate and the ultimate solid utilization as well. Within a 1 h exposure time, a full CaO utilization ($X = 100\%$) could be obtained with the hydrated/recalcined calcine as compared to the 70% conversion of the unhydrated one under the same sulfation conditions (1,123 K and 0.31 vol. % SO_2).

By plotting the initial reaction rates, taken as the slopes of the curves in Figures 6 and 7 at the origin against SO_2 concentrations (0.11–0.31 vol. %), the reaction between both unhydrated and hydrated/recalcined calcines were found to be first-order with respect to SO_2 concentration at constant O_2 partial pressure of 5.07 kPa (5 vol. %).

Figures 6 and 7 also show that although both the unhydrated and hydrated/recalcined calcines initially exhibited high reactivity with SO_2, the sulfation rates of the unhydrated calcines (Figure 6) experienced a significant drop after 10–20 min reaction time indicating to some extent diffusional limitations. On the contrary, the sulfation of the hydrated/recalcined sample (Figure 7) proceeded with comparatively less diffusional limitations and reached more than 90% conversion in 1 h. The high reactivity of the hydrated/recalcined dolomitic calcine is presumably due to the enhanced pore characteristics developed during the hydration/recalcination reactions (see Figure 2), which facilitated SO_2 diffusion into the calcine and thus allowed sulfation to proceed even to completion. t is sulfation time, min.

The effect of reaction temperature on the dolomitic calcines, both unhydrated and hydrated/recalcined due to sulfation in 0.31 vol. % SO_2-containing gases, are shown in Figures 8 and 9, respectively. With the unhydrated calcine (Figure 8) increasing the reaction temperature in the 1,073–1,173 K range enhanced both the initial and ultimate (after 1 h reaction) CaO conversions. The ultimate CaO utilization in the unhydrated calcine was nearly 79% at around 1,173 K. Through all the test temperatures, after 10–15 min sulfation the unhydrated calcine experienced a significant drop in its sulfation rate most likely due to the pore diffusional limitations. This was evidenced by the sharp drop in the apparent activation energy E_a (kJ/mol) from 149 to 85 kJ/mol in the temperature ranges of 1,073–1,123 K to 1,123–1,223 K, respectively, as shown in Table 2. The fact that the apparent activation energy dropped to about one-half (from 149 to 85 kJ/mol) is consistent with the theoretical derivation under strong pore diffusion limitation

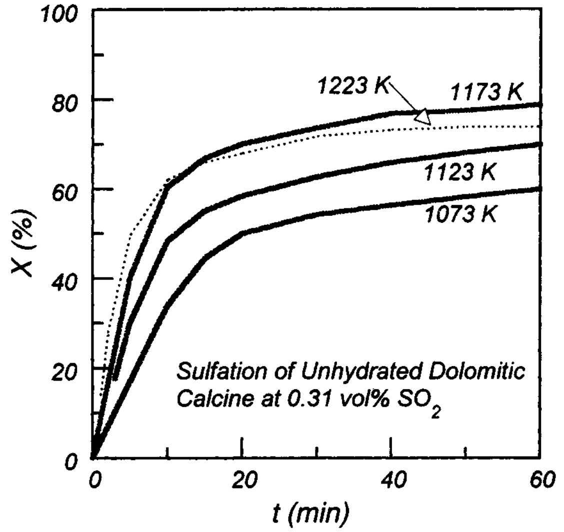

Figure 8. Sulfation temperature effect on CaO conversion in unhydrated dolomitic calcines sulfated at 0.31 vol. % SO_2.

$$E_a = \frac{E + E_d}{2} \approx \frac{E}{2} \tag{3}$$

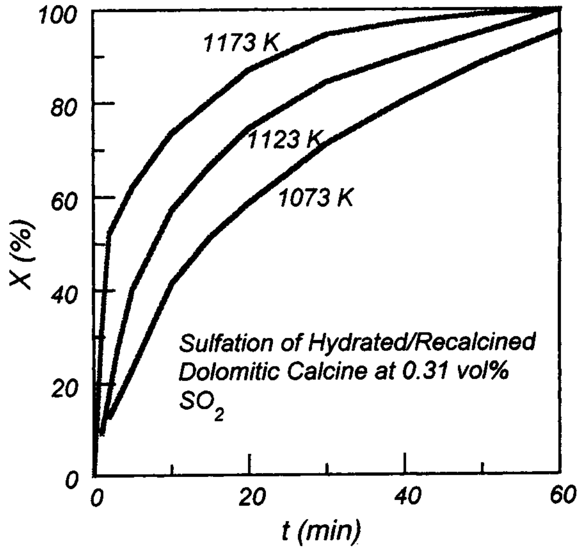

Figure 9. Sulfation temperature effect on CaO conversion in hydrated/recalcined dolomitic calcines sulfated at 0.31 vol. % SO_2.

Table 2. Calculated Apparent Activation Energies (E_a) of Dolomitic Calcines Reactions with SO_2 (0.31 Vol. %)

Dolomitic Calcine	Temp., K	E_a (kJ/mol)
Unhydrated	1,073–1,123	149
	1,123–1,223	85
Hydrated/recalcined	1,073–1,173	198

assuming E_d (kJ/mol) (gas diffusion through pores) $\ll E$ (activation energy, kJ/mol). Stouffer and Yoon (1989) showed that the onset of pore diffusion control of Dravo-100 mesh limestone-derived calcines (of surface areas between 13 and 55 m^2/g) was around 1,075 K where the apparent activation energy was approximately halved.

It is also necessary to examine if the E_a drop in the unhydrated calcine/SO_2 reaction is in part due to pore mouth plugging, and because larger small pore fraction in the unhydrated calcine was detected compared to the hydrated/recalcined one (see Figure 3). The pore mouth plugging phenomenon is usually associated with porous calcines owing to the relatively greater molar volume of the sulfate ($CaSO_4$, 52.2 cm^3/mol) over the initial solid reactant (CaO, 16.9 cm^3/mol) as reported by Hartman and Coughlin (1976). Zarkanitis and Sotirchos (1989), moreover, showed that small pores were more prone to deactivation by pore mouth plugging since less $CaSO_4$ is required for complete blockage. Over the experimental conditions of this work, nevertheless, at least the initial (or early) reaction course seems to be free from pore plugging because an apparent activation energy significantly less than 75 kJ/mol (Eq. 3: 149/2) would be expected if pore mouth plugging occurred. In prior experimental results, which were based on initial sulfation-time data (Stouffer and Yoon, 1989), a premature pore mouth plugging was indicated by activation energies lower than 40 kJ/mol.

Now, unlike the unhydrated calcines, the CaO ultimate conversions in the hydrated/recalcined calcines, demonstrated in Figure 9, seem to be insensitive to the temperature increase indicating the nonexistence of significant pore diffusion limitations nor pore mouth plugging by the impervious sulfation product ($CaSO_4$). This was also verified by a linear Arrhenius relationship and the relatively high apparent activation energy of 198 kJ/mol throughout the whole test temperatures (see Table 2). The insignificant pore diffusion resistance in the hydrated/recalcined calcine is probably because of its improved pore shape (plate-like pores) over that of the unhydrated one (spherical pores) as was discovered by Bruce et al. (1989). In a previous communication (Al-Shawabkeh et al., 1994), we also measured the adsorption/desorption isotherms of the calcines (CaO) derived from both a hydrate (H-CaO) and a carbonate (C-CaO), and proved that the specific surface areas and volumes of the plate-shaped pores in the H-CaO calcine were larger than those of the spherical pores in the C-CaO calcine.

In summary, the current TGA study calls attention to water hydration/recalcination of dolomitic calcine as a highly effective and inexpensive method for curtailing SO_2 emissions from a coal-fired FBC. Upon sulfation tests for 1 h under different SO_2 concentrations (0.11–0.31 vol. %) and temperatures (1,073–1,173 K), the achieved SO_2 capture (as CaO conversion into $CaSO_4$) by the hydrated/recalcined dolomitic calcine was 1.3–1.6 times higher in comparison to that of the unhydrated one.

Conclusions

Water hydration/recalcination of a dolomitic sorbent to improve its affinity for SO_2 removal in a TGA was investigated. Parameters affecting hydration, such as hydration temperature and time, were studied, and findings showed that 1 h and 80°C were the best hydration parameters as they led to fourfold and fivefold increases in the specific pore surface area and volume of the hydrated/recalcined samples, respectively. Due to these improved pore characteristics, the SO_2 capture (in terms of CaO conversion into $CaSO_4$) achieved by the hydrated/recalcined calcine was 1.3–1.6 times higher than that of the unhydrated one after a 1 h exposure to different SO_2 concentrations (0.11–0.31 vol. %) at different temperatures (1,073–1,173 K).

The enhanced CaO utilization in the hydrated/recalcined sample was attributed to the absence of significant pore diffusional limitations, at least during the early reaction times, evidenced by the high apparent activation energy of 198 kJ/mol. On the contrary, the relativey low CaO utilization in the unhydrated calcine was ascribed to the severe pore diffusional limitations that resulted in a drop in its apparent activation energy from 149 to 85 kJ/mol at temperatures higher than 1,123 K.

Acknowledgments

The authors gratefully acknowledge the generous financial support from NEDO (New Energy and Development Organization, Japan) without which this work would not have been possible.

Literature Cited

Al-Shawabkeh, A., H. Matsuda, and M. Hasatani, "Comparative Reactivity of $Ca(OH)_2$-Derived Oxides for SO_2 Capture," *J. Chem. Eng. Japan*, **27**(5), 650 (1994).

Al-Shawabkeh, A., H. Matsuda, and M. Hasatani, "Utilization of Highly Improved Fly Ash for SO_2 Capture," *J. Chem. Eng. Japan*, **28**(6), 53 (1995).

Borgwardt, R. H., "Kinetics of the Reaction of SO_2 with Calcined Limestone," *Environ. Sci. Technol.*, **4**(1), 59 (1970).

Borgwardt, R. H., and R. D. Harvey, "Properties of Carbonate Rocks Related to SO_2 Reactivity," *Environ. Sci. Technol.*, **6**(4), 350 (1972).

Bruce, K. R., B. K. Gullett, and L. O. Beach, "Comparative SO_2 Reactivity of CaO Derived from $CaCO_3$ and $Ca(OH)_2$," *AIChE J.*, **35**(1), 37 (1989).

Chang, E. Y., and G. Thodos, "Complex Nature of the Sulfation Reaction of Limestone and Dolomites," *AIChE J.*, **30**(3), 450 (1984).

Ciambelli, P., D. Lucarelli, and R. Valentino, "Sulfur Dioxide Reactivity of Carbonate Rocks: 3. Influence of Porosity and Purity of Sorbents," *Fuels*, **64**, 816 (1985).

Cole, J. A., J. C. Kramlich, W. R. Seeker, G. D. Silcox, G. H. Newton, D. J. Harrison, and D. W. Pershing, "Fundamental Studies of Sorbent Reactivity in Isothermal Reactors," *Proc. Joint Symp. on Dry SO_2 and Simultaneous SO_2/NO_x Control Technol.*, EPRI CS-4966, Electrical Power Research Inst., Palo Alto, CA (1986).

Couturier, M. F., D. L. Marquis, F. R. Steward, and Y. Volmerange, "Reactivation of Partially-Sulphated Limestone Particles from a CFB Combustor by Hydration," *Can. J. Chem. Eng.*, **72**, 91 (1994).

Dean, J. A., *Lange's Handbook of Chemistry*, 12th ed., McGraw-Hill, New York (1979).

Dennis, J. S., and A. N. Hayhurst, "The Effect of CO_2 on the Kinetics and Extent of Calcination of Limestone and Dolomite Particles in Fluidized Beds," *Chem. Eng. Sci.*, **42**(10), 2361 (1987).

Dogu, T., "The Importance of Pore Structure and Diffusion in the Kinetics of Gas-Solid Non-Catalytic Reactions: Reaction of Calcined Limestone with SO_2," *Chem. Eng. J.*, **21**, 213 (1981).

Hartman, M., and R. W. Coughlin, "Reaction of Sulfur Dioxide with Limestone and the Influence of Pore Structure," *Ind. Eng. Chem. Process Des. Dev.*, **13**(3), 248 (1974).

Hartman, M., and R. W. Coughlin, "Reaction of Sulfur Dioxide with Limestone and the Grain Model," *AIChE J.*, **22**(3), 490 (1976).

Howard, J. R., *Fluidized Beds: Combustion and Applications*, 1st ed., Applied Science Publishers, Barking, Essex, England, p. 221 (1983).

Montagna, J. C., J. F. Lenc, G. J. Vegel, and A. A. Jonke, "Regeneration of Sulfated Dolomite from a Coal-Fired FBC Process by Reductive Decomposition of Calcium Sulfate in a Fluidized Bed," *Ind. Eng. Chem. Process Des. Dev.*, **16**(2), 230 (1977).

Münzner, H., B. Bonn, and H. Schilling, "Reduction of Sulphur Dioxide by Addition of Limestone in Fluidized Bed Combustion," *Ger. Chem. Eng.*, **8**, 104 (1985).

Murthi, K. S., D. Harrison, and R. K. Chan, "Reaction of Sulfur Dioxide with Calcined Limestones and Dolomites," *Environ. Sci. Technol.*, **5**(9), 776 (1971).

Pigford, R. L., and G. Sliger, "Rate of Diffusion Controlled Reaction between a Gas and a Porous Solid Sphere," *Ind. Eng. Chem. Process Des. Dev.*, **12**(1), 85 (1973).

Potter, A. E., "Sulfur Oxide Capacity of Limestone," *Am. Ceramic Soc. Bull.*, **48**, 855 (1969).

"Powder Diffraction File," *Hanawalt Search Manual*, International Center for Diffraction Data, Newtown Square, PA (1993).

Schmal, D., "Improving the Action of Sulfur Sorbents in Fluidized-Bed Combustion of Coal," *Ind. Eng. Chem. Process Des. Dev.*, **24**(1), 72 (1985).

Shearer, J. A., G. W. Smith, K. M. Myles, and I. Johnson, "Hydration Enhanced Sulfation of Limestone and Dolomite in the Fluidized-Bed Combustion of Coal," *J. Air Pollut. Control Assoc.*, **30**, 684 (1980).

Stouffer, M. R., and H. Yoon, "An Investigation of CaO Sulfation Mechanisms in Boiler Sorbent Injection," *AIChE J.*, **35**(8), 1253 (1989).

Yang, R. T., "Enhancement of Sorbent Utilization in Fluidized-Bed Combustion," *Fuel*, **57**, 709 (1978).

Yang, R. T., and M. S. Shen, "A Regenerative Process for Fluidized-Bed Combustion of Coal with Lime Additives," *Ind. Eng. Chem. Process Des. Dev.*, **18**(2), 312 (1979).

Yaverbaum, L., *Fluidized-Bed Combustion of Coal and Waste Materials*, Noyes Data Corporation, Park Ridge, NJ (1977).

Zarkanitis, S., and S. V. Sotirchos, "Pure Structure and Particle Size Effects on Limestone Capacity for SO_2 Removal," *AIChE J.*, **35**(5), 821 (1989).

Manuscript received Apr. 22, 1996, and revision received July 19, 1996.