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Effects of Flue Gas Components on the Reaction of $\text{Ca}(\text{OH})_2$ with SO_2

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A differential fixed-bed reactor was employed to study the effects of the flue gas components, H_2O , CO_2 , NO_x , and O_2 , on the reaction between $\text{Ca}(\text{OH})_2$ and SO_2 under conditions similar to those in the bag filters of a spray-drying flue gas desulfurization (FGD) system. The presence of CO_2 with SO_2 in the gas phase enhanced the sulfation of $\text{Ca}(\text{OH})_2$ only when NO_x was also present. When either NO_x (mainly NO) or O_2 was present with SO_2 , the enhancement effect was slight, but became great when both NO_x and O_2 were present, and was even greater when CO_2 was also present. The great enhancement effect exerted by the presence of NO_x/O_2 resulted from the rise in the NO_2 concentration, which enhanced the oxidation of HSO_3^- and SO_3^{2-} to SO_4^{2-} in the water layer adsorbed on $\text{Ca}(\text{OH})_2$ surface and the formation of deliquescent salts of calcium nitrite and nitrate. The enhancement effect due to the presence of NO_x/O_2 was more pronounced when the relative humidity was above that at which the salts deliquesced; the extent of sulfation was more than twice that obtained when SO_2 alone was present. The presence of H_2O , CO_2 , NO_x , and O_2 in the flue gas is beneficial to the SO_2 capture in the low-temperature dry and semidry FGD processes. The presence of NO_x/O_2 also enhanced CO_2 removal when SO_2 was absent.

Introduction

SO_2 is one of the major air pollutants emitted from power stations burning fossil fuels. Hydrated lime ($\text{Ca}(\text{OH})_2$) is the commonly used sorbent for SO_2 removal in flue gas desulfurization (FGD) processes, such as the dry and semidry FGD processes. In the low-temperature dry process or in the dry stage of the semidry process, SO_2 is captured by $\text{Ca}(\text{OH})_2$ particles through the reaction between them under humid conditions.

Besides SO_2 and H_2O , the gaseous species in flue gas, NO_x , CO_2 , and O_2 ,¹ also take part in the reaction of $\text{Ca}(\text{OH})_2$. However, most studies on the sulfation of $\text{Ca}(\text{OH})_2$ at low temperatures have been carried out without the presence of NO_x , CO_2 , and O_2 .^{2,3} Nevertheless, there are some reports on the effects of these species on the sulfation of $\text{Ca}(\text{OH})_2$.

The study of Chu and Rochelle⁴ revealed that the presence of NO_x in the gas phase has a negligible effect on the reaction of $\text{Ca}(\text{OH})_2$ with SO_2 . They reacted $\text{Ca}(\text{OH})_2$ with a gas mixture containing 14% H_2O , 500 ppm SO_2 , 7% O_2 , 10% CO_2 , and 500 ppm NO_x at 66 and 92 °C for 1 h. However, when NO_2 was used instead of NO_x , Nelli and Rochelle⁵ found that the SO_2 removal by $\text{Ca}(\text{OH})_2$ at 70 °C and 60% relative humidity (RH) is enhanced by NO_2 , but the enhancement effect is reduced when O_2 is also present. Ishizuka et al.⁶ pointed that NO_x barely affects the SO_2 removal efficiency in the low-temperature semidry FGD process, but NO_x significantly enhances the SO_2 removal efficiency in the high-temperature dry FGD process: the SO_2 removal efficiency is very low without the presence of NO_x . They also reported that the main product of the semidry FGD is CaSO_3 and that of the high-temperature dry FGD is CaSO_4 .

Ho and Shih⁷ found that, with the presence of O_2 , the SO_2 capture of $\text{Ca}(\text{OH})_2$ increases when the RH is above 60% and decreases when the RH is lower, but the O_2 concentration (1–5.4%) does not affect the reaction. Ho et al.⁸ found that the

total conversion of $\text{Ca}(\text{OH})_2$ increases when both SO_2 and CO_2 are present with or without O_2 . Later, Liu and Shih⁹ reported that the presence of CO_2 with SO_2 increases the total conversion of $\text{Ca}(\text{OH})_2$, but does not affect the yield of CaSO_3 . However, Klingspor et al.¹⁰ and Irabien et al.¹¹ reported that CO_2 and O_2 have no influence on the reaction, and Moyeda et al.¹² and Seeker et al.¹³ reported a decrease in the SO_2 capture with the presence of CO_2 .

Understanding the effects of the flue gas components on the reaction of $\text{Ca}(\text{OH})_2$ is important to the design and operation of the FGD processes. However, the effects reported in the literature are inconsistent. Thus, it is worthwhile to undertake a more thorough study on this subject. In the present study, $\text{Ca}(\text{OH})_2$ was reacted with gas mixtures containing different combinations of the gaseous species SO_2 , CO_2 , NO_x , and O_2 in addition to H_2O , in order to elucidate the effects of H_2O , CO_2 , NO_x , and O_2 on the reaction of $\text{Ca}(\text{OH})_2$ with SO_2 at low temperatures. The major findings of this study are that the presence of $\text{CO}_2/\text{NO}_x/\text{O}_2$ has a positive effect on the sulfation of $\text{Ca}(\text{OH})_2$, especially at high RHs, and that the presence of NO_x/O_2 enhances CO_2 removal by $\text{Ca}(\text{OH})_2$ with SO_2 absent.

Experimental Section

Sulfation Test. The hydrated lime used was reagent-grade $\text{Ca}(\text{OH})_2$ (purity > 95%; Hayashi Pure Chemical Industries, Ltd.), which had a BET surface area of 10.4 m²/g.

Experiments for the reaction of the sorbent were carried out using a differential fixed-bed reactor made of glass. The experimental setup is shown in Figure 1. About 40 mg of $\text{Ca}(\text{OH})_2$ powder was used for each run. The $\text{Ca}(\text{OH})_2$ powder was dispersed into quartz wool; the wool was then set into the sample pan. The sample pan had dimensions of 10 mm o.d. and 15 mm height and was perforated at the bottom to facilitate the passage of the sweep gas. The sweep gas entered the bottom of the reactor, passed through the 25 mm i.d. and 365 mm length outer tube, and went downward through the sample pan and the 10 mm i.d. and 315 mm length inner tube. The reactor was heated by a heating tape. The gas mixture comprised SO_2 , CO_2 , NO_x , O_2 , H_2O , and N_2 . The H_2O vapor was provided by a water

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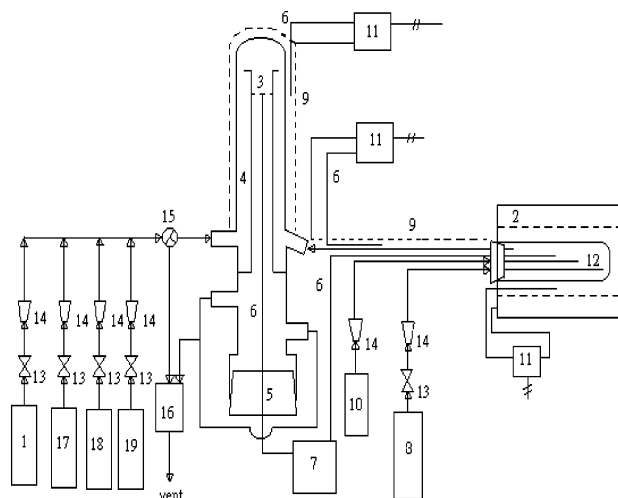


Figure 1. Schematic diagram of experimental apparatus: 1, SO₂ cylinder; 2, furnace; 3, Pyrex sample pan; 4, reactor; 5, rubber stopper; 6, thermocouple; 7, temperature recorder; 8, N₂ cylinder; 9, heating tape; 10, syringe pump; 11, temperature controller; 12, evaporator; 13, needle valve; 14, rotameter; 15, three-way valve; 16, SO₂ absorber; 17, O₂ cylinder; 18, CO₂ cylinder; 19, NO_x cylinder.

evaporator, and the other gases, with purities >99%, were supplied from cylinders. The NO_x gas consisted of NO (>97%) and NO₂. The concentrations of the components in the gas mixtures were controlled by adjusting their flow rates. As shown in Table 1, the concentrations of SO₂, CO₂, NO_x, and O₂ were in the typical concentration ranges in the flue gas evolved in burning medium-sulfur coal.¹

Prior to each run, the sample bed was humidified for 30 min with humid N₂ at a selected relative humidity and temperature under which the subsequent reaction experiment was performed. After humidification, the reactive gases were admitted into the reactor to start the run. The total gas flow rate was 4 L/min (STP). The reaction time was 1 h. At least two repeated runs were undertaken for each set of experimental conditions.

Chemical and Physical Analyses. After the reaction ended, the sample was vacuum-dried before it was subjected to analysis. The amount of Ca(OH)₂ remaining in a reacted sample was determined by acid/base titration. The amount of sulfite formed was determined by iodimetric titration, the amounts of sulfate, nitrite, and nitrate were determined by ion chromatography, and the amount of Ca was determined by EDTA titration. From the results of the above analyses, the mole fractions of Ca(OH)₂ remaining (X_{HL}), calcium sulfite (X_{S1}), calcium sulfate (X_{S2}), calcium nitrite (X_{N1}), and calcium nitrate (X_{N2}) were calculated, and the mole fraction of calcium carbonate and/or trace amount of inert substance (X_C) was $1 - X_{HL} - X_{S1} - X_{S2} - X_{N1} - X_{N2}$. The detailed procedures of the analyses are described elsewhere.¹⁴ The reacted samples were also analyzed by X-ray diffraction (XRD) and observed by scanning electron microscopy (SEM).

Results and Discussion

Effects of Flue Gas Components on the Reaction of Ca(OH)₂. The mole fractions of reaction products and Ca(OH)₂ remaining after Ca(OH)₂ had reacted with various gas mixtures at 60 °C and 80% RH for 1 h are listed in Table 1. The gas mixtures contained different combinations of SO₂, CO₂, NO_x, and O₂ in addition to water vapor and N₂. The 1 h reaction time was long enough for the sulfation of Ca(OH)₂ to reach the ultimate extent.^{3,14} The absolute errors of the mole fractions measured were about 0.02; thus a value of mole fraction around

0.02 shown in Table 1 indicates just the presence of the species instead of its true value.

As shown in Table 1, when SO₂ alone reacted with Ca(OH)₂, calcium sulfite was formed, and X_{S1} was 0.29. When either NO_x or O₂ was also present, a small amount of calcium sulfate ($X_{S2} = 0.05$) was generated, and X_{S1} slightly increased with the presence of O₂. Similar results have been reported for Ca(OH)₂ reacted with SO₂ alone^{2,3} and with SO₂ and O₂.⁷

Ca(OH)₂ is also reactive toward CO₂.^{8,15} Table 1 shows that X_C was 0.34 when CO₂ alone was present. However, when both SO₂ and CO₂ were present, X_C was small (about 0.06), and X_{S1} was almost the same as that obtained when SO₂ alone was present. Therefore, CO₂ nearly did not affect the ultimate SO₂ capture of Ca(OH)₂. It has been reported that when both SO₂ and CO₂ are present, Ca(OH)₂ reacts with both gases to form sulfite and carbonate in the initial stage of reaction, but the carbonate formed reacts further with SO₂ to form sulfite; thus the ultimate X_C is small.^{8,9}

The gas mixture containing SO₂, CO₂, and O₂ was to simulate the flue gas after the NO_x removal unit and before the SO₂ removal unit. Under this gas mixture, the total conversion to sulfite and sulfate (about 0.34) was close to that obtained when only SO₂ and O₂ were present (about 0.37), but smaller than that obtained (about 0.40) when the gas mixture contained SO₂, CO₂, and NO_x.

As seen in Table 1, Ca(OH)₂ barely reacted with NO_x when NO_x presented alone. However, the conversion of Ca(OH)₂ to form calcium nitrite and nitrate was appreciable when both NO_x and O₂ were present; X_{N1} and X_{N2} were about 0.15 and 0.03, respectively. The reacted sample appeared as yellow mud, indicating an excessive amount of water had been collected by the sample. It is known that calcium nitrite and nitrate are deliquescent salts and the color of calcium nitrite is yellow.¹⁶

The presence of NO_x and O₂ together with SO₂ markedly increased the SO₂ captured by Ca(OH)₂. As shown in Table 1, both X_{S1} and X_{S2} were about 0.28, but nitrite and nitrate were hardly detected. The sample became a wet white cake with some yellow spots after the reaction. This appearance indicates that the deliquescent species played an important role during the reaction.

When Ca(OH)₂ reacted with the NO_x, O₂, and CO₂ mixture, the major product was CaCO₃. The value of X_C , 0.84, was much larger than that obtained when CO₂ presented alone. The reacted sample appeared as white mud. This again indicates that a great quantity of water had been collected by the sample during the reaction when the gas mixture contained both NO_x and O₂.

The gas mixture containing SO₂, NO_x, CO₂, and O₂ was to simulate the typical flue gas before entering the NO_x and SO₂ removal units. As shown in Table 1, under this gas mixture, X_{S1} and X_{S2} were 0.34 and 0.32, respectively, X_C was small, and X_{N1} and X_{N2} were nearly zero. Evidently, this gas mixture greatly enhanced the extent of sulfation of Ca(OH)₂, which was more than twice that obtained when SO₂ alone was present, and was 0.10 greater than that obtained when only SO₂, NO_x, and O₂ were present. Therefore, the presence of NO_x, CO₂, and O₂ together with SO₂ in the flue gas would be beneficial to the SO₂ removal using hydrated lime. The reacted sample in this case also became a cake similar to that observed when only SO₂, NO_x, and O₂ were present.

The effects of the component gas-phase concentrations on the ultimate sulfation extent of Ca(OH)₂ were also studied by varying the SO₂ concentration from 100 to 1000 ppm, NO_x from 300 to 600 ppm, CO₂ from 3.2 to 12.6%, and O₂ from 1.0 to 5.4%, and negligible effects were found.

Table 1. Mole Fractions of Calcium Hydroxide (X_{HL}), Sulfite (X_{S1}), Sulfate (X_{S2}), Nitrite (X_{N1}), Nitrate (X_{N2}), and Carbonate (X_C) in Reacted Samples after $\text{Ca}(\text{OH})_2$ Samples Reacted with Different Gas Mixtures at 60 °C for 1 h

| RH, % | SO_2 , ppm | NO_x , ppm | CO_2 , % | O_2 , % | X_{HL} | X_{S1} | X_{S2} | X_{N1} | X_{N2} | X_C |
|-------|---------------------|---------------------|-------------------|------------------|----------|----------|----------|----------|----------|-------|
| 80 | 1000 | 0 | 0 | 0 | 0.68 | 0.29 | 0 | 0 | 0 | 0.03 |
| 80 | 1000 | 0 | 12.6 | 0 | 0.65 | 0.29 | 0 | 0 | 0 | 0.06 |
| 80 | 1000 | 600 | 0 | 0 | 0.63 | 0.29 | 0.05 | 0.01 | 0 | 0.02 |
| 80 | 1000 | 0 | 0 | 5 | 0.60 | 0.32 | 0.05 | 0 | 0 | 0.03 |
| 80 | 1000 | 600 | 0 | 5 | 0.41 | 0.28 | 0.28 | 0 | 0 | 0.03 |
| 80 | 1000 | 600 | 12.6 | 0 | 0.53 | 0.34 | 0.06 | 0.01 | 0 | 0.07 |
| 80 | 1000 | 0 | 12.6 | 5 | 0.61 | 0.27 | 0.07 | 0 | 0.01 | 0.04 |
| 80 | 0 | 0 | 12.6 | 0 | 0.66 | 0 | 0 | 0 | 0 | 0.34 |
| 80 | 0 | 600 | 0 | 0 | 0.95 | 0 | 0 | 0.01 | 0.01 | 0.03 |
| 80 | 0 | 600 | 0 | 5 | 0.77 | 0 | 0 | 0.15 | 0.03 | 0.05 |
| 80 | 0 | 600 | 12.6 | 5 | 0.14 | 0 | 0 | 0.01 | 0.01 | 0.84 |
| 80 | 1000 | 600 | 12.6 | 5 | 0.29 | 0.34 | 0.32 | 0 | 0.01 | 0.04 |
| 70 | 1000 | 600 | 12.6 | 5 | 0.35 | 0.30 | 0.32 | 0 | 0.01 | 0.02 |
| 50 | 1000 | 600 | 12.6 | 5 | 0.58 | 0.20 | 0.09 | 0 | 0.01 | 0.12 |
| 30 | 1000 | 600 | 12.6 | 5 | 0.73 | 0.11 | 0.05 | 0 | 0 | 0.11 |
| 70 | 1000 | 0 | 0 | 0 | 0.76 | 0.21 | 0 | 0 | 0 | 0.03 |
| 50 | 1000 | 0 | 0 | 0 | 0.80 | 0.17 | 0 | 0 | 0 | 0.03 |
| 30 | 1000 | 0 | 0 | 0 | 0.87 | 0.10 | 0 | 0 | 0 | 0.03 |

Effect of RH on the Reaction of $\text{Ca}(\text{OH})_2$. The effect of RH or water vapor on the reaction of $\text{Ca}(\text{OH})_2$ was studied with two gas mixtures: one containing SO_2 alone and one simulating the typical flue gas composition. The results for 1 h reaction at 60 °C and 30–80% RH are also listed in Table 1.

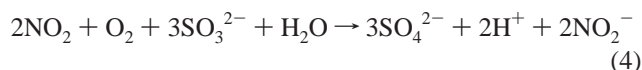
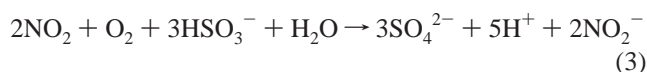
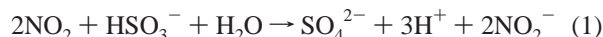
As seen in Table 1, under either gas mixture the conversion of $\text{Ca}(\text{OH})_2$, $1 - X_{HL}$, increased as RH increased, but the conversion under the synthesized flue gas was much greater at each RH, especially when the RH was high ($\geq 70\%$). Both X_{S1} and X_{S2} increased with increasing RH, but there were no marked changes in X_{S1} and X_{S2} when RH increased from 70 to 80%. X_{S2} was smaller than 0.09 when $\text{RH} \leq 50\%$, but increased drastically to 0.32 when RH increased to 70%. The $\text{CaSO}_3/\text{CaSO}_4$ molar ratio was about 1 at 70 and 80% RH, but was about 2 at 30 and 50% RH. X_C was about 0.12 when RH was low ($\leq 50\%$), but was very small when RH was high, indicating that high RH favored the sulfation of $\text{Ca}(\text{OH})_2$ instead of the carbonation. The mole fractions of $\text{Ca}(\text{NO}_2)_2$ and $\text{Ca}(\text{NO}_3)_2$ were very small (≤ 0.01) at each RH. Nevertheless, these two species were helpful to the conversion of $\text{Ca}(\text{OH})_2$.

SEM Observations. The unreacted $\text{Ca}(\text{OH})_2$ sample is a white powder. When NO_x and O_2 were not present simultaneously in the gas phase, the sulfated samples were still white powders. The SEM micrographs shown in Figure 2 reveal that the sample particles after reacting with SO_2 (Figure 2a), CO_2 (Figure 2b), and $\text{SO}_2/\text{CO}_2/\text{NO}_x$ (Figure 2d) are similar in morphology: the product grains densely cover the particle surface. However, the particles that reacted with SO_2/CO_2 have a quite different appearance (Figure 2c): rods and plates of calcium sulfite appear on the particle surface.

The samples after reacting with $\text{SO}_2/\text{NO}_x/\text{O}_2$ or $\text{SO}_2/\text{CO}_2/\text{NO}_x/\text{O}_2$ at $\text{RH} \geq 70\%$ became a wet white cake with some yellow spots of calcium nitrite. The samples were vacuum-dried at 60 °C and ground to fine particles. As shown in Figure 2e,f, the particles seem to have larger grains and pores.

Effects of the Presence of both NO_x and O_2 . At low temperatures, the reaction between $\text{Ca}(\text{OH})_2$ and SO_2 requires the presence of water vapor; the higher the RH, the greater the extent of reaction of $\text{Ca}(\text{OH})_2$. Under humid circumstances, water molecules are adsorbed on the surface of $\text{Ca}(\text{OH})_2$, forming a thin water layer, e.g., 2.3 monolayers thick at 70% RH.² SO_2 molecules in the gas phase are adsorbed onto the water layer and combine with water to form $\text{SO}_2 \cdot \text{H}_2\text{O}$. $\text{SO}_2 \cdot \text{H}_2\text{O}$ may then dissociate to H^+ , HSO_3^- , and SO_3^{2-} , and these ions subsequently react with $\text{Ca}(\text{OH})_2$ to form CaSO_3 .^{2,3} When O_2 or NO_x (mainly NO) is also present in the gas phase, some O_2

or NO_x molecules are also present in the water layer and oxidize HSO_3^- and SO_3^{2-} to SO_4^{2-} ; however, the extent of oxidation is low due to the low solubility of O_2 or NO_x in water. When both O_2 and NO_x are present in the gas phase, the tendency of approach to the equilibrium of the $\text{O}_2/\text{NO}/\text{NO}_2$ system raises the concentration of NO_2 in the gas phase to a higher value.¹⁷ As NO_2 is a much stronger oxidant and more soluble in water than NO and O_2 ,^{17,18} there are more NO_2 molecules present in the water layer, and the oxidation of HSO_3^- and SO_3^{2-} to SO_4^{2-} is enhanced, which induces more SO_2 molecules to be captured into the water layer. The reactions that take place in the water layer involving NO_2 can be represented by the following stoichiometric equations:^{17,18}



As seen in the above equations, H^+ , NO_2^- , and NO_3^- are formed when NO and NO_2 react with HSO_3^- , SO_3^{2-} , and water. These ions react with $\text{Ca}(\text{OH})_2$ to form $\text{Ca}(\text{NO}_2)_2$ and $\text{Ca}(\text{NO}_3)_2$. Since $\text{Ca}(\text{NO}_2)_2$ and $\text{Ca}(\text{NO}_3)_2$ are deliquescent salts, their deliquescence would collect a great quantity of water on the sample surface, and thus greatly enhance the reaction of $\text{Ca}(\text{OH})_2$ with the reactive gases. This is thought to be another reason for the increase in SO_2 capture by $\text{Ca}(\text{OH})_2$ with NO_x/O_2 present, besides the oxidation of bisulfite and sulfite to sulfate mentioned previously. The high extent of carbonation when $\text{Ca}(\text{OH})_2$ reacted with the $\text{CO}_2/\text{NO}_x/\text{O}_2$ mixture is believed to be also caused by the deliquescence of these salts.

The marked difference in the conversion of $\text{Ca}(\text{OH})_2$ between 50 and 70% RH as shown in Table 1 indicates that the deliquescence RH, i.e., the RH at which a salt starts to deliquesce,¹⁸ of $\text{Ca}(\text{NO}_2)_2$ or $\text{Ca}(\text{NO}_3)_2$ is in this RH range. This was also confirmed by that the samples reacted at $\text{RH} \geq 70\%$ became a white cake, whereas those reacted at $\text{RH} \leq 50\%$ were

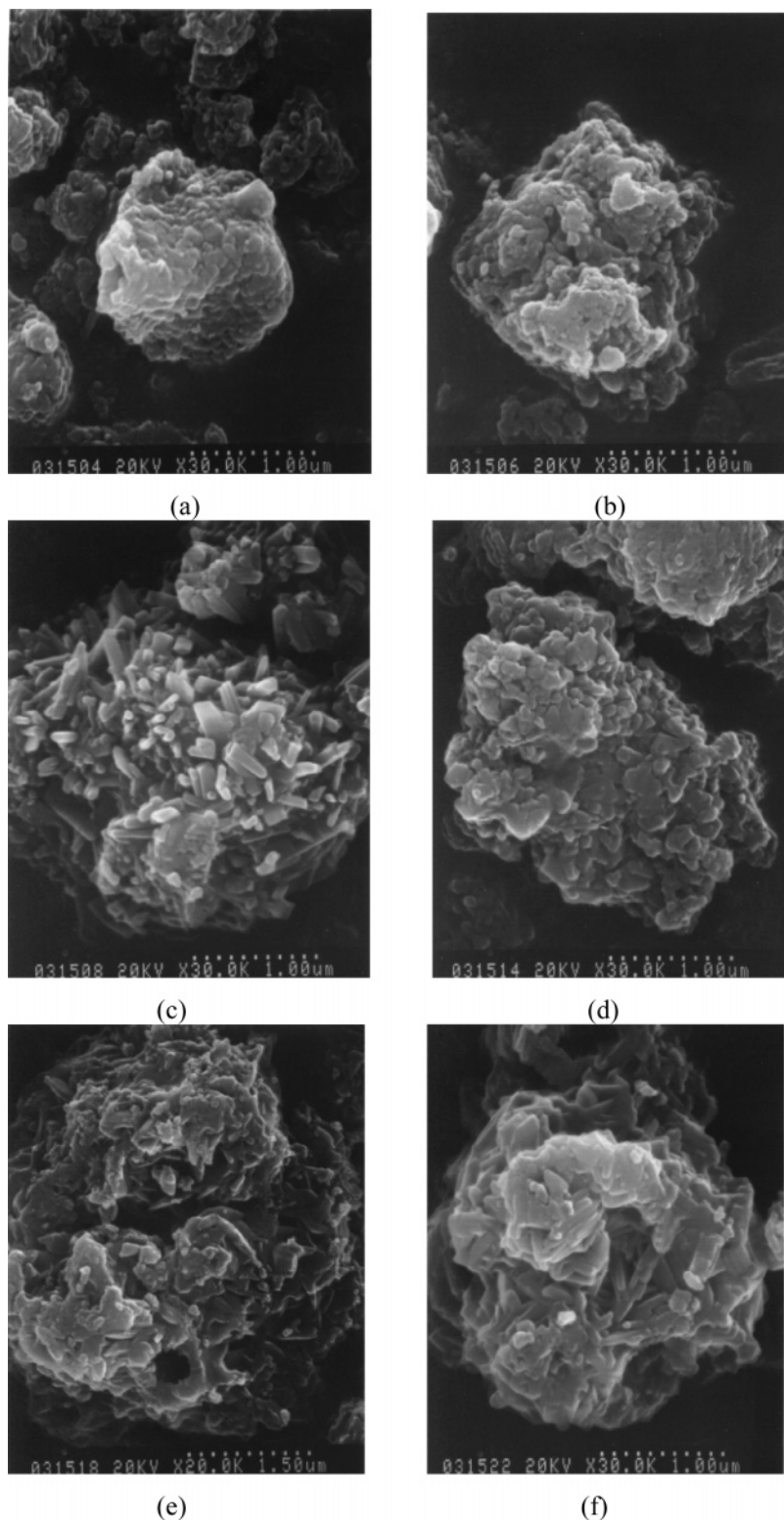


Figure 2. SEM micrographs of $\text{Ca}(\text{OH})_2$ reacted at 60 °C, 80% RH, and different gas compositions for 1 h: (a) 1000 ppm SO_2 ; (b) 12.6% CO_2 ; (c) 12.6% CO_2 and 1000 ppm SO_2 ; (d) 12.6% CO_2 , 600 ppm NO_x , and 1000 ppm SO_2 ; (e) 5% O_2 , 600 ppm NO_x , and 1000 ppm SO_2 ; (f) 12.6% CO_2 , 600 ppm NO_x , 5% O_2 , and 1000 ppm SO_2 .

still in powder form. The deliquescence RH of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ has been reported to be 50.8% at 25 °C;¹⁹ its deliquescence RH at 60 °C would be higher according to the prediction equation (9.72) given in ref 18 because its heat of solution is negative.²⁰

This study has shown that the presence of NO_x/O_2 in the gas phase can enhance the reaction of $\text{Ca}(\text{OH})_2$ with SO_2 . This finding is different from that reported by Chu and Rochelle,⁴

Nelli and Rochelle,⁵ and Ishizuka et al.⁶ This discrepancy probably is due to the differences in the relative humidity and the reaction temperature used. Chu and Rochelle carried out the reaction experiments at 54% RH (66 °C) and 19% RH (92 °C), and Nelli and Rochelle at 60% RH (70 °C). Their relative humidity at each temperature may be lower than the deliquescence relative humidity of $\text{Ca}(\text{NO}_2)_2$ or $\text{Ca}(\text{NO}_3)_2$ at that

temperature; thus the enhancement effect due to the presence of NO_x/O_2 was absent.

During the reaction of $\text{Ca}(\text{OH})_2$, most of the sulfite, sulfate, and carbonate ions in the water layer on the $\text{Ca}(\text{OH})_2$ surface precipitate, once in contact with calcium ions, to form a product layer of calcium salts, due to the relative insolubility of these salts. The buildup of the product layer impedes the reaction between hydrogen ions and hydroxide ions or $\text{Ca}(\text{OH})_2$ and thus slows the overall reaction rate. Meanwhile, the water layer is gradually acidified. When the product layer becomes impervious, the reaction ceases, leaving part of $\text{Ca}(\text{OH})_2$ unreacted.^{3,15} This is the reason for the incomplete conversion of $\text{Ca}(\text{OH})_2$ at reaction time as long as 1 h.

As pointed out by Ho et al.⁸ and Liu and Shih,⁹ when CO_2 is present with SO_2 , CaCO_3 crystals form in the early stage of reaction and react again to form sulfite in the latter stage, leaving less carbonate at higher RHs. The mole fractions of CaCO_3 measured for the reacted samples in this study are in agreement with the previous results.

The additional SO_2 capture when CO_2 was added together with NO_x or NO_x/O_2 may be due to NO_x enhancing the formation of CaCO_3 and the re-reaction of CaCO_3 to form CaSO_3 and CaSO_4 causing the impervious product layer to form at higher extents of reaction.

Although calcium nitrite and nitrate played an important role in collecting water when samples reacted with gas mixtures containing NO_x and O_2 , only small mole fractions of calcium nitrite and nitrate were measured for the reacted samples, except for the case when $\text{Ca}(\text{OH})_2$ reacted with the NO_x/O_2 mixture. This outcome is thought to be due to their high solubilities. Thus, as the water layer was acidified by the absorption of SO_2 or CO_2 in the latter stage of reaction, the high concentrations of nitrite and nitrate ions would cause them to form HNO_2 and HNO_3 or to react in the reverse direction of reactions 5 and 6, resulting in low concentrations of these ions. Furthermore, the reacted samples were vacuum-dried before being subjected to analysis. During vacuum-drying of a wet reacted sample, the nitrite and nitrate ions might transform to NO , NO_2 , HNO_2 , and HNO_3 , which subsequently evaporate. The above processes, therefore, would result in small amounts of calcium nitrite and nitrate contained in a dried sample which had reacted with SO_2 or CO_2 with the presence of NO_x and O_2 .

Conclusion

The presence of CO_2 with SO_2 in the gas phase enhanced the sulfation of $\text{Ca}(\text{OH})_2$ only when NO_x was also present. When either NO_x (mainly NO) or O_2 was present with SO_2 , the enhancement effect was slight, but became great when both NO_x and O_2 were present, and was even greater when CO_2 was also present. The great enhancement effect exerted by the presence of NO_x/O_2 resulted from the rise in the NO_2 concentration, which enhanced the oxidation of HSO_3^- and SO_3^{2-} to SO_4^{2-} in the water layer adsorbed on $\text{Ca}(\text{OH})_2$ surface and the formation of deliquescent salts of calcium nitrite and nitrate. The enhancement effect due to the presence of NO_x/O_2 was more pronounced when the relative humidity was above that at which the salts deliquesced. The presence of H_2O , CO_2 , NO_x , and O_2 in the flue gas is beneficial to the SO_2 capture in the low-temperature dry and semidry FGD processes. The presence of NO_x/O_2 also enhanced CO_2 removal by $\text{Ca}(\text{OH})_2$ when SO_2 was absent.

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Notation

RH = relative humidity

X_C = molar fraction of CaCO_3 and/or trace amount of inert substance

X_{HL} = molar fraction of $\text{Ca}(\text{OH})_2$

X_{N1} = molar fraction of $\text{Ca}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$

X_{N2} = molar fraction of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$

X_{S1} = molar fraction of $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$

X_{S2} = molar fraction of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$

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