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THERMOGRAVIMETRIC STUDIES OF THE REACTION OF CaO WITH SO_2

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Abstract

The high temperature sulfation of CaO with SO_2 was investigated under vacuum by TG. Experimental data indicated that the sulfation process was a two-stage reaction, a very fast surface reaction in the beginning, and followed by a product-layer diffusion-controlled reaction. The initial period was about 7 s. This process of sulfation was affected by type of limestone, micro structure, particle size and temperature, but hardly affected by SO_2 concentration. A 59% CaO conversion can be achieved in 30 s at 1000°C and 1 mbar.

Keywords: high temperature sulfation, reaction of CaO with SO_2, TG

Introduction

The emissions of SO_2 from the combustion of high sulfur coals in industrial boilers and furnaces are generally regarded as a major source of acid rain. Furnace dry-sorbent injection is a potentially attractive retrofit technology for the reduction of these emissions [1]. In this process, limestone sorbents are injected into the high-temperature regions of a combustion chamber. The sorbent is rapidly calcined to form highly porous CaO, which reacts subsequently with the gaseous SO_2 to produce calcium sulfate according to the following equation:

$$CaO(s)+SO_2(g)+1/2O_2(g) \rightarrow CaSO_4(s) \qquad (1)$$

The sulfation of CaO with SO_2, which seems to be a simple reaction, is now recognized as a complex, high-temperature, short-time heterogeneous process limited by gas-phase and solid-phase diffusion with simultaneous physical transformations of the solid [2]. Because of the complexity of the sulfation, some results provided by different investigators [3–5] are somewhat confusing and even contrary. Clearly the understanding of this sulfation is far from complete.

In this study, TG technique was used to investigate the reaction of CaO with SO_2 under the condition of eliminating the gas phase resistance and most of the pore diffusion resistance.

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Table 1 Chemical (wt%) and physical properties of the samples

Limestone	$CaCO_3$	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	S	BET surface /m^2g^{-1}	Mean particle size /μm
Forsby	95.6	0.26	0.30	0.23	0.88	0.01	0.09	0.11	10.3	2.1
Ignaberga	82.8	12.4	0.89	0.66	0.35	0.17	0.11	0.03	10.3	2.0
Limhamn	89.3	7.37	0.23	0.28	0.95	0.02	0.06	0.04	12	3.3

Experimental

Test sorbent

Three specimens of limestone were used in most of the study. A summary of the chemical physical properties of these materials is presented in Table 1.

TG measurement

TG used in the study was a Cahn-2000 electrobalance with a sample basket made of a fine Pt-net. The basket was hanging in a quartz reactor, surrounded by a furnace which could raise the temperature up to 1250°C. The reactant gases, which were stoichiometrically premixed in the gas mixer, could be fed to the system via two inlet ports, one connected to the balance casing and the other to the quartz reactor. A schematic diagram of the TG system was shown in Fig. 1.

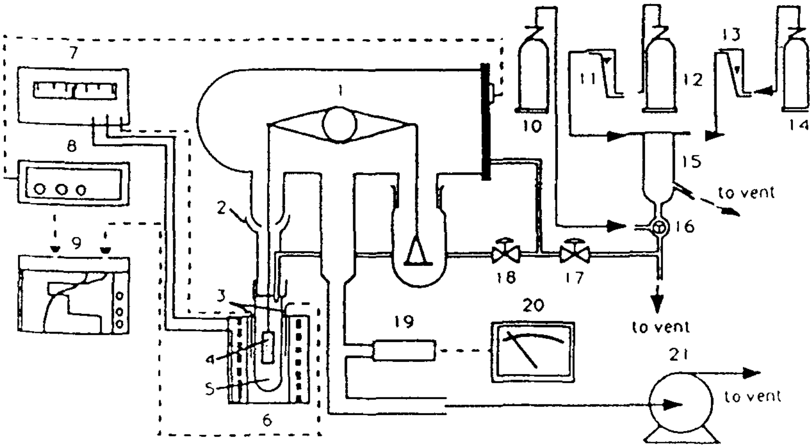

Fig. 1 Diagram of TG equipment. 1 Cahn 2000 electrobalance, 2 hemispherical connector, 3 thermocouples, 4 sample holder, 5 quartz reactor, 6 electric furnace, 7 thermostat, 8 Cahn control unit, 9 strip chart recorder, 10 N_2, 11 rotameter for SO_2, 13 rotameter for O_2, 14 O_2, 15 reactant gas mixer, 16 three-way valve, 17 valve for upper inlet, 18 valve for reactor inlet, 19 pressure transducer, 20 manometer, 21 vacuum pump

In order to eliminate the gas phase resistance and most of the pore diffusion resistance, the TG system was kept at low pressure. The total pressure in a standard experiment was 1 mbar both for the inert and the reactant gases, and the partial pressure SO_2 was kept at 0.67 mbar to maintain a stoichiometric reactant gas mixture. During the sample preparation, the basket was dipped in a slurry containing 10–15 wt% of limestone with about 5 mg of solid particles adhered to the basket. The basket was then dried under IR radiation in order to form a very thin layer of sample.

The sample in the quartz reactor was first heated to 400°C in a relatively slow heating rate at normal atmosphere with N_2 as sweeping gas. This period lasted for about 5 min to evaporate water possibly contained in the sample. The reactor was then heated at 200 deg·min^{-1} to 800–900°C where the calcination took place. After the calcination was completed, the system was evacuated and kept at a desired pressure. The temperature was then brought up to the sulfation temperature. By switching a three-way valve, the N_2 flow was cut off and the reactant gases were introduced into the reactor. The sulfation was continuously monitored by the weight increase of the basket. In order to effect the offset of gas flow on weighing, a blank run was conducted under the same conditions as in sulfation except that there was no sample on the basket.

BET measurement

Both the BET surface area and pore volume measurements were conducted in a Chan-2000 electrobalance-based system. In the BET method, nitrogen was used as the adsorption gas. From the adsorption/desorption isotherm, the pore volume and the pore size distribution were calculated.

Grinding

Finer particles were obtained by grinding the limestone slurry in a small bead mill. The optimum grinding conditions were: a slurry containing 100 g solid in 150 ml water; a stirring speed of 3000 rpm; a ceramic bead diameter range of 1–1.5 mm; 1200 ml beads; a grinding time of 7 h.

Results and discussion

Limestone type

Every TG curve was analysed by the method of the dynamic force analysis [6], and transferred to a CaO conversion *vs.* time relationship. Figure 2 shows the reactivity comparisons of three tested samples at 1000°C and 1 mbar. These results indicate that there are significant differences between CaO conversion with each samples. Forsby calcine exhibits the highest sulfation reactivity. The reactivity differences are mainly attributed to the micro structural properties of

Table 2 BET surface area and pore volume of the calcines

	Forsby	Ignaberga	Limhamn
BET surface area /m^2g^{-1}	44	35	30
Pore volume /$10^{-3}cm^3g^{-1}$	64	51	45

the calcined samples, as shown in Table 2. These results confirm the BET surface area and pore volume of calcines play a significated role in sulfation. It can be concluded that the surface area and pore volume produced in the simple calcination experiment provide a reasonable estimate of sorbent reactivity in an actual sulfation process.

Figure 2 also shows that for the three samples 34–59% CaO conversion are achieved after 30 s sulfation. The ultimate conversion of Forsby calcine is higher than 50% conversion limit predicted by the theoretically available pore

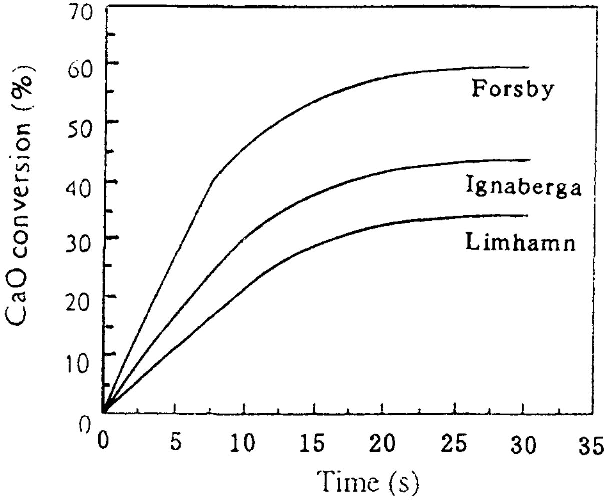

Fig. 2 CaO conversions *vs.* time for three different samples at 1000°C and 1 mbar

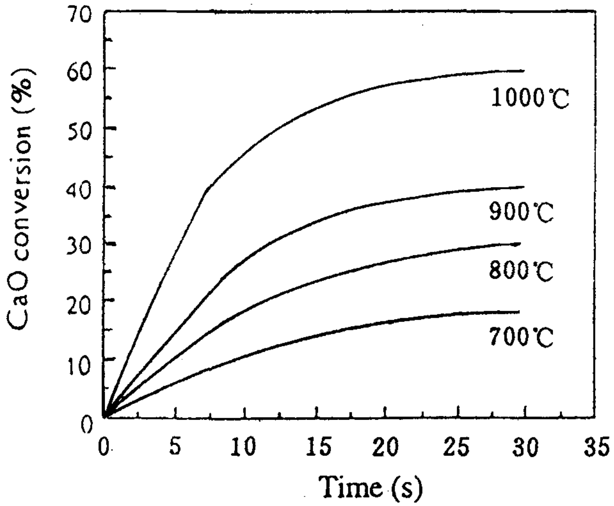

Fig. 3 CaO conversion *vs.* time for Forsby sample at different temperature and 1 mbar

volume [7]. The particle volume has probably expanded at higher conversions. The particle expansion during sulfation has been observed by several researchers [3, 4, 8].

Reaction time and temperature

Figure 3 shows that the overall rate of sulfation is strongly influenced by reaction time and temperature for Forsby calcine in the region 700–1000°C at 1 mbar total pressure. These curves show that the CaO conversion rate is very high in the initial stage of exposure, and then decreases as the sulfation process proceeds. This reduction in the reaction rate is more apparent at higher temperatures. This is similar to that observed by McClellan [9]. The initial rapid reaction results from the high surface area of the calcine, acting in combination with rapid intrinsic kinetics. The $CaSO_4$ product builds up the surface of unreacted CaO, and leads to pore closure or plugging in the interior of the reacting particles. Consequently the sulfation rate may be decreased in the succeeding period. The sulfation rate may be controlled by solid state diffusion through the growing $CaSO_4$ product layer. The sulfation can therefore be described as a two-stage reaction, starting with a very fast surface reaction, and followed by a product layer diffusion controlled reaction. The initial period was about 7 s.

The effect of temperature is also emphasized in Fig. 4. The experimental data indicate that CaO conversion increases with temperature up to 1000°C and then levels off. Similar results were obtained by Borgwardt up to 970°C [10].

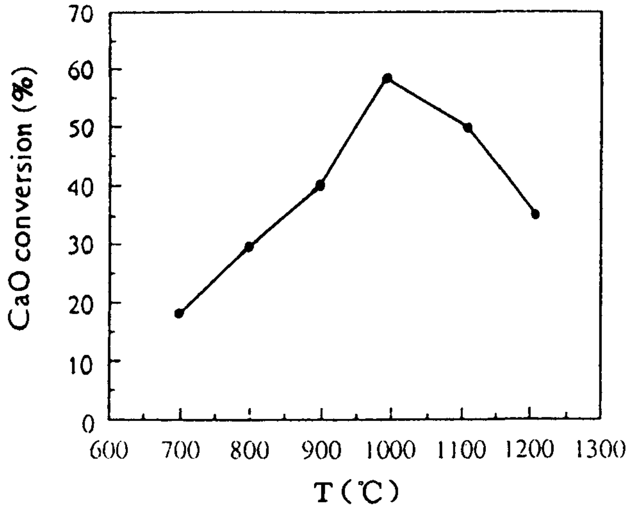

Fig. 4 The effect of temperature on CaO conversions for Forsby sample after 30 s sulfation at 1 mbar

The optimum temperature is likely to be different for various types of sorbents and can only be found for each sorbent by experiment [2, 7, 9, 10].

SO_2 concentration

The effect of SO_2 concentration on CaO conversion was investigated for Forsby calcine at 1000°C by controlling the total pressure of the TG system, shown in Fig. 5. As the system pressures were changed in the region 1–4 mbar, the corresponding SO_2 fractions of reactant gases are between 670 ppm and 2680 ppm. Figure 5 shows that the initial reactivity is insensitive to an increase of SO_2 concentration, but the ultimate reactivity shows a weak with increasing SO_2 concentration. These results are similar to those observed by Newton *et al.* [11].

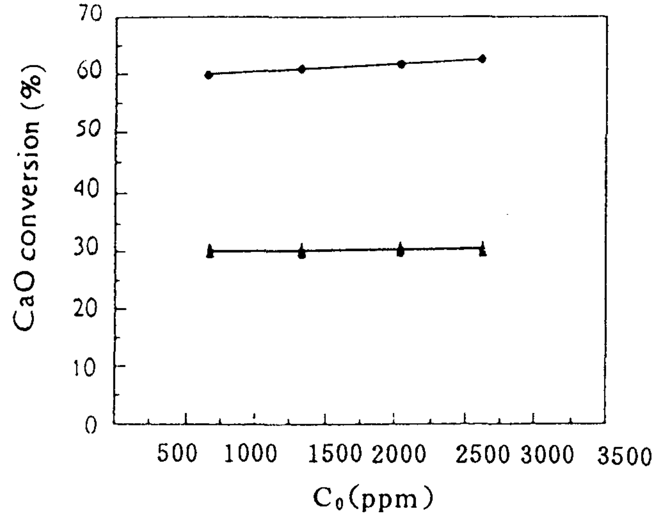

Fig. 5 The effect of SO_2 concentration on CaO conversions for Forsby sample at 1000°C: ▲ 5 s; ● 30 s

Particle size

Figure 6 shows that the sulfation rate of ground sample is faster than that of unground sample. It is clear that the reduction of sorbent size is indeed helpful in promoting the CaO/SO_2 reaction, as many researchers have reported [2, 12]. This effect is likely due to decreasing resistance against gas phase diffusion, and allowing the surface SO_2 concentration of the particle to approach that of the gas bulk as the particle size decreases. In addition, decreasing particle size leads to larger surface area (75 m^2g^{-1}) and pore volume (111.01×10^{-3} cm^3g^{-1}) of Forsby calcine (ground 7 h) than that of unground sample (Table 2).

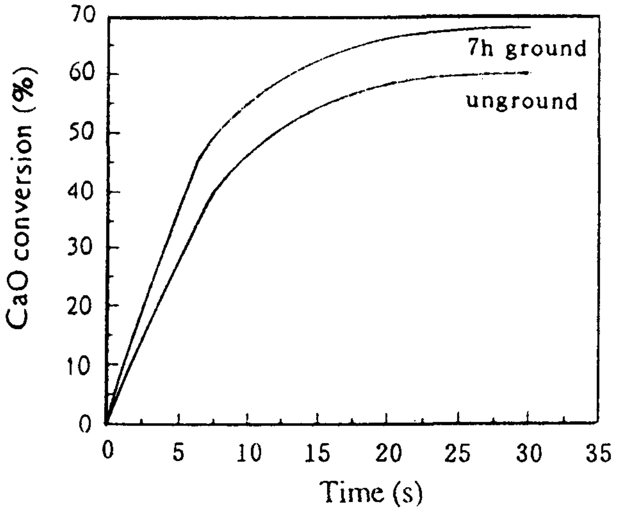

Fig. 6 The effect of particle size on CaO conversions for Forsby sample at 1000°C and 1 mbar

Conclusions

Under the conditions developed in this study, the sulfation process is found to be a two-stage reaction, first with a very fast surface reaction, and followed by a product-layer diffusion-controlled reaction. The initial period is about 7 s. This process of sulfation is affected by limestone type, micro structure, particle size and temperature, but hardly affected by SO_2 concentration. The optimum reaction temperature is about 1000°C. The BET surface area and pore volume of calcined limestones have profound effect on the SO_2 uptake capacity for a given limestone. A 59% CaO conversion can be achieved in 30 s for Forsby calcine at 1000°C and 1 mbar.

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Zusammenfassung — Mittels TG wurde in Vakuum die Hochtemperatursulfatierung von CaO mit SO_2 untersucht. Die entsprechenden experimentellen Daten zeigen, daß der Sulfatierungsprozeß eine zweischrittige Reaktion ist, bestehend aus einer sehr schnellen Oberflächenreaktion zu Beginn, gefolgt von einer produkteschichtkontrollierten Reaktion. Die Dauer der Initiierungsperiode beträgt ca. 7 s. Dieser Sulfatierungsprozeß wird durch den Kalksteintyp, Mikrostruktur, Partikelgröße und Temperatur, stark jedoch durch die SO_2-Konzentration beeinflußt. In 30 s kann bei 1000°C und 1 mbar ein CaO-Umsatz von 59 % erzielt werden.