Korean J. of Chem. Eng., **4**(2) (1987) *143-148*

REACTIVITY OF CALCINED LIMESTONE AND DOLOMITE WITH SULFUR DIOXIDE

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(Received 10 November 1986 • accepted 29 May 1987)

Abstract—Under the conditions prevailing in in-situ desulfurization of fluidized bed combustion two types of limestone and two types of dolomite were tested for their reactivity with sulfur dioxide. Experimental variables were sorbent size, sulfur dioxide concentration and reaction temperature. In general reactivity increased with temperature with activation energy ranging 15.9 to 19.5 kcal/mol for initial reaction rate. Reaction order with respect to sulfur dioxide was close to one and reactivity decreased with increase of sorbent size. With continuous feeding of coal and sorbent sulfur dioxide concentration in the effluent gas decreased with increase of Ca/S ratio.

INTRODUCTION

Through extensive research and development efforts during last two decades fluidized bed combustion (FBC) has become a vital alternative in the utilization of coal [1]. One of merits using FBC is *in-situ* desulfurization: the ability to significantly reduce sulfur dioxide emissions by injecting limestone or dolomite particles directly into the combustor.

Although detailed mechanism of desulfurization reaction is not well understood, it is generally accepted that the reaction involves two steps: calcination and sulfation. Including combustion of coal, SO_2 is a byproduct of it, we can summarize chemical reactions *involving* SO_2 *retention as shown below.*

combustion of coal

$$\text{COAL (C, H, O, N, Mineral)} + \text{AIR } (O_2 + N_2) \xrightarrow{\sim 850^\circ\text{C}} N_2 + CO_2 + O_2 + SO_2 + CO + NO + \text{ASH} \quad (1)$$

calcination

$$\text{(Limestone)} \quad CaCO_3 \longrightarrow CaO + CO_2 \quad (2a)$$

$$CaCO_3 \cdot MgCO_3 \rightarrow CaO \cdot MgO + 2CO_2 \quad (2b)$$

sulfation

$$CaO + SO_2 + \tfrac{1}{2} O_2 \rightarrow CaSO_4 \quad (3a)$$

$$CaO \cdot MgO + SO_2 + \tfrac{1}{2} O_2 \rightarrow CaSO_4 \cdot MgO \quad (3b)$$

Upon entering a fluidized bed combustor which is operated around 850°C, sorbent particles (such as limestone or dolomite) experience rapid temperature rise owing to excellent heat transfer. Because of their small size (a few milimeter or smaller in largest demension) calcination of sorbent particles is rather fast and completed within a few minutes. By calcination sorbent particles become porous because they do not shrink in size while molar volume of CaO is smaller than that of $CaCO_3$. Reactivity of sorbent particles is closely related to this pore structure developed by calcination [2,3].

Experimental findings from various studies on sulfation reaction can be summarized as below. Reaction rate of sorbent particles with SO_2 is much slower compared to that of calcination. Mean residence time of sorbent particels in a FBC is in the order of hours; sulfation reaction can proceed even hours after calcination although reaction rate is slower compared to that of the freshly calcined. However, molar volume of $CaSO_4$ is much larger than that of CaO ($86.4cm^3/mol$ vs $30.5cm^3/mol$) and sorbent particles change their size very little, if ever, during sulfation. Thus sulfation can either fill or plug pores which were generated by calcination. Moreover in the case of nonporous limestone sulfation cannot proceed to completion because molar volume of $CaSO_4$ is larger than that of $CaCO_3$ ($86.4cm^3/mol$ vs $59.5cm^3/mol$). On top of that pore plugging proceeds from the outer surface of sorbents because gaseous reactants are involved in the sulfation. The result is that sulfation rate becomes virtually zero even before all pores in the calcined sorbent particles are plugged. Pore mouths are plugged even while there are unplugged pores inside those particles. Reactant gases have difficulties in reaching to those inside pores, resulting extremely low reaction rate well below the maximum conversion expected from the consideration of molar volume changes. Additionally it is well documented that reactivity of sorbents vary widely depending on the type and origin of sorbents and reactivity can be significantly different among sorbents which have seemingly similar chemical composition [2,3,4,5]. For these reasons as well as importance in practical terms calcination and sulfation of sorbents (limestone or dolomite) have been the object of intensive research works, both experimentally and theoretically [6]. In this paper we present results from sulfation experiments with limestones and dolomites produced in Korea for which systematic studies have not been published in the literature up to now.

EXPERIMENTAL

A small scale (78mm ID) fluidized bed comustor and a fixed bed reactor were used for the measurement of sulfation reaction rate. The FBC has accessories such as screw-feeder for coal feeding, electric air preheater which can raise fluidizing air temperature up to coal ignition temperature, inside cooling water tube, thermocouples and pressure taps for the measurement of temperature and pressure in the bed. Bed temperature, air flow rate and coal feed rate can be changed independently within a certain range maintaining proper combustion of coal.

Schematic diagram of the FBC is shown in Figure 1. The fixed bed reactor consists of 25mm ID tube in which a 22mm diameter basket made of stainless steel mesh hung from above. Sorbent particles are put in this basket and the reactor is jacketed by electrical heaters. For the continuous measurement of SO_2 and CO_2 in the gas stream CO_2 analyzer (Horiba VIA 300IR ESDA-104) and SO_2 analyzer (Horiba VIA 300IR ESDA-103) were used (see Figure 1).

In this study we used four different types of sorbent; two kinds of limestone, and two kinds of dolomite. We selected these based on the availability and geographic diversification. Properties of sorbents are listed in Table 1. As we have confirmed in preliminary experiments calcination of sorbents in the fixed bed is rather slow thus necessitating precalcination of them for use in fixed bed studies. Characteristics for uncalcined sorbent is generally very poor compared to those of precalcined. For the precalcination we put sorbent particles in a ventilated furnace at 980°C for two hours. Properties of calcined sorbents are listed in Table 1. we can observe that BET area of dolomite increases sharply with calcination, but much less so with limestone.

The FBC in this study was used for two purposes: firstly for the in-situ desulfurization, and secondly for the generation of reactant gases for the fixed bed reactor. Procedure for the operation of FBC is as follows. To start up the FBC fluidizing air is heated while it passes through air preheater. At the same time electric heating elements surrounding the FBC is activated. When bed temperature reaches coal ignition temperature (~500°C) coal feeding begins. Then bed temperature reses further owing to combustion of coal. By adjusting flow rate of water through cooling tube and power input to the heaters bed temperature can be controlled. At steady combustion state CO_2 concentration from the FBC stabilizes to a certain value. Because SO_2 concentration cannot be changed at will by burning coal only, cylinder SO_2 is introduced to the fluidizing air for the adjustment of SO_2 concentration level in the combustion gas.

When the fixed bed reactor is employed a small fraction of combustion gas is diverted from the freeboard and cooled, then sent to the fixed bed reactor with the aid of gas sampler (see Fig. 1). Flow rate of gases coming to the fixed bed reactor is measured with a rotameter. Temperature of the fixed bed reactor can be set to desired values by a temperature controller. About 0.5 gram of precalcined sorbent (amount just enough to form monolayler on the basket bottom) is put into the basket when the reaction conditions such as temperature and gas composition are stabilized. Meanwhile SO_2 concentration in the effluent gas is measured continuously. Conversion of sorbent by sulfation is calculated as follows:

Table 1. Properties of sorbents.

Designation	Species	Production site	Chemical Analysis (wt%)		wt loss by calcination(wt%)	BET Area(m^2/g)		Color	
						before	after	before	after
			Ca	Mg		calcination		calcination	
A	Limestone	Danyang	39.9	0.12	41.3	1.56	2.56	gray	light gray
B	Limestone	Wulgin	39.1	0.078	43.1	1.17	2.58	white	light gray
C	Dolomite	Danyang	21.2	13.1	47.3	0.18	14.00	brown	light brown
D	Dolomite	Wonsung	21.4	12.9	47.1	0.42	13.65	white	light gray

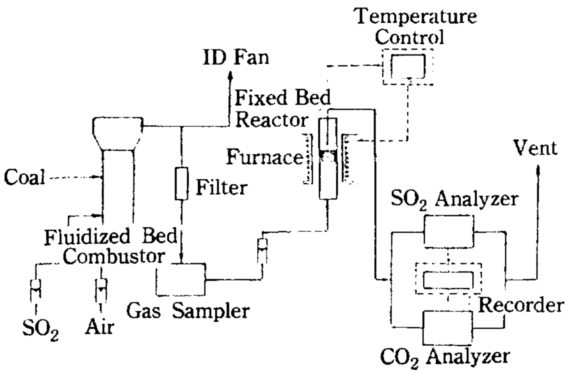

Fig. 1. Schematic diagram of experimental setup.

$$X(t)=\frac{G}{M}\int_0^t [C_o - C(t')]\ dt' \qquad (4)$$

where $X(t)$ = conversion at time t
G = molar gas flow rate through the reactor (mol/s)
M = Ca mole in the basket
C_o = mol fraction of SO_2 before the introduction of sorbent into the basket.
$C(t)$ = mol fraction of SO_2 after the introduction of sorbent into the basket.

The conversion calculated from equation (4) was checked with the value obtained by measuring weight gain of the sorbent after each run. It was found that conversion obtained by gravimetric method is upto 10% higher compared to that of given by equation (4). We suspect the difference is due to drifting of SO_2 base line of SO_2 analyzer. Preliminary tests show no loss of SO_2 when sorbent is not put into the basket. In this study conversions calculated from equation (4) are used.

RESULTS AND DISCUSSIONS

For each sorbent experimental results were converted to conversion, X, vs time to investigate the effect of SO_2 concentration, reaction temperature and sorbent size. Figure 2 shows X vs time for four kinds of sorbent for the base conditions (-45+60 mesh, 850°C, 3600ppm). This figure shows typical behavior of sorbents in sulfation: initial reaction rate is relatively high, but reaction rate falls off as X increases with time and reaction rate becomes extremely slow after one hour or so. We can also observe in Figure 2 that dolomites, sorbent C and D, are more reactive than limestones, sorbent A and B, (on the basis of CaO conversion to $CaSO_4$, not on weight basis). This is not surprising if we look into calcination reaction (Equation 2a and 2b) and BTE area change as listed in Table 1. As X vs time curve flattens after 90 minutes in most cases, we chose X at 90 minutes to compare sorption capacity of sorbents. We also obtained initial sulfation rate from the slope at time zero.

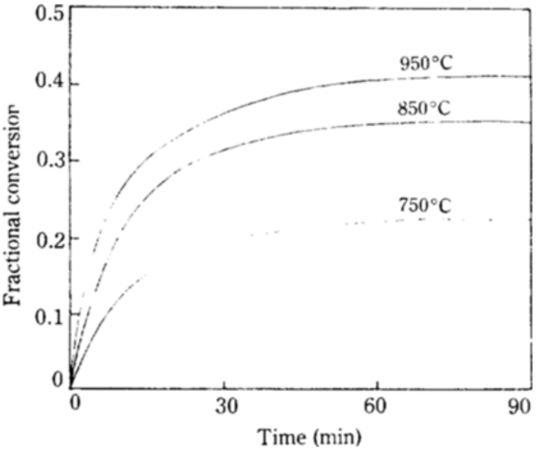

Fig. 2. Sulfation conversion vs time for four types of sorbents.

Effect of Reaction Temperature

A typical effect of reaction temperature on sulfation is shown in Figure 3 which is for sorbent C. We can see that sorption capacity and reaction rate increases with reaction temperature. Other sorbents showed similar temperature effect

Figure 4 shows sorption capacity at 90 minutes depends on bed temperature, while Figure 5 shows Arrhenius plot of initial sulfation rate. Compared to limestones (sorbent A and B) dolomites (sorbent C and

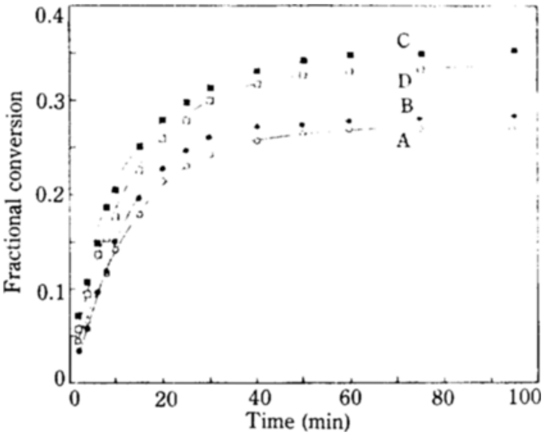

Fig. 3. Conversion vs time for sorbent C at different temperatures (Particle size: -45+60 mesh; SO_2: 2700 ppm).

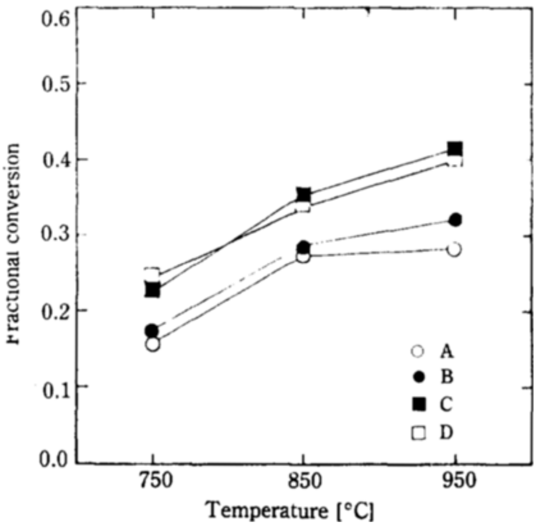

Fig. 4. Effect of temperature on sorption capacity for four types of sorbents.

D) give higher sorption capacity and initial sulfation rate.

Activation energy calculated from Figure 5 are listed in Table 2, together with those reported in the literature. Activation energy of this study (15.7 ~ 19.5 kcal/mol) is comparable to those in the literature (8.1 ~ 19.5 kcal/mol). These values suggest that the effect of external mass transfer resistance is not significant. However, these values are much smaller compared to what Borgwardt and Bruce reported for much smaller size particles (1 μm) [7]. Their value of activation energy is 37.6 kcal/mol for temperature ranging 800 to 1125°C. Because of small particle size the value reported by Borgwardt and Bruce can represent "true" activation energy devoid of pore diffusion influence. In this case, that values listed in Table 2 are only one half of true one suggests strong effect of pore diffusion.

Table 2. Activation energy of sulfation under FBC environment.

Investigators		Activation (Kcal/mol) energy	Operating temperature(°C)
Borgwardt(1970) [5]		8.1-18.1	650-980
Wen and Ishida (1973) [8]		17.5	590-860
Marsh and Ulrichson(1985) [9]		19.1	740-930
This Study			
Sorbent	A	15.9	750-950
	B	15.7	
	C	16.2	
	D	19.5	

Effect of SO_2 Concentration

Initial sulfation rates show close to first order dependence on SO_2 concentration (Figure 6) which is consistent with the findings by other (see e.g. Borgwardt [4], Marsh and Ulrichson [9], Kojima et al. [10]), but sorption capacity does not increase linearly with SO_2 concentration (Figure 7). This implies that morphological change of sorbents such as pore plugging comes into play as sulfation proceeds.

Effect of Sorbent Size

As stated earlier four size ranges (-14+18; -25+35; -45+60; -120+170 mesh) were employed for each type of sorbent. Size of sorbent ranges from 0.1 mm to 1.2 mm (estimated from mesh openings), which is typical for use in FBC. Within experimental range sorption capacity decreases with the increase of sorbent size for all sorbent types (see Figure 8). It is interesting that difference in sorption capacity among sorbent types decreases with the increase of sorbent size.

The effect of particle size on the initial sulfation rate is shown in Figure 9. For all sorbents initial reaction rate is inversely proportional to particle size. This is

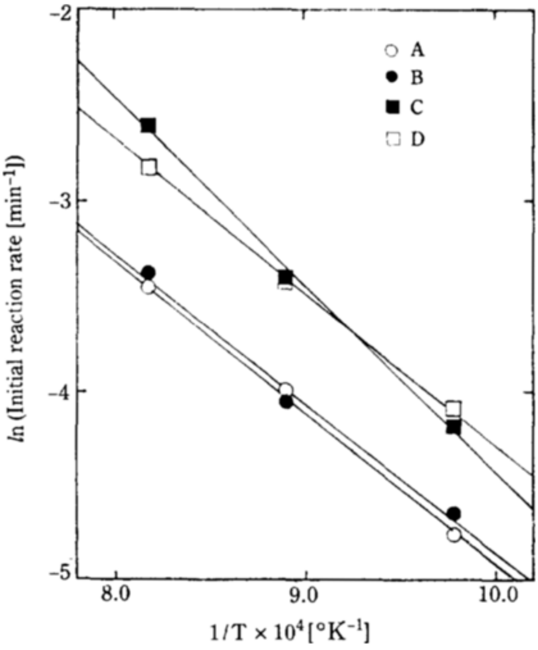

Fig. 5. Arrhenius plot of initial sulfation reaction rate for four types of sorbents.

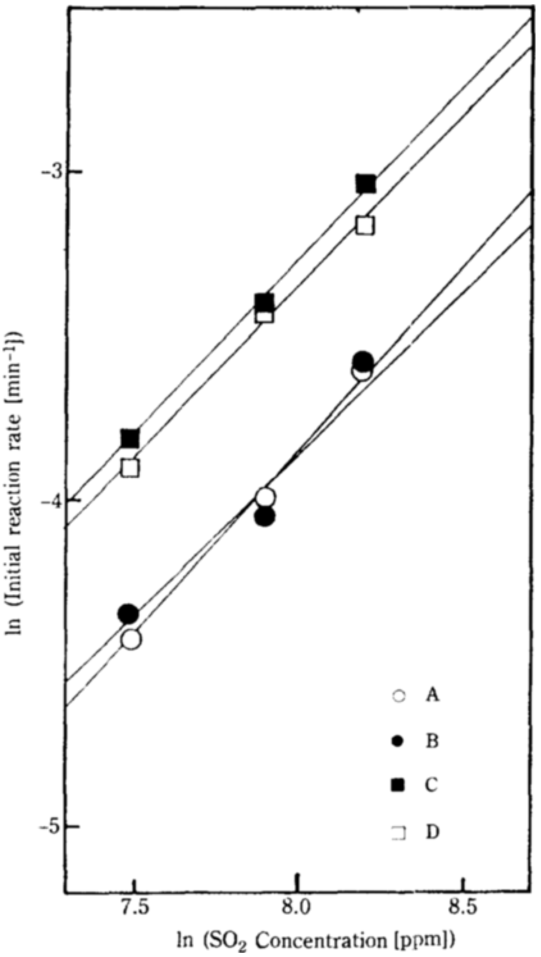

Fig. 6. Dependence of initial sulfation rate on SO_2 concentration.

consistent with the trend of sorption capacity shown in Figure 8.

Desulfurization with Continuous Feeding of Sorbent in the FBC

For a FBC with desulfurization in continuous operation sorbent as well as coal should be continuously fed. In this case the most important parameter is so-called Ca/S ratio, which is the ratio of molar feed rate of calcium in sorbent to that of sulfur in coal. Thus zero Ca/S ratio means no sorbent feeding. From stoichiometry we have

$$Y = (Ca/S) \quad \bar{X} \tag{5}$$

where Y = Sulfur retention (conversion of SO_2 to $CaSO_4$)

$\bar{X}$ = average conversion to $CaSO_4$ of CaO in sorbent particles leaving the combustor

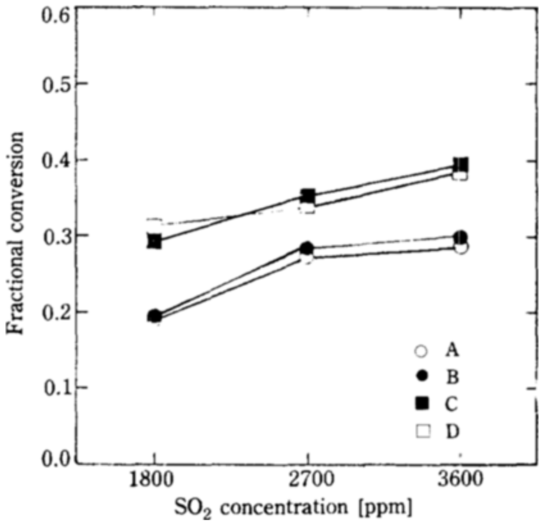

Fig. 7. Dependence of sorption capacity on SO_2 concentration.

The result of continuous desulfurization using the FBC with continuous feeding of sorbent A and coal is shown in Figure 10. Figure 10 shows sulfur retention efficiency increases with Ca/S ratio as expected from results of others (see e.g. Lee and Georgakis. [11]).

CONCLUSIONS

Four different types of calcium containing sorbent (two types of limestone and dolomite, respectively)

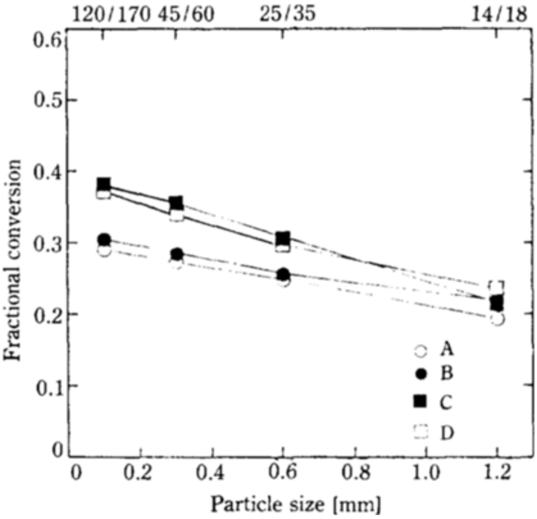

Fig. 8. Effect of sorbent particle size on sorption capacity.

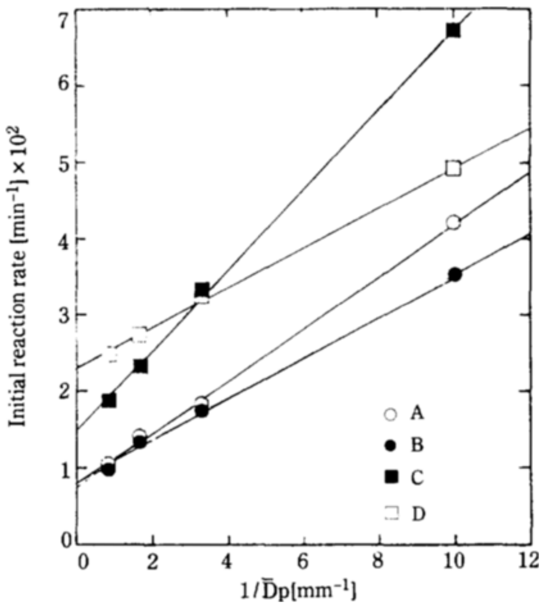

Fig. 9. Effect of sorbent particle size on initial sulfation rate.

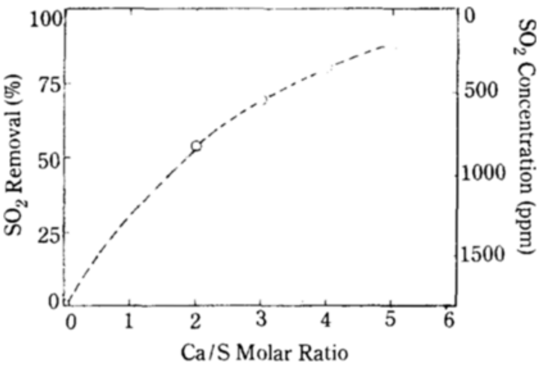

Fig. 10. Effect of Ca/S ratio on sulfation efficiency.

were tested for the reactivity with sulfur dioxide. Based on weight of CaO in sorbent dolomites were more reactive than limestones.

Initial sulfation rate increased linearly with sulfur dioxide concentration and activation energy of it ranged from 15.9 to 19.5 kcal/mol which was comparable to those reported in the literature. Initial sulfation rate also showed significant effect of sorbent particle size: initial rate vs inverse of particle size showed linear relationship. With continuous feeding of coal and sorbent into a FBC SO$_2$ concentration in the effluent decreased with increase of Ca/S ratio.

NOMENCLATURE

C_O, C : mol fraction of SO$_2$ in the gas stream
$\bar{D}_p$: mean sorbent size [mm]
G : molar gas flow rate through the reactor [mol/s]
M : moles of Ca in the basket
X, $\bar{X}$: fractional conversion of sorbent [CaO to CaSO$_4$]
Y : sulfur retention by the bed

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