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A THERMOGRAVIMETRIC STUDY OF THE SULFATION OF LIMESTONE AND DOLOMITE—THE EFFECT OF CALCINATION CONDITIONS*

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ABSTRACT

A pressurized thermogravimetric analysis system, constructed to operate with corrosive gases and connected to a programmable calculator used as a data acquisition system, has been used to study the isothermal reaction of sulfur dioxide with limestones and dolomites at pressures from 1.01×10^5 Pa to 1.01×10^6 Pa (1 to 10 atm), and temperatures from 750 to 1050 °C. The sulfation reactions have been studied (a) under conditions where calcium carbonate is the stable form of the reacting solid, and (b) where calcium oxide is the stable form of the sorbent.

The data show that both sample size and gas flow-rate strongly influence the observed kinetics. However, the dominant influence on the sulfation reaction of calcined sorbents is the carbon dioxide pressure in which the stone is originally calcined. The results are discussed in the light of previous studies on the sulfation of lime, and the application of this reaction to pollution abatement by removal of sulfur dioxide from hot gases.

INTRODUCTION

Sulfur dioxide pollution from coal combustion may be largely prevented when the coal is burned in a fluidized bed of limestone or dolomite. More than 90% of the fuel sulfur is fixed as solid calcium sulfate, and the process is attractive from the energy conservation standpoint because pressurized fluidized bed combustors have the potential to increase the efficiency of electric power generation in a combined cycle power plant[1].

The range of experimental conditions under which sulfur capture occurs—outlined in Table 1, lies outside the range of previous laboratory experimental studies of the sulfation of lime[2–5]. This work is concerned with a study of the sulfation reaction at pressures up to 10 atm and temperatures up to 1000 °C—and is principally directed at factors which influence the utilization of calcium, or the percent conversion to calcium sulfate which occurs under technically feasible conditions. The study of the

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sulfation reaction requires the design and construction of a thermogravimetric analysis system which can operate at pressure and can monitor the course of reaction of a solid sample exposed to hot flowing corrosive gases.

TABLE 1

EXPERIMENTAL CONDITIONS OF INTEREST FOR DESULFURIZATION IN FLUIDIZED BED COMBUSTION

Temperature:	730 °C → 950 °C → ?
Pressure :	1 atm → 10 atm → 15 atm
SO_2 :	0.5% → 0.1%
O_2 :	~3% → 12%
Particle size :	~300 μm → 3 000 μm diameter
Sorbent :	limestone: half-calcined dolomite calcined limestone: calcined dolomite
CO_2 :	up to 1.5 atm

Previous studies have indicated three interesting features of the sulfation reaction. The primary limit on utilization of the calcium is caused by the space available within pores of (0.1–2 μm radius) for accommodation of the sulfate ion, and leads to an upper value of ~40% sulfation at a particle size of 500 micron diameter. However, several laboratory studies have found a very low calcium utilization ~18% or 11% at this particle size, using a particular limestone designated as limestone 1359, while fluidized bed tests on the same sorbent have shown a utilization greater than 30%. Further, a temperature maximum in the desulfurizing action has been observed in the temperature range 800–850 °C, at atmospheric pressure[10,11]. Two mechanisms have been advanced to explain this behavior, and since one invokes the reducing action in oxygen-deficient regions of the fluidized-bed combustor, investigation of the effect in an oxidizing atmosphere should assist identification of the actual mechanism.

EXPERIMENTAL

The apparatus as outlined in Fig. 1 consists of a reaction gas manifold; a custom built pressure shell (304 SS) through which the gases are ducted: the shell contains a Du Pont 951 thermobalance modified to accept corrosive gases after the design of Ruth[7]; and an exhaust/depressurization system which contains sampling ports, and traps. The controller and recorder are supplied by a Du Pont 990 thermal analyzer. The system has been described previously[12]. In addition to the analog recorder, the weight and temperature signals are fed to a Fluidyne multichannel interface. The signals are digitized and input to a Wang 2200 calculator with an 8 k memory, and cassette tape recorders. The data may be conditioned, or reduced, before recording. After a run, the data are reduced and analyzed through the Wang calculator and graphically output on a typewriter plotter which has a precision of 0.01 in. in both x and y axes. Development of this system is in an early stage, but it is equipped with output relays to enable extension to system control (i.e., pressure temperature, gas or flow changes), at a later date.

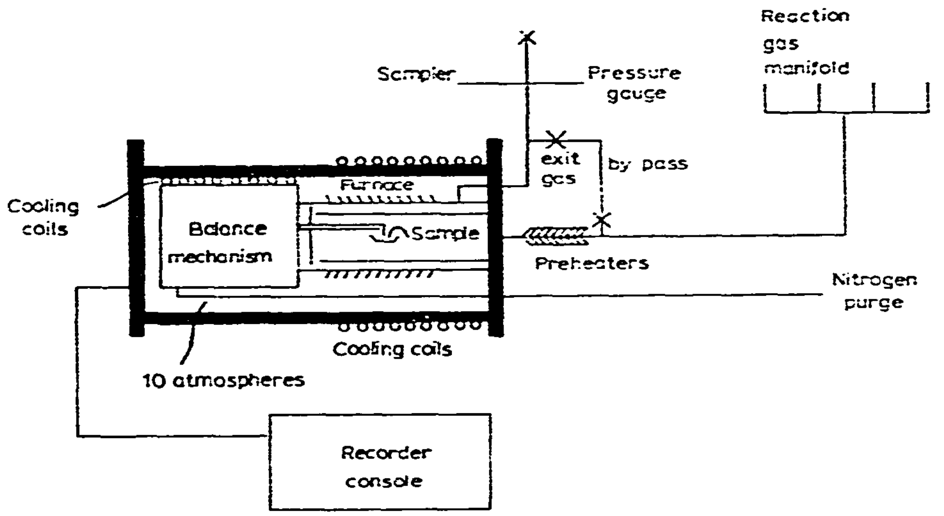


Fig. 1. Diagram of the TG system.

Because corrosive gases rapidly destroy the thermocouple it was sheathed in a quartz capillary. The resulting error was found to be minor in two kinds of test. The Curie point of "specpure" iron (Johnson Matthey), was found to be 773 °C at 10 atm pressure (literature value 771 °C)[13]. Cycling experiments on the decomposition pressure of CO_2 over $CaCO_3/CaO$ at 0.956 atm of CO_2 gave a value of 892 °C, in relatively good agreement with literature values, (891 °C derived from Curran's Kp data[14] and 901 °C derived from Hill's[15] data).

In all the work reported here, the samples were fully calcined in the TG apparatus before sulfation. (Further work on half-calcined dolomites will be reported later.)

Materials

The materials studied are natural limestones and dolomites, as described in Table 2. Their choice was dictated by their extensive use as sorbents in fluidized-bed combustion studies[8,9,11]. The petrographic and mineralogical properties have been described by Harvey[16]. Samples of the material were ground and sieved to the desired size range. In view of the small sample size (20 mg of raw stone) eventually studied, sample homogeneity is of concern. The weight loss on calcination of limestone 1359 was 43.59±0.20 (16 samples), indicating that sample variability should not affect the study.

Sulfur dioxide, carbon dioxide, oxygen and nitrogen were used as supplied from cylinders. The rotameters were calibrated for pressurized operation using a back pressure regulator and a Brooks flowmeter calibrator.

The sample container was a platinum gauze bag which showed no weight change on exposure to the sulfating gas mixture in a blank run.

TABLE 2

SORBENTS USED TO STUDY THE SULFATION REACTION

Sorbent	*Ca*	*Mg*	*Ignition wt. loss*	*Principal impurities*
Limestone 1359 Stephens City, Va.	38.4	.04	43.4	Silica
Tymochtee Dolomite Huntsville, Ohio	20.5	11.9	44.4	Silica, pyrites, alumino silicates
Glasshouse Dolomite (Dolomite 1337) Gibsonberg, Ohio	21.5	12.5	47.7	Silica, pyrites, alumino silicates

Experimental results

Initial trials on the sulfation of calcined dolomite 1337 at pressure, using ~100 mg samples gave results inconsistent with previous studies: the initial rate of reaction was about one-fifth of those reported by Borgwardt[9]. Further experimentation using non-isothermal calcination of limestone as a probe reaction showed that flow-rates over the sample of ~2 l min^{-1} (S.T.P.) at pressure were required to replicate atmospheric pressure calcination curves. Experiments with the sulfation reaction showed that if a small sample of raw sorbent, 20 mg or less were used, much faster sulfation rates were noted as shown in Fig. 2. The sulfation reaction at atmospheric pressures was independent of flow-rate in the range 200–600 ml min^{-1} and the rate of sulfation at 5% was close to that reported by Borgwardt[3] for the same dolomite in a differential bed reactor. With the small sample size, the rate of sulfation at 10 atm was almost independent of flow-rate in the range 2–4 l min^{-1}.

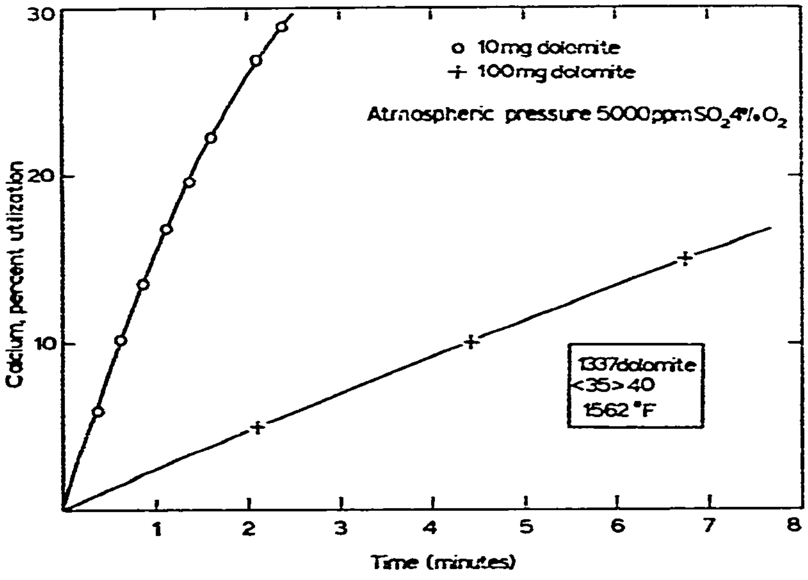


Fig. 2. Effect of sample size on sulfation of calcined dolomite 1337 in the TG.

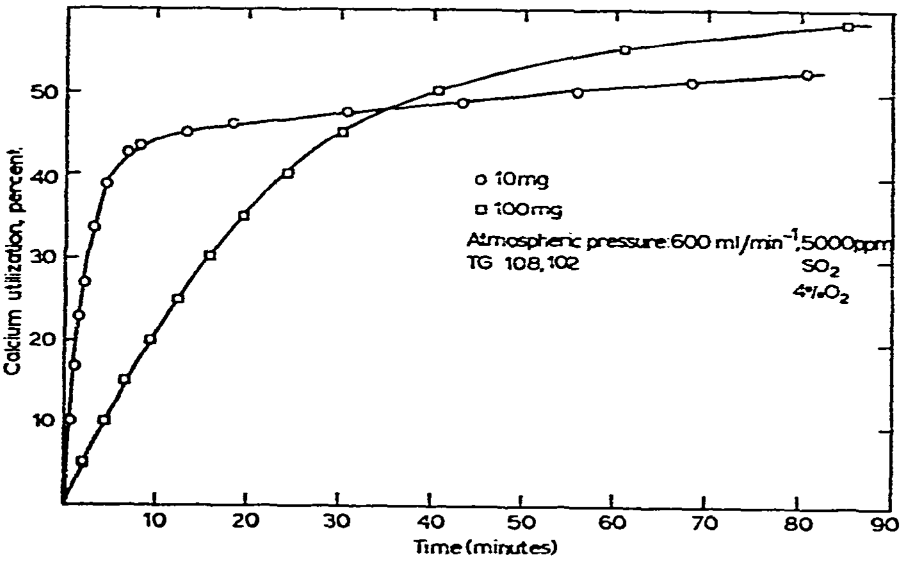


Fig. 3. Sulfation of calcined dolomite 1337.

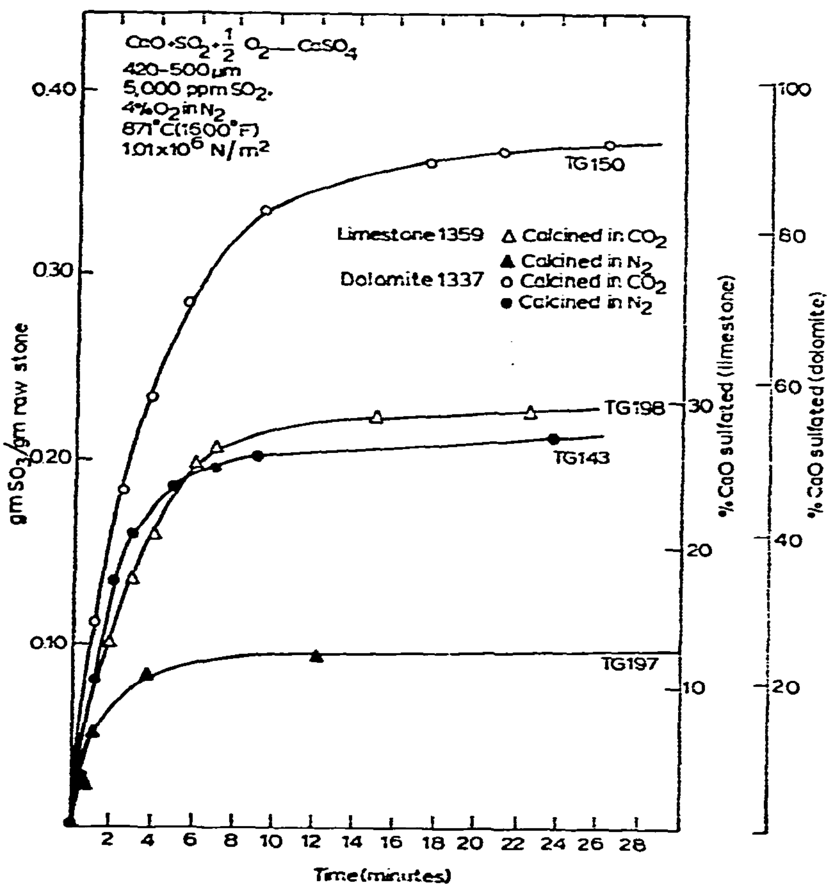


Fig. 4. Comparison of pressurized sulfation of limestone and dolomite.

The sample size exerted a second important influence on sulfation as shown in Fig. 3. Although sulfation is initially slower with the large sample, it does not suffer the abrupt decline in reaction rate of the small sample, and a higher calcium utilization is obtained.

The sulfation of calcined dolomite 1337 was then studied and three factors were noted. The effect of pressure on the initial rate of sulfation was less than double the rate observed at atmospheric pressure. Temperature had a slight effect on the rate of reaction at 10% utilization of the calcium. The reaction was first order with respect to sulfur dioxide concentration, and zero order with respect to oxygen concentration in the range 2–11% O_2. However, in some experiments, at the 500 micron diameter level, the calcium utilization achievable was ~40% and in others about 90%. Attention focused on the calcination conditions preceding sulfation. The approach taken was to calcine the stone in either an atmosphere containing 1 atm of carbon dioxide or in nitrogen. The results are shown in Fig. 4, and demonstrate that slow calcination in CO_2 greatly enhances the capacity of limestone and dolomite as sulfur sorbents. Slow calcination in CO_2 also increased the capacity of the impure stone, Tymochtee dolomite in sulfation.

In order to show that this activation process was not per se the result of sulfation at pressure, experiments were carried out at atmospheric pressure on the sulfation of limestone 1359 after calcination under different partial pressures of CO_2. The results show a strong dependence of sulfation on the carbon dioxide environment during calcination, as illustrated in Fig. 5 and Table 3.

To assess the influence of temperature, a set of experiments was carried out on calcined limestone 1359: the samples were brought to 900°C under carbon dioxide,

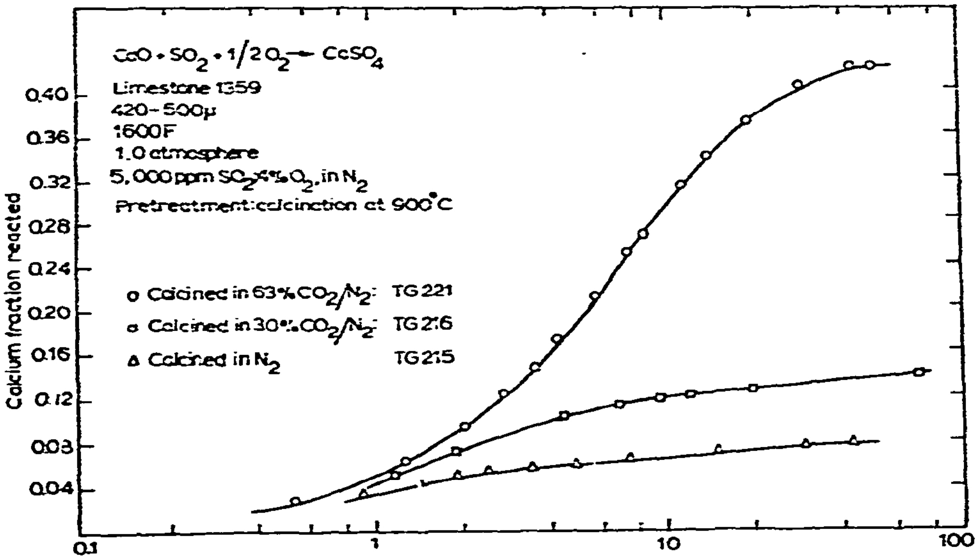


Fig. 5. Atmospheric pressure sulfation of limestone 1359—the effect of calcination history.

TABLE 3

LIMESTONE 1359 SULFATION RUNS

TG No.	*Pressure kPa (atm)*	*Particle size*	*Calnination*			*Sulfation*	
			Temperature °C (°F)	*Atmosphere*	*Time (min)*	*Temperature °C (°F)*	*Utilization % Ca*
196	1013 (10.0)	420–500	900(1652)	N_2	4.0	871(1600)	14.0
197	1013 (10.0)	420–500	680–870 (1256–1598)	N_2	~12.0	871(1600)	14.0
198	1013 (10.0)	420–500	930(1706)	10% CO_2/N_2	8.0	871(1600)	32.0
199	1013 (10.0)	420–500	930(1706)	10% CO_2/N_2	8.0	871(1600)	~37.0
215	101.3 (1.0)	420–500	900(1652)	N_2	2.5	871(1600)	9.0
216	101.3 (1.0)	420–500	900(1652)	30% CO_2 in N_2	5.0	871(1600)	14.0
220	101.3 (1.0)	420–500	871(1600)	55–30% CO_2 in N_2	80.0	871(1600)	34.5
221	101.3 (1.0)	420–500	900(1652)	60% CO_2 in N_2	30.0	871(1600)	42.0
229	101.3 (1.0)	420–500	954(1749)	15% CO_2 in N_2	~1.2	954(1749)	12.0
230	101.3 (1.0)	420–500	843(1549)	15% CO_2 in N_2	34.0	843(1549)	14.0
231	101.3 (1.0)	420–500	899(1650)	15% CO_2 in N_2	3.0	900(1652)	11.0

calcined in 0.6 atm of CO_2 and were then sulfated at temperatures in the range 750 to 950°C, in random order. The results are shown in Fig. 6. The calcium utilization noted after 1 h at each temperature, is shown in Fig. 7.

DISCUSSION

Comparison with other data

The rate of sulfation at atmospheric pressure noted in this study is comparable to the fastest rates reported in the literature: there is an order of magnitude spread in the published data. For limestone calcined and sulfated at 850°C and atmospheric pressure, the calculated rate is 1.92×10^{-5} mol SO_3 g calcined dolomite^{-1} sec^{-1} in agreement with the value of ~2.1 read from Borgwardt's graphs[3]. The comparison with data reported by the National Coal Board (U.K.) investigators[8] is more interesting. They reported an initial rate (at 4.6% calcium utilization) of 0.112 m^3 kg^{-1} sec^{-1}, compared to the value obtained here of 0.45 m^3 kg^{-1} sec^{-1}, under comparable conditions. However, they suspected that SO_2 stagnation in their apparatus had limited the rate to a maximum value of 0.131 m^3 kg^{-1} sec^{-1}. It is, therefore, appropriate to compare the rates at higher utilization. For TG107 at atmospheric pressure, the rate at 22% calcium utilization was 1.1×10^{-1} m^3 kg^{-1} sec^{-1}. For NCB run 53 at 23% utilization, the rate was 9.77×10^{-2} m^3 kg^{-1} sec^{-1}.

The effect of pressure

The direct influence of system pressurization on reaction rate in the sulfation of lime or calcined dolomite is relatively minor: it is the sorbent capacity which may

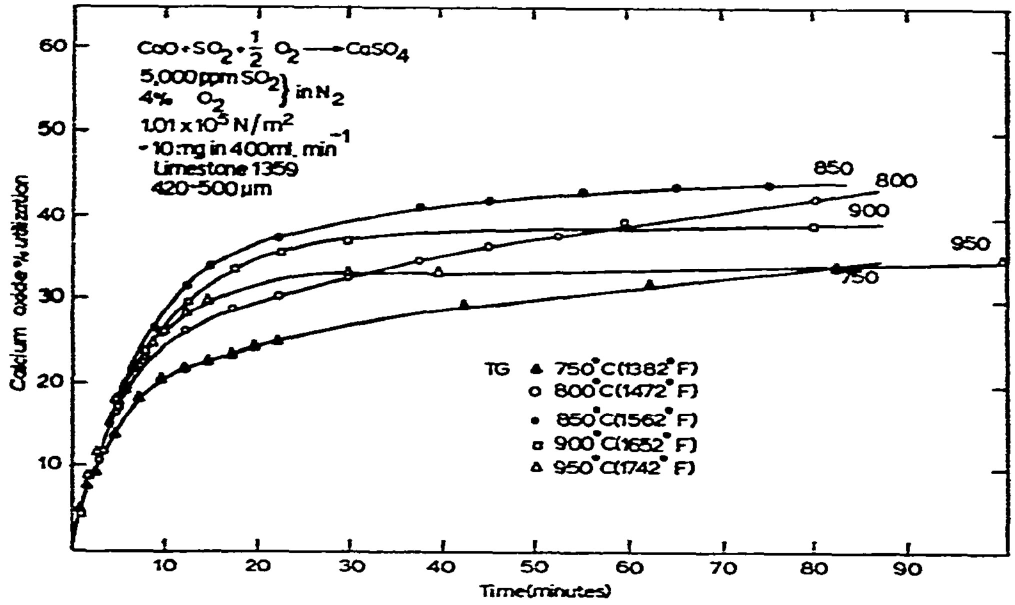


Fig. 6. The effect of temperature on limestone sulfation.

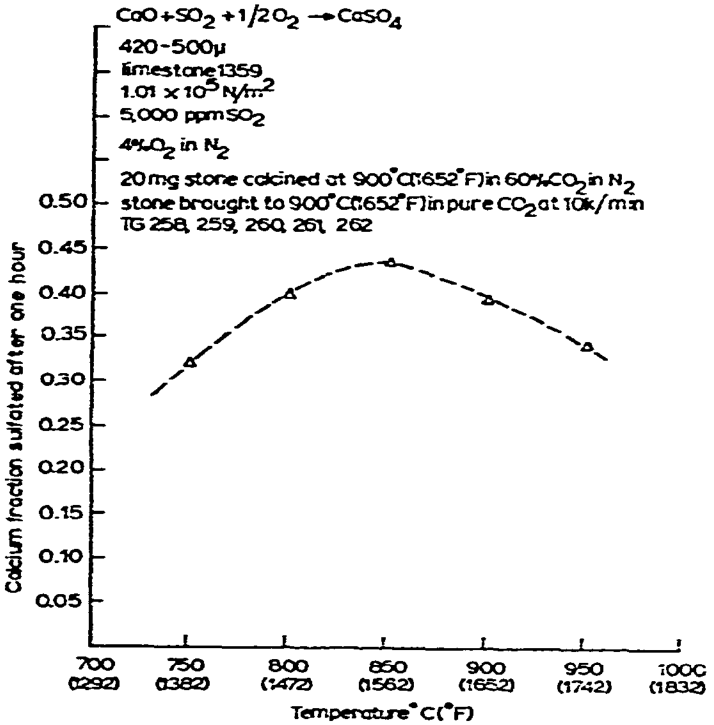


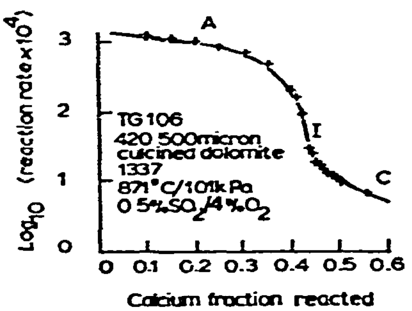
Fig. 7. The effect of temperature on CaO utilization in sulfation.

be most directly affected. McKewan[17] noted that increasing system pressure from 1 to 10 atm increased the rate of reduction of magnetite with hydrogen by a factor of 1.88.

The study by Borgwardt and Harvey[4] shows clearly that large pores which can accommodate the sulfate ion govern the capacity of calcium oxide to react with sulfur dioxide. Sorbents which form pores of fine radii may have high initial rates of reaction: however, the entrance to these pores rapidly becomes clogged leaving a sulfated shell which prevents further utilization of the stone's theoretical capacity. If this picture is accepted then it means that when limestone is calcined under a high partial pressure of CO_2 relative to the equilibrium partial pressure of $CaCO_3/CaO$, there is sufficient time for the oxide lattice to adjust so that large pores grow at the expense of small pores, and while the initial rate of reaction may be somewhat lower, the ultimate capacity of the stone is increased. (A 500 micron particle of limestone calcines in 2 min at 900°C under a fast nitrogen flow: in 60% CO_2, the limestone calcines in about 90 min.)

This may explain the data shown in Fig. 3. Because the 100 mg sample is relatively bulky and consists of a heap of dolomite particles, its calcination is retarded by the relatively poor ability of the nitrogen flow to remove the CO_2: thus an active dolomite with high pore volume capacity for sulfate is created. When exposed to the SO_2-containing stream, the reaction is slow because of poor mass transfer to the stone surface. However, the decline in reaction rate is not abrupt as it is with the fast calcined 10 mg sample which sulfates initially at a high rate but has a low pore volume capacity for calcium sulfate.

The overall rate of reaction of the sulfating gas with dolomitic calcium oxide is typified by Fig. 8. It shows an initial reaction rate in the region A which is probably limited by mass transfer from the gas to the stone surface. The apparent activation energy for this phase of the reaction is 5 kcal mol^{-1}. The rate is virtually independent of the substrate stone (limestone or dolomite), and while the reaction is first order with respect to sulfur dioxide, increasing the system pressure to 10 atm increases the rate by a factor of two, not ten. This latter change in rate is of the order predicted by



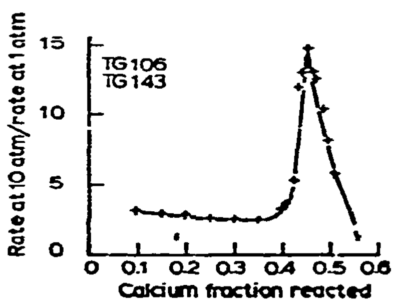


Fig. 8. The decline in rate of reaction (calcium fraction reacting per minute) as calcined dolomite sulfates.

Fig. 9. The effect of pressure on sulfation of calcined dolomite 1337 (420 μm; 0.5% SO_2/4% O_2; 871°C).

mass transfer to the surface of a sphere using standard correlations for the reactor and gas flow conditions used.

As the pores become lined with calcium sulfate, an additional barrier to reaction arises—the available exposed surface area of CaO within the solid decreases. The sulfur gases conducted down the pores no longer react rapidly with the walls and eventually the pressure of SO_2 within the pores rises to equal that in the gas stream. Consequently the rate of reaction in this phase should be proportional to the partial pressure of SO_2 in the system and an increase in system pressure to 10 atm should cause a ten-fold increase in reaction rate, as long as reaction on a CaO surface is the dominant reaction path. Figure 9 shows that this effect is observed. In each of three cases tested, the ratio of rates at 10 and 1 atm total pressure rose to a value greater than or equal to 10. In the final phase of reaction, C, when the only route to reaction is by diffusion through the product layer pressure should exert no effect, since the diffusion coefficient of the gas is inversely proportional to the pressure. This effect is also noted in Fig. 9.

If the variation in the sorbent porosity causes the capacity of the limestone in sulfation to vary from 7 to 35% of the theoretical value, then the use of quantitative models of the rate of reaction as a function of sorbent utilization is made extremely difficult. Current models[18,19] require the use of a void fraction or fractional porosity in the solid. Before meaningful definition of the rates of sulfation for a particular limestone can be made, an experimental study of the development of porosity during calcination is required.

The effect of temperature

The effect of temperature on the sulfation of lime, as originally observed by Moss[10] is accurately duplicated by the TG experiments as shown in Fig. 7. It is not necessary to invoke an oxidizing/reducing cycle in the fluidized bed combustor to explain the temperature maximum phenomenon: (however, there is no doubt that such an oxidizing/reducing cycle is a characteristic of the bed). Moss found the maximum temperature for efficient SO_2 absorption at a given Ca/S mol ratio fed to a fluidized bed was 856°C, in agreement with the data shown here. It is important to note that the CO_2 partial pressure generated in a fuel combustion experiment at atmospheric pressure ($\sim$0.2 atm) is high relative to the equilibrium partial pressure over $CaCO_3$/CaO up to $\sim$830°C: thus when calcination occurs at higher temperatures, the sorbent will have a lower capacity for SO_2. The decline in sulfur removal efficiency will be more marked than Fig. 7 shows.

The reason for the temperature maximum observed in fluidized bed combustion may be attributed in part to the calcination conditions of the sorbent. However, since the curves in Fig. 6 were obtained on sorbents calcined under uniform conditions, the chemistry of the reaction must be important. Moss has attributed the maximum to the concentration of sulfur trioxide, SO_3 in the system. However, if the SO_3 concentration which ranges (at equilibrium), from 20% of the input sulfur at 750°C to 6% at 950°C, is dominant, then its influence should be evident in the early stages of the reaction:

in the first 20% of sulfation the reaction increases monotonically with temperature. An alternative suggestion is that reaction occurs by adsorption of SO_2 on the surface to form relatively unstable calcium sulfite $CaSO_3$ (reaction 1). The sulfite immediately disproportionates to CaS and $CaSO_4$. A competition then exists between the reaction[14]

$$\tfrac{1}{4}CaS+\tfrac{3}{4}CaSO_4 \rightarrow CaO+SO_2 \tag{2}$$

and oxidation of calcium sulfide

$$CaS+2O_2 \rightarrow CaSO_4 \tag{3}$$

As Fig. 10 shows, reaction 1 has a rate maximum at 820°C. While reaction (2) is as fast as reaction (1) at 890°C, the sulfide oxidation reaction would upset the equilibrium and cause continued sulfation, but at a lower rate.

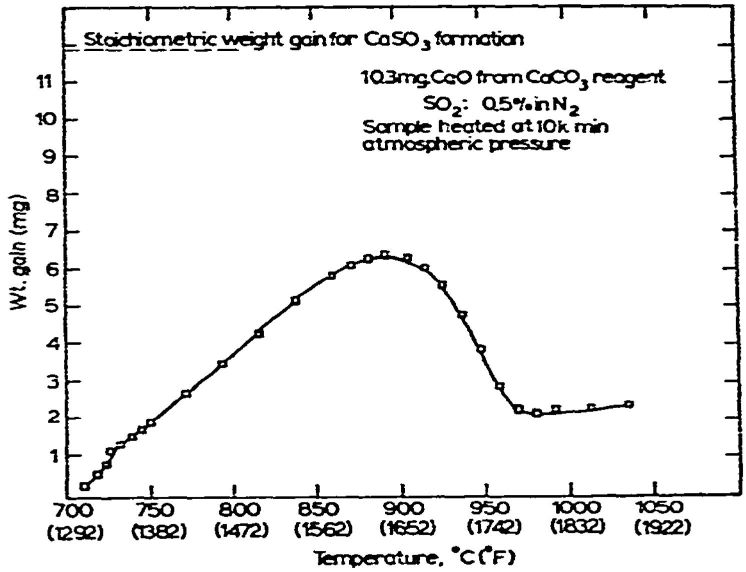


Fig. 10. The effect of temperature on the course of the reaction between SO_2 and CaO.

CONCLUSIONS

A high partial pressure of carbon dioxide during calcination of limestone and dolomite is a key factor in increasing the sorbent capacity in sulfation. Since high partial pressures of carbon dioxide are generated in the fluidized bed combustion of fossil fuels at pressure, sorbent utilization should be enhanced, by pressurized operation. The increase in partial pressure of SO_2 caused by system pressurization leads to modest increases in reaction rate during most (~ four fifths) of the sulfation reaction. Thermogravimetric studies qualitatively replicate the effect of temperature on sulfur dioxide retention in fluidized bed combustion. Further studies on the quantitative prediction of fluidized bed desulfurization from thermogravimetric data will be reported.

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