

## Kinetic Study of Domestic Limestone (Daesung)

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(Received 20 May 1999 • accepted 1 September 1999)

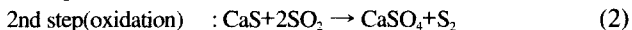
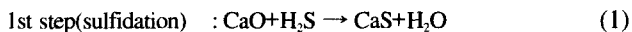
**Abstract**—Sulfidation and sulfation reactions of Daesung limestone, which is a calcium-based sorbent chosen out of domestic limestone for the removal of  $H_2S$  and  $SO_2$ , were investigated by using TGA (thermal gravimetric analyzer). Effects of  $H_2$  and  $H_2S$  on the sulfidation were also investigated. The conversion rate of  $CaS$  to  $CaSO_4$  in oxidation was low since the concentration of  $SO_2$  used for this study was low and  $CaO$  was not completely converted into  $CaS$ . It was observed that the effects of  $H_2$  concentration on the sulfidation were relatively small and the maximum conversion rate and reaction rate increased with increase of  $H_2S$  concentration. In the sulfation reaction, conversion rate could be raised with the injection of air at a sulfation reaction temperature above  $800^\circ C$ . However, the conversion rate decreased without the injection of air due to the blockage of sorbent pores.

Key words: Calcium-Based Sorbent, Sulfidation, Sulfation, Oxidation

### INTRODUCTION

The development of coal utilization technology has been extensively pursued worldwide since coal is abundant over the world compared to petroleum and will be available over the next 250 years. Environmentally attractive new coal utilization technologies such as IGCC (integrated coal gasification combined cycle) and PFBC-CC (pressurized fluidized bed combustion-combined cycle) emerged as a result of clean coal technology development. PFBC-CC has advantages of both atmospheric fluidized bed combustion and pressurized system such as minimization of system size, short constructive period, enhanced total heat efficiency, pollutant reduction and so on. With a consideration of the advantages, next generation PFBC-CC based on the gasification concept of IGCC was developed through extensive research in several countries such as UK, USA, and Sweden [Robert et al., 1983; Williamson, 1992].

Two pivotal technologies of new coal utilization, IGCC and PFBC-CC, have not been fully developed on a commercial scale, and still require study. One of main investigation areas is the development of sorbent used in the desulfurization process. Most coal contains sulfur naturally and the sulfur is converted to either  $H_2S$  by gasification or  $SO_2$  by combustion. In fluidized bed combustion, usually limestone as calcium based sorbents is infused directly to combustor in order to convert sulfur to  $CaS$  and/or  $CaSO_4$ . However, in the next generation PFBC system developed recently, the infusion method has a limitation due to the difference in process operation that some of coal is gasified in the first step like IGCC. The following method of desulfurization is called high temperature dry type desulfurization [DOE, 1993, 1994].



First,  $CaO$  is converted to  $CaS$  by reacting with  $H_2S$  and then  $CaS$  is converted to  $CaSO_4$  and sulfur element by reacting with  $SO_2$  in the oxidation step.  $SO_2$  produced in the regeneration process is used in the oxidation step [Ham and Heesink, 1996; Kim and Park, 1987].

The development of sorbent is one research field we can catch up with the level of developed countries' technology in a short period of time. It is urgently important to develop a sorbent since the desulfurization process is the only one which needs to be completed in the development of coal utilization combined cycle technologies [Lee et al., 1997; Kang et al., 1997; Yi et al., 1999].

The objective of this study is to investigate the reaction mechanism needed to apply new desulfurization concepts to the next generation PFBC. To fulfill this objective, reactivity of typical domestic Daesung limestone has been investigated in sulfation and sulfidation experiments.

### EXPERIMENT

Daesung (North Choongchung province, Danyang) limestone, a typical domestic limestone, was chosen as the experimental raw material. The size of sample was less than  $44\ \mu m$  and z-mill was used for crushing.

In this study, a thermal gravimetric analyzer (TGA) as shown in Fig. 1 was used. Gas flow rates were controlled by using MFCs (mass flow controller), and reaction gases were injected to TGA after being mixed in a mixing tank. To prevent the weight sensor of TGA from being corroded by the sulfur compounds, nitrogen gas flows from the back of the weight sensor to the vent line.

Total gas flow rate was 150 ml/min and limestone sample weight was about  $11 \pm 1\ mg$ . Composition of simulated gas was 30.7 vol%  $H_2$ , 6.8 vol%  $CO_2$ , 0.3 vol%  $H_2S$ , and balance  $N_2$ . Sulfidation temperature was  $850^\circ C$ , which has been reported as a typical desulfurization condition in a gasifier [KIER, 1996].

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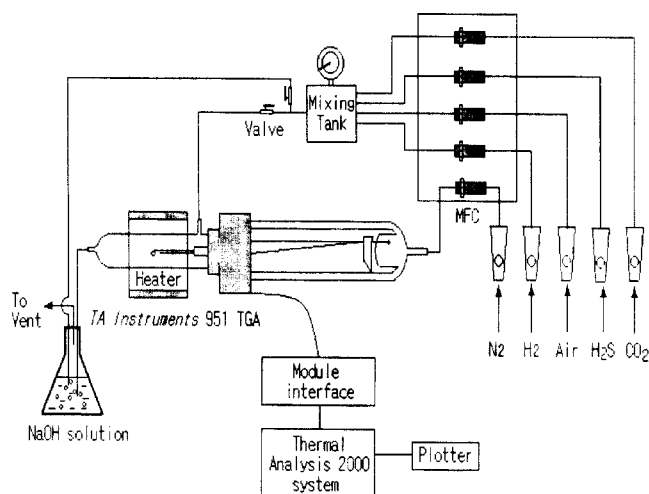


Fig. 1. Schematic diagram of TGA system.

H<sub>2</sub> was used instead of CO in simulated gas for safety. H<sub>2</sub>S concentration was changed as 0.3, 0.5, 0.8, and 1 vol%, respectively, at 850 °C.

To investigate effects of H<sub>2</sub>, isothermal experiments were carried in 850 °C at several H<sub>2</sub> concentrations of 0, 6.3, 12.6, 25.2, and 30.7 vol%, respectively. Gas composition for sulfation was 0.3 vol% SO<sub>2</sub> and balance N<sub>2</sub>. To investigate effects of air injection, experiments were carried out at the conditions of 0 and 5 vol% air.

In this study, both sulfidation and sulfation were performed without calcination. After a sample was loaded in TGA, isothermal reaction was performed right after the temperature reached to the sulfidation and sulfation reaction temperature in which the increment of temperature was 100 °C/min.

## RESULTS AND DISCUSSION

Results of the sulfidation experiment obtained with various H<sub>2</sub>S concentrations are shown in Figs. 2 and 3. When temperature reached to 850 °C where sulfidation experiment started,

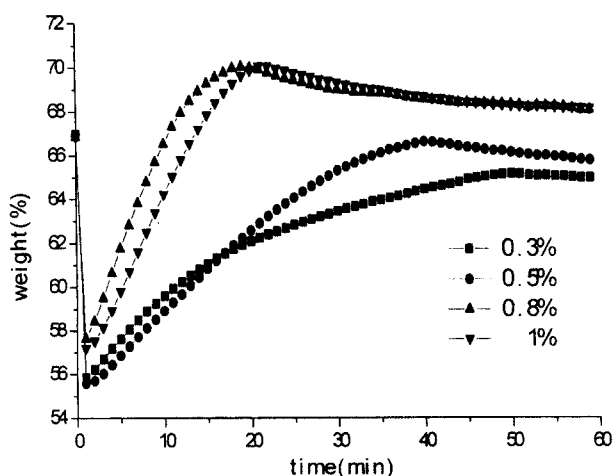


Fig. 2. Effects of H<sub>2</sub>S concentration on sulfidation reaction of Daesung limestone at 850 °C.

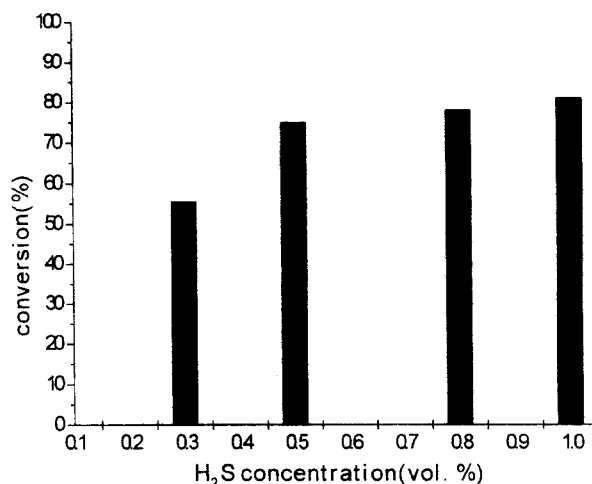


Fig. 3. Effects of H<sub>2</sub>S concentration on conversion of Daesung limestone at 850 °C.

weight loss of CaCO<sub>3</sub> was 42-44%, which indicates that CaCO<sub>3</sub> decomposed to CaO completely. The conversion rates of CaO to CaS with various H<sub>2</sub>S concentrations are shown in Fig. 3. Maximum conversion and reaction rate increase with increasing H<sub>2</sub>S concentrations. Maximum conversions were 55.6%, 75%, 78%, and 81% when H<sub>2</sub>S concentrations were 0.3 vol%, 0.5 vol%, 0.8 vol%, and 1 vol%, respectively. At this point it is not clear why low H<sub>2</sub>S concentration resulted in low maximum conversion.

The effects of H<sub>2</sub> concentrations on the sulfidation at 850 °C were not significant as shown in Fig. 4. Though higher H<sub>2</sub> concentration resulted in less decomposition of CaCO<sub>3</sub> to CaO, the sulfidation reaction rates were little different. Maximum conversion rates range about 78-82% at various H<sub>2</sub> concentrations. Ruth et al. reported a similar result that H<sub>2</sub> does not affect the sulfidation reaction significantly [Ruth et al., 1972].

Results of sulfidation and oxidation reactions in a newly proposed regenerable desulfurization process are shown in Fig. 5. It was observed that the conversion of CaO to CaS was 53-65%. Conversion of CaS to CaSO<sub>4</sub> was quite low. This low conversion is ascribed to the relatively low concentrations of H<sub>2</sub>S

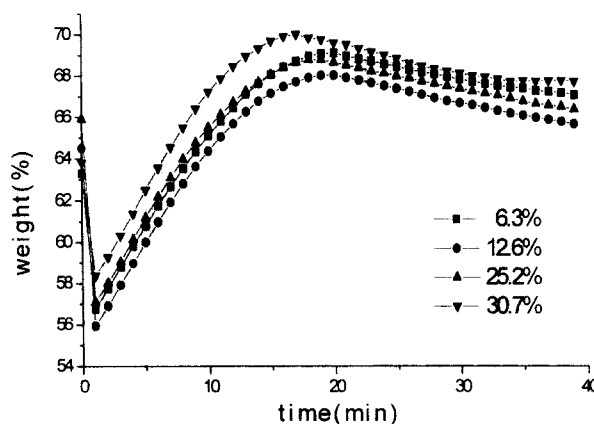


Fig. 4. Effects of H<sub>2</sub> concentration on sulfidation of Daesung limestone at 850 °C.

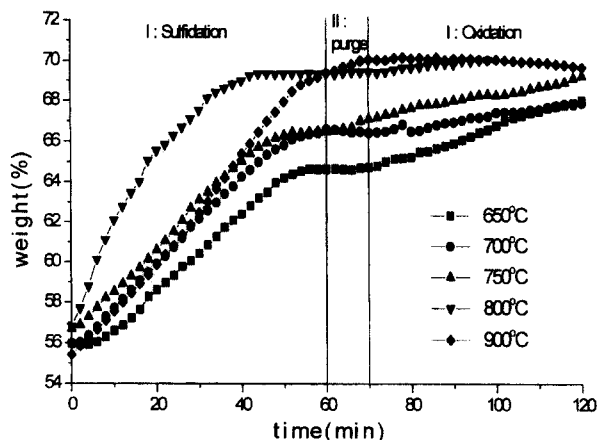


Fig. 5. Sulfidation and oxidation of Daesung limestone at various temperatures.

and  $\text{SO}_2$ . Ham et al. obtained maximum conversion of 80% in sulfidation reaction of  $\text{CaO}$  into  $\text{CaS}$  by using 2.4 vol%  $\text{H}_2\text{S}$  and maximum conversion of 50% in sulfation reaction of  $\text{CaS}$  to  $\text{CaSO}_4$  by using 10 vol%  $\text{SO}_2$ . They reported that when oxidation reactions above  $700^\circ\text{C}$  occurred in a pressurized reactor of which total reaction pressure was 30 bar, pores of sorbent were blocked since the size of  $\text{CaSO}_4$  is larger than that of  $\text{CaS}$  [Ham et al., 1996]. Since our study has been performed under atmospheric pressure, a comparison with pressurized experiment data cannot be given here.

Effects of  $\text{CO}_2$  concentration on sulfation of limestone are shown in Fig. 6 where conversion increases with increasing  $\text{CO}_2$  concentration. Conversion decreases with increasing sulfation temperature under the condition of constant  $\text{CO}_2$  concentration. The conversion shows its maximum value when  $\text{CO}_2$  concentration is 20% and reaction temperature is  $800^\circ\text{C}$ . It is believed that diffusion of  $\text{SO}_2$  into the inside of pores could not occur, which would cause a decrease of  $\text{SO}_2$  removal since large size of  $\text{CaSO}_4$  was formed at the pore inlet during the reactions of  $\text{CaS}$  with  $\text{SO}_2$  above  $800^\circ\text{C}$  [Ham et al., 1996; Newton et al., 1989].

Effects of air injection on sulfation are shown in Fig. 7. When limestone reacted with  $\text{SO}_2$  for 2 hours without air, con-

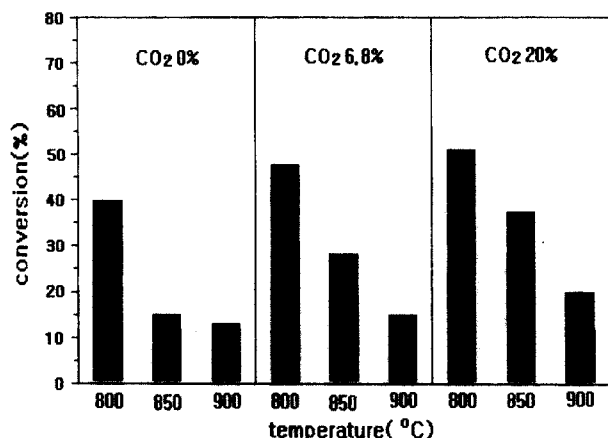


Fig. 6. Effects of  $\text{CO}_2$  concentration on sulfation of Daesung limestone.

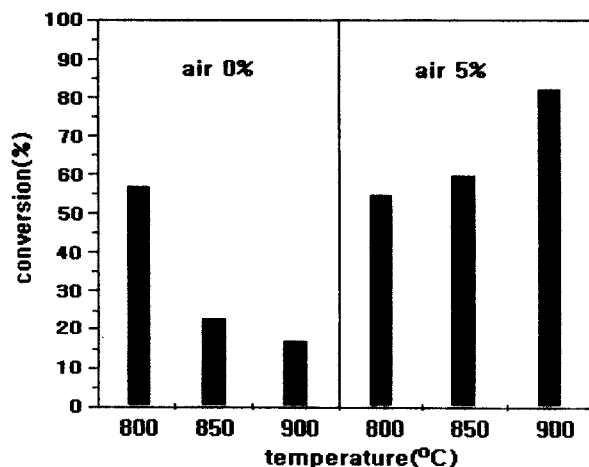


Fig. 7. Effects of air injection on sulfation of Daesung limestone.

versions were 57% at  $800^\circ\text{C}$ , 23% at  $850^\circ\text{C}$ , and 17% at  $900^\circ\text{C}$ , respectively. Conversion decreased rapidly at a reaction temperature above  $800^\circ\text{C}$ . This might result from pore blockage caused by high temperature where the diffusion of  $\text{SO}_2$  into pores of limestone is inhibited [Chang et al., 1984; Ham et al., 1996]. Zarkanitis et al. showed that surface areas of limestone decreased with increasing the calcination temperature. They also explained that this behavior was due to the formation of inaccessible pore space when closure of the small pores of the aperture-cavity structure takes place at  $850^\circ\text{C}$  [Zarkanitis et al., 1989].

It was observed that the conversion rate with air injection increased as the temperature increased. This result is opposite to that of experiment without air injection. Consequently, in the PFBC system, it is desirable to remove  $\text{SO}_2$  over  $800^\circ\text{C}$  by loading limestone into the combustor and reacting with air which will be blown from the bottom of combustor. Conversions with air injection were 55% at  $800^\circ\text{C}$ , 60% at  $850^\circ\text{C}$ , and 82.5% at  $900^\circ\text{C}$ , respectively.

## CONCLUSION

Sulfidation and sulfation experiments were performed with Daesung limestone to investigate their reaction mechanisms. Effects of  $\text{H}_2$  and  $\text{H}_2\text{S}$  concentrations on sulfidation reaction at  $850^\circ\text{C}$  isothermal condition and effects of air injection and  $\text{CO}_2$  concentration on sulfation reaction were analyzed. Effects of  $\text{H}_2$  concentration on sulfidation reaction were not significant. Maximum conversion increased as  $\text{H}_2\text{S}$  concentration increased. Low conversion of  $\text{CaS}$  to  $\text{CaSO}_4$  was caused by low concentrations of  $\text{H}_2\text{S}$  and  $\text{SO}_2$ , incomplete conversion of  $\text{CaO}$  to  $\text{CaS}$ , and atmospheric pressure. It was possible to raise the conversion in sulfation reaction with air injection at a reaction temperature above  $800^\circ\text{C}$ .

## ACKNOWLEDGEMENT

This work was supported by the Korea Science and Engineering Foundation (Grant No. KOSEF 971-1109-057-2).

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