

Kinetic Study of Domestic Limestone (Daesung)

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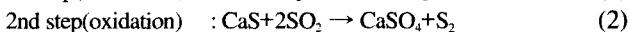
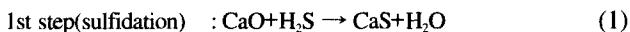
Abstract—Sulfidation and sulfation reactions of Daesung limestone, which is a calcium-based sorbent chosen out of domestic limestone for the removal of H_2S and SO_2 , were investigated by using TGA (thermal gravimetric analyzer). Effects of H_2 and H_2S on the sulfidation were also investigated. The 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 °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 μm 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 ± 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 °C, which has been reported as a typical desulfurization condition in a gasifier [KIER, 1996].

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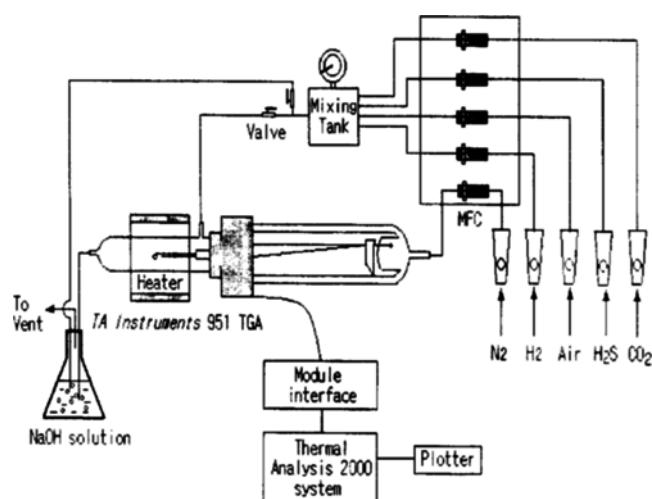


Fig. 1. Schematic diagram of TGA system.

H_2 was used instead of CO in simulated gas for safety. H_2S concentration was changed as 0.3, 0.5, 0.8, and 1 vol%, respectively, at 850 °C.

To investigate effects of H_2 , isothermal experiments were carried in 850 °C at several H_2 concentrations of 0, 6.3, 12.6, 25.2, and 30.7 vol%, respectively. Gas composition for sulfation was 0.3 vol% SO_2 and balance N_2 . 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_2S concentrations are shown in Figs. 2 and 3. When temperature reached to 850 °C where sulfidation experiment started,

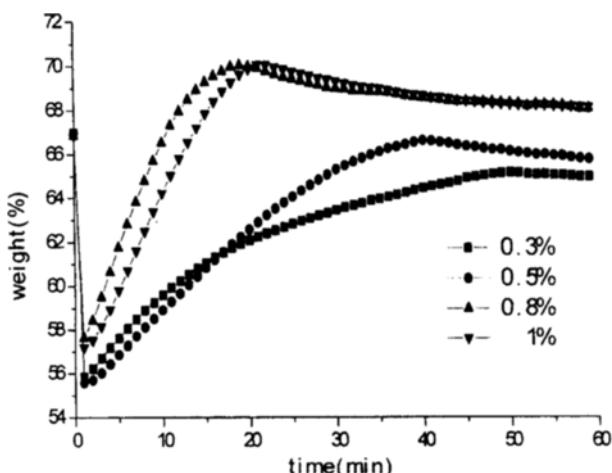


Fig. 2. Effects of H_2S concentration on sulfidation reaction of Daesung limestone at 850 °C.

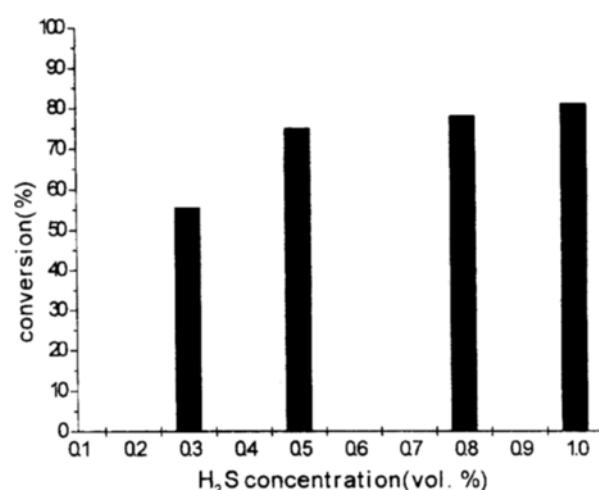


Fig. 3. Effects of H_2S concentration on conversion of Daesung limestone at 850 °C.

weight loss of $CaCO_3$ was 42-44%, which indicates that $CaCO_3$ decomposed to CaO completely. The conversion rates of CaO to CaS with various H_2S concentrations are shown in Fig. 3. Maximum conversion and reaction rate increase with increasing H_2S concentrations. Maximum conversions were 55.6%, 75%, 78%, and 81% when H_2S 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_2S concentration resulted in low maximum conversion.

The effects of H_2 concentrations on the sulfidation at 850 °C were not significant as shown in Fig. 4. Though higher H_2 concentration resulted in less decomposition of $CaCO_3$ to CaO , the sulfidation reaction rates were little different. Maximum conversion rates range about 78-82% at various H_2 concentrations. Ruth et al. reported a similar result that H_2 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 $CaSO_4$ was quite low. This low conversion is ascribed to the relatively low concentrations of H_2S

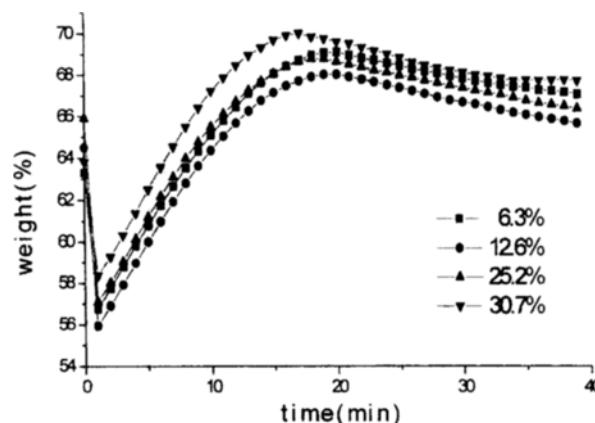


Fig. 4. Effects of H_2 concentration on sulfidation of Daesung limestone at 850 °C.

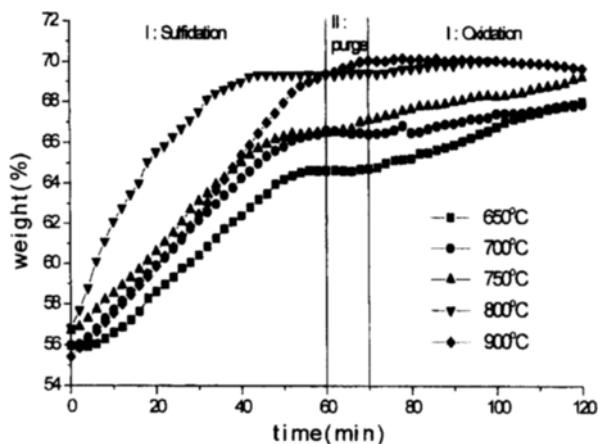


Fig. 5. Sulfidation and oxidation of Daesung limestone at various temperatures.

and SO_2 . Ham et al. obtained maximum conversion of 80% in sulfidation reaction of CaO into CaS by using 2.4 vol% H_2S and maximum conversion of 50% in sulfation reaction of CaS to CaSO_4 by using 10 vol% SO_2 . They reported that when oxidation reactions above 700 °C occurred in a pressurized reactor of which total reaction pressure was 30 bar, pores of sorbent were blocked since the size of CaSO_4 is larger than that of 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 CO_2 concentration on sulfation of limestone are shown in Fig. 6 where conversion increases with increasing CO_2 concentration. Conversion decreases with increasing sulfation temperature under the condition of constant CO_2 concentration. The conversion shows its maximum value when CO_2 concentration is 20% and reaction temperature is 800 °C. It is believed that diffusion of SO_2 into the inside of pores could not occur, which would cause a decrease of SO_2 removal since large size of CaSO_4 was formed at the pore inlet during the reactions of CaS with SO_2 above 800 °C [Ham et al., 1996; Newton et al., 1989].

Effects of air injection on sulfation are shown in Fig. 7. When limestone reacted with SO_2 for 2 hours without air, con-

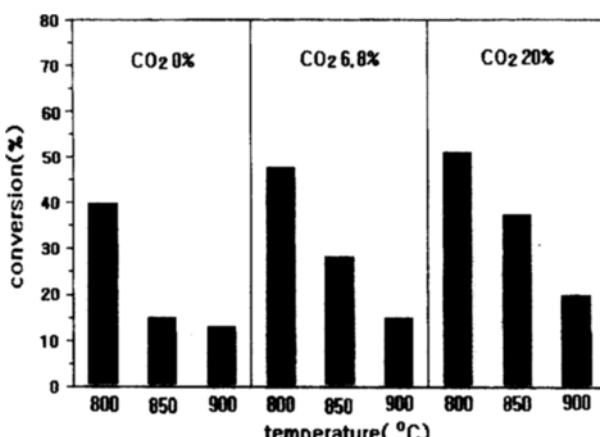


Fig. 6. Effects of CO_2 concentration on sulfation of Daesung limestone.

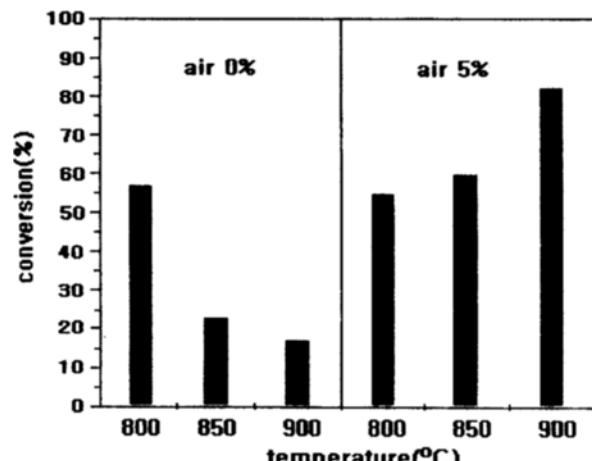


Fig. 7. Effects of air injection on sulfation of Daesung limestone.

versions were 57% at 800 °C, 23% at 850 °C, and 17% at 900 °C, respectively. Conversion decreased rapidly at a reaction temperature above 800 °C. This might result from pore blockage caused by high temperature where the diffusion of 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 °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 SO_2 over 800 °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 °C, 60% at 850 °C, and 82.5% at 900 °C, respectively.

CONCLUSION

Sulfidation and sulfation experiments were performed with Daesung limestone to investigate their reaction mechanisms. Effects of H_2 and H_2S concentrations on sulfidation reaction at 850 °C isothermal condition and effects of air injection and CO_2 concentration on sulfation reaction were analyzed. Effects of H_2 concentration on sulfidation reaction were not significant. Maximum conversion increased as H_2S concentration increased. Low conversion of CaS to CaSO_4 was caused by low concentrations of H_2S and SO_2 , incomplete conversion of CaO to CaS , and atmospheric pressure. It was possible to raise the conversion in sulfation reaction with air injection at a reaction temperature above 800 °C.

ACKNOWLEDGEMENT

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