

Kinetics of lime-limestone sulfation: review of lime reactivity and sulfation kinetics in the dry limestone desulfurization processes

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Abstract. The necessity for the control of the growing problem of atmospheric pollution by sulfur dioxide is emphasized, and the advantages and disadvantages of the widely accepted dry limestone desulfurization process are indicated. Various important properties of limestone and the reaction parameters influencing SO_2 reactivity are critically discussed. The kinetics of the lime-sulfation reaction and the probable reaction mechanism based on recent experimental investigations are briefly summarized. The present knowledge of the SO_2 reactivity and related phenomena is presented, together with examples of possible areas of improvement of the process.

1 Introduction

The development of economic and practical methods for the solution of the growing problem of atmospheric pollution by sulfur dioxide emission is one of the major unmet needs in air-pollution control today. Statistics reveal that in 1970 the discharge of sulfur oxides to the atmosphere in the United States amounted to about thirty-four million tons and is likely to reach almost double of this value in 1990 with the continuation of present practices for control of SO_2 pollution (Ludwig and Spaite 1967). Of the various emission sources—coal and oil power plants, ore smelting, refinery operations, and others—the generation of electric power is the largest single contributor with approximately one-half of the emission of 1970; and this contribution is likely to reach ~70% of total SO_2 emission in 1990 (Hangebrauck and Spaite 1967). This alarming situation has stimulated a large amount of research and development on methods of removing this pollutant from power-plant waste gases. Various schemes have been proposed, and a comparative description of these, along with an economic assessment, has been given elsewhere (Cortelyou 1969; Newell 1969).

The lime-limestone processes are widely applied to flue-gas desulfurization because of their inherent advantages, such as the simplicity of the process, low capital investment, and ready availability of the material at low cost. These processes can be of either dry or wet type, but the wet processes have been more widely adopted. Several modifications of both the processes have been achieved in recent years, in order to make these more efficient and economical (Hubble et al 1975; Lummus Co. 1967; Alvin et al 1969; Plumley 1967). Two serious drawbacks of the dry desulfurization processes are the low efficiencies of desulfurization and of additive utilization. A good understanding of the parameters affecting the reactivity of lime with respect to SO_2 , and a clear picture of the mechanism of the lime-sulfation reaction will go a long way towards solving the above problems. It has therefore been attempted here to bring together the salient points of the various investigations relating to the above two aspects of the dry limestone desulfurization processes in form of a technical review, as an article of this nature does not exist in the literature.

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2 Reactivity of limestone with respect to SO_2

In the development of limestone desulfurization process, it became apparent that some limestones are better absorbents than others, and that selective recommendation of limestones would be necessary to optimize full-scale field trials in power boilers. The sorption capacity (which will be referred to simply as 'capacity') of limestone depends on its reactivity. Potter (1969) defined SO_2 capacity as the gain in weight of a sample of fresh or precalcined limestone when exposed to a stream of SO_2 .

The important properties of limestone and reaction parameters which have been found to influence the reactivity of SO_2 are:

- (i) chemical composition of limestone;
- (ii) limestone calcination time and temperature;
- (iii) physical properties of calcines;
- (iv) sulfation reaction temperature;
- (v) miscellaneous properties.

The above effects have been investigated by Borgwardt and Harvey (1972), Drehmel (1971), Falkenberry and Slack (1969), Hammons and Skopp (1972), Harrington et al (1968), Hartman (1976), Hartman and Coughlin (1974), Ishihara (1975), O'Neill (1975), and Potter (1969). These effects will be examined in turn in the following sections.

2.1 *Chemical composition of limestone*

Harrington et al (1968) attempted to explain the wide range of reactivities exhibited by the different test stones in view of their varying chemical composition. Single-component and multiple-component correlation studies between the reactivity of a material and its content of calcium, magnesium, silicon, and aluminium failed to establish any composition dependency. The only correlation obtained was a very weak relationship between increasing reactivity and increasing content of iron oxide. Relatively high reactivities of stones low in iron content indicated that other characteristics of the stones are equally important. Potter (1969) observed that, of the chemical components only the iron is significantly related to the SO_2 capacity of limestone at or above the 90% confidence level. Whether the contribution of the iron is physical or chemical has not been established.

Falkenberry and Slack (1969) noted that high-calcium limestones are more reactive than dolomitic limestones. Silica was found to be the most undesirable impurity, as it appeared to fuse and glass-over the calcine and thus reduced the effectiveness of the limestone particles in reacting with SO_2 . Murthi et al (1971) observed that the presence of 10% moisture in calcined limestone substantially reduced SO_2 capacity. The main undesirable impurities in the carbonate rocks are silica and alumina. These impurities combine with CaO at temperatures $> 1080^\circ\text{C}$ to form slags which reduce the amount of active lime and occlude pores in the lime thereby reducing its reactivity (Nicholls and Reid 1932).

2.2 *Limestone calcination time and temperature*

Work by Boynton (1966) on limestone calcination has shown that the time and temperature of calcination have significant effects on reactivity, and that the reactivity increased when the calcination time was increased from 1 h to 2 h. These investigations also indicated that maximum reactivity was generally obtained when the samples were calcined for ~ 2 h at 980°C . It was also observed that an increase in calcination temperature from 930°C to 980°C resulted in equal numbers of particles with increasing and decreasing reactivities, for particle sizes in the range 0.6-1.7 mm.

Potter (1969) conducted fixed-bed calcinations at 1360°C for 16 h in order to evaluate the effect of high-intensity calcination on the SO_2 capacity and physical properties of the calcines. The samples were tested in the fixed-bed reactor both in

the calcined form and in the uncalcined form. The correlation coefficient between capacities of uncalcined and calcined samples was found to be 0.73; the mean loadings of uncalcined and calcined samples were 41.7 and 43.1 g SO₂/100 g sample, respectively. These values suggested that for these conditions the relative capacity of a sample is unaffected by calcination.

Modification of the SO₂ capacity of limestone was achieved by O'Neill (1975), who adopted a technique in which limestone or dolomite was calcined in an atmosphere of high CO₂ concentration. The calcination was performed at a partial pressure of 3 mol% and a partial pressure of CO₂ that is greater than the equilibrium partial pressure of CO₂ over CaCO₃ at 900 °C. After such calcination, 90% of the sulfur contaminants were removed from the flue gas used to test the capacity of the stone.

Investigations by Drehmel (1971) also emphasized the importance of calcination conditions in improving the stone reactivity. Dead-burning, or overburning, of the stone was found to be harmful as it made the lime unreactive. The loss in reactivity observed at high calcination temperatures was attributed to the loss in surface area and pore volume. Murthi et al (1971) also indicated that the capacity of individual samples varied with calcination time and temperature. With elevation of the calcination temperature to 1230-1430 °C, the lime sinters. This causes the particle size to decrease, thus increasing the bulk density and reducing the porosity or surface area and the SO₂ sorption capacity. To prevent this, dead-burning must be avoided in calcination.

2.3 *Physical properties of calcines and additives*

Petrographic examination and grain-size distribution measurements were made by Borgwardt and Harvey (1972) on eleven specimens representing a wide spectrum of limestones and dolomites. Stones of various geological types yielded calcines of distinctly different physical structures and showed correspondingly large differences both in rate of reaction and in SO₂ capacity. Pore size and particle size together determined the extent to which the interior of individual particles reacted. Variations in effectiveness for flue-gas desulfurization were explained in terms of the physical properties of the calcines which, in turn, were related to the crystal structure of the original rock. These authors suggested that the presence of imperfections and grain boundaries in crystalline rocks tends to enhance their reactivity, possibly by facilitating the conversion from anisotropic calcite to isotropic lime during calcination.

Potter (1969) conducted experiments at various calcination temperatures; various physical properties of the calcines obtained were tested. In all cases, a loss in surface area and an increase in the mean mercury-intrusion pore size were observed when the calcination temperature was increased from 980 °C to 1320 °C. The variations in SO₂ capacity that resulted from changes in the calcination procedure are well explained by consideration of pore volumes >0.3 μm; the minimum pore diameter measured was 0.017 μm. Those samples whose number of large pores was reduced showed a corresponding loss of capacity, whereas samples whose SO₂ capacity increased as a result of high-temperature calcination were found to have increased numbers of pores that had diameters >0.3 μm.

Modification of reactivity of the nonreactive limestones by changing the porosity and thereby increasing the quantity of sulfur capture has also been investigated. Two methods have been demonstrated: (a) a slow calcination of the stone (O'Neill et al 1976); and (b) addition of salts (Johnson 1977). In the slow-calcination method, the stone would probably be precalcined in a separate vessel specially constructed for this purpose. In the second method, additives such as NaCl, Na₂CO₃, Na₂SO₄, KCl, and CaCl₂ have effectively increased the utilization of calcium by 25-200%. The chlorides of sodium and potassium appear to be the most effective salts for this

purpose. Van Houte et al (1978) also observed a large increase in the degree of transformation from 20% to 90% when limestone was doped with ~2 wt% CaCl₂.

2.4 Sulfation reaction temperature

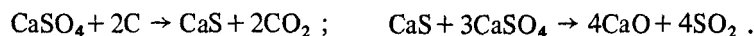
The temperature of the sulfation reaction is a variable of major importance in comparing the reactivities of various stones. Extensive studies have been made by Harrington et al (1968) and by Potter (1969). In order to evaluate the effects of temperature, Harrington et al prepared samples by calcining at 980 °C for 2 h; the calcines were then tested for SO₂ capacity at temperatures of 760, 870, and 980 °C. The reactivity was found to increase with temperature between 760 °C and 870 °C. A further increase of temperature to 980 °C produced mixed results. The reaction temperature was found to influence the reactivity to a much greater extent than the calcining conditions.

Potter (1969) investigated various materials based on calcium and magnesium—including the carbonate, oxide, and hydroxide forms, a high-calcium stone, and a dolomite stone—at reaction temperatures of 430, 700, 980, and 1090 °C. The following observations were made:

- (i) The hydrates exhibit greater capacity than the oxides and carbonates throughout the temperature region examined.
- (ii) Below 900 °C, the capacity of the calcined stone is greater than that of the carbonate.
- (iii) Above 1000 °C, the SO₂ loading generally decreases with increasing temperature. This reduced capacity may result either from changes in physical properties or from thermodynamic limitations.

2.5 Miscellaneous properties

The effect of regeneration of sulfated lime on its SO₂ capacity was investigated by Hammons and Skopp (1972). The SO₂ capacity of the larger stone increases following the first regeneration but decreases slowly thereafter. This initial increase in capacity is possibly related to a more favourable crystal lattice resulting from the elimination of SO₃ from the sulfated material, compared with the crystal lattice of calcined limestone. However, Montagna et al (1977) have found that a regeneration procedure reduces the reactivity of lime to a certain extent. Chen and Yang (1979) report on a two-step reaction mechanism describing the regeneration of sulfated lime:



Kinetic investigations lead to the conclusion that the second equation represents the rate-determining step.

Ishihara (1975) studied the effects of variables such as the injection-site temperature, the amount of injected additive, and the iron oxide content of additive on the reactivity of CaO. The reactivity was found to increase as the iron oxide content of the limestone increased. Ishihara also proposed power-law relationships between CaO reactivity and limestone particle size (with exponent values 0.25-0.33), and between CaO reactivity and SO₂ concentration in the flue gas (with exponent values 0.3-0.5).

3 Kinetics of the lime-sulfation reaction

During the last decade, a number of investigations have been made on the kinetics of the reaction of SO₂ with limestone in the dry desulfurization processes. The most important are those by Bethell et al (1973), Borgwardt (1970), Borgwardt and Harvey (1972), Chen and Saxena (1977), Hammons and Skopp (1972), Hartman and Coughlin (1976), Jonke (1972), Murthi et al (1971), Pigford and Sliger (1973), Potter (1969), Reid (1970), Wen and Ishida (1973), and Whitten and Hagstrom (1970).

Two major directions have been emphasized in these investigations:

- (a) the study of the effect of various process variables on the reaction rate;
- (b) identification of the reaction mechanism with the help of a suitable model.

The absorption of SO_2 by limestone involves two consecutive reaction steps:

- (i) dissociation of calcium carbonate; and
- (ii) reaction of CaO with SO_2 . The rate of this second step is the important factor in all the pollution-control processes. These two steps will be examined separately below.

3.1 *Dissociation of calcium carbonate (calcination)*

Potter (1969) suggested that calcination and sulfation occur sequentially and therefore compete for the limited period of time of the high-temperature calcination treatment. The optimum calcination temperature was found to vary by several hundred degrees for different naturally occurring limestones. It was also observed that high temperatures increase calcination rates, but that excessive temperatures result in dead-burning. Dead-burning of limestone is responsible for low sorbent utilization, with equilibrium levels <1 ppm SO_2 at temperatures <760 °C. Reid (1970) found that raw limestone can also desulfurize flue gas. Hence, as far as thermochemistry is concerned, it would appear that calcination is not necessary for sulfur fixation. A similar observation was made by Whitten and Hagstrom (1970) as regards calcination. They further observed that the degree of calcination was almost independent of particle size above 1150 °C, but was mainly controlled by residence time and temperature. Murthi et al (1971) studied the calcination parameters of limestones and dolomites in a small rotary kiln and found the optimum conditions for this process to be a calcination time of 2 h at 850 °C. They emphasized the importance of calcination in developing a reactive lime or magnesia to capture SO_2 from flue gas by the dry injection process.

3.2 *Contact between the sorbent and SO_2 (sulfation)*

The contact between sorbent and flue gas can be accomplished in either a fixed or a fluidized bed. SO_2 sorption rates were determined by Murthi et al (1971) in a fixed-bed reactor. Miyajima (1974) obtained the optimum operating conditions for desulfurization by limestone in another fixed-bed process. Absorption of SO_2 in a fluidized-bed reactor has been studied by various investigators, including Bethell et al (1973), Chen and Saxena (1977), Ghose et al (1971), Hammons and Skopp (1972), Hartman and Coughlin (1974, 1976), Jonke (1972), Vejvoda et al (1968), and Whitten and Hagstrom (1970). The objectives of these studies can be summarized as follows:

- (a) To determine how sulfur retention is affected by independent fluidized-bed variables such as bed temperature, gas velocity, bed height, and additive particle size;
- (b) to determine how the sorption reaction is affected by the additive feed rate, presence of water vapour, residence time, impurities in lime, sorbent injection temperature, and injection air velocity;
- (c) to obtain information on limestone utilization and desulfurization efficiency;
- (d) to obtain information on the mechanism of the lime-sulfation reaction.

The important conclusions obtained from these investigations include the following:

- (i) The rates of sorption of SO_2 were dependent on reaction temperature and limestone (or dolomite) particle size, for tests in a fixed bed reactor. The average rate of sorption was estimated to be 2×10^{-4} g SO_2 (g calcined sample) $^{-1}$ s $^{-1}$, up to 15% conversion of CaO .
- (ii) Above 760 °C, the sulfation of lime appears to be a first-order reaction.
- (iii) In fixed-bed desulfurization of a flue gas containing 2000 ppm SO_2 with powdered limestone of particle size 1-2 mm, maximum desulfurization was obtained at 1050 °C with a Ca/S mole ratio of 2.

(iv) A maximum recovery of 30% of the sulfur present in a high-sulfur coal (3-5 wt% sulfur) was achieved by keeping the absorbing medium (ie limestone) in the fluidized-bed condition at a temperature of 500 °C. Under identical conditions the above recovery increased to 42% when sodium carbonate was used as the absorbent.

(v) The carbon dioxide liberated from the decomposition of lime hinders the sulfation reaction by blocking the diffusion of SO₂ into the interior of the particle. Water vapor introduced into the system acts catalytically, and at 8 mol% water vapor the adverse effect of CO₂ is more than compensated.

(vi) The adverse effect of silica, which forms slag at elevated temperatures and reduces the active surface area for the lime-sulfation reaction, is corrected by the addition of a small quantity of ferric oxide. The presence of ~2 wt% Fe₂O₃ also improves the flow characteristics of powdered additives.

(vii) Use of limestones, dolomites, or chalks as dry additives in quantities 1.5-2.0 times in excess of stoichiometric, properly injected for good distribution, at temperatures of 1150-1370 °C, can reduce the SO₂ content of flue gas up to 65% in small combustion installations. The optimum particle size and injection temperature for maximum desulfurization are characteristic of the additives.

3.3 Kinetics of the sulfation reaction

The kinetics of the lime-sulfation reaction has been quite extensively investigated by most of the above-mentioned authors. The results can be discussed under the following headings.

3.3.1 *Temperature effects.* The sorption of SO₂ by CaO in the presence of oxygen proceeds as follows (Reid 1970):



The equilibrium constant, K , is related to the free energy change, ΔG_T° , by the equation

$$\ln K = -\frac{\Delta G_T^\circ}{RT} \quad (2)$$

where R is the gas constant and T is the absolute temperature. For reaction (1), the value of K calculated from equation (2) can be related to the composition of the system by the equation

$$K = \frac{a_{\text{CaSO}_4}}{a_{\text{CaO}} x_{\text{SO}_2} x_{\text{O}_2}^{1/2} (p/p^\circ)^{3/4}} \quad (3)$$

where a_{CaSO_4} and a_{CaO} are the activities of the solids; x_{SO_2} and x_{O_2} are the mole fractions of SO₂ and O₂ in the gas phase; p is the pressure; and p° (= 1.01325 bar) is the standard pressure. At $p = p^\circ$ and with the solid activities taken to be unity, equation (3) simplifies to

$$x_{\text{SO}_2} = \frac{1}{K x_{\text{O}_2}^{1/2}} \quad (4)$$

By using the value of K from equation (2), the mole fraction of SO₂ in the flue gas containing x_{O_2} mole fraction of O₂ can be calculated for any temperature. Calculations of SO₂ equilibrium concentration for CaO and MgO sorbents in 2.7 mol % O₂, performed by Reid (1970), are reproduced in figure 1 (Murthi et al. 1971). At low temperatures, the equilibrium concentrations of SO₂ are favourably small. However, the time required to reach equilibrium would be impracticably long because of kinetic considerations. An upper temperature limit of desulfurization is determined by the initial concentration of SO₂ in the flue gas (in these calculations, a value of

2700 ppm was assumed). The lower temperature limit corresponds approximately to an equilibrium concentration of 1 ppm. Thus the desulfurization temperature ranges are chosen to be 980-1230 °C for CaO and 650-820 °C for MgO. Above 820 °C, CaO seems to be the more effective desulfurizing agent.

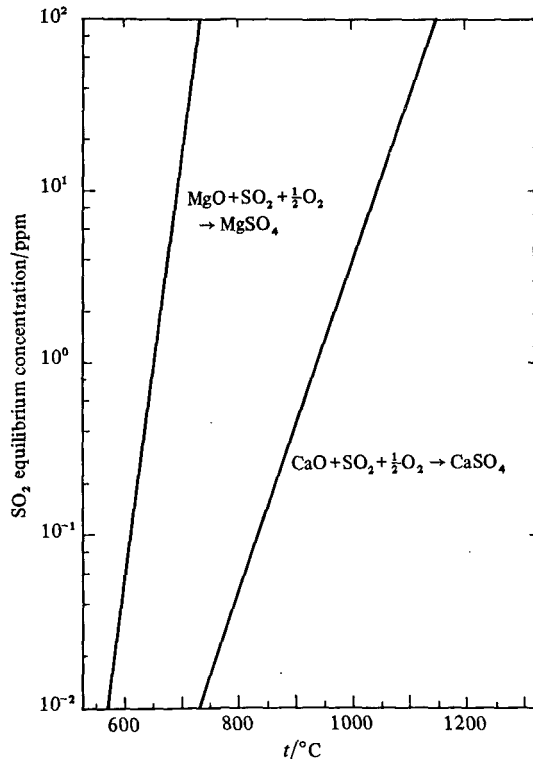


Figure 1. Calculated equilibrium concentration of SO_2 in flue gas, containing 2.7 mol% O_2 , in contact with CaO and MgO. After Reid (1970).

3.3.2 *Effects of particle size and pore size.* Borgwardt (1970) used the differential reactor technique to measure the rate of reaction with four normal specimens of limestone after calcination at standardized conditions. The effect of particle size on reaction rate was determined by plotting the rate, r , of reaction at a constant sulfate loading against the inverse of particle diameter (figure 2). It was observed that the rate was not proportional to the specific surface; and for fine particles ($d < 500 \mu\text{m}$) the rate was only weakly dependent on particle size.

Later, Borgwardt and Harvey (1972) studied the desulfurization reaction kinetics of eleven different calcines at 530 °C. The variations in the physical structure of the calcines resulted in large differences in the rate of reaction as well as in the capacity for SO_2 sorption. As stated in section 2.3, pore size and particle size together determine the extent to which the interiors of individual particles react. Particles smaller than 100 μm with pores larger than 0.1 μm react throughout their internal pore structure at a rate directly proportional to the surface area as measured by the Brunauer-Emmett-Teller (BET) method. Small pores result in a high reaction rate, but if the particles are large, their capacity is low. Large pores give lower reaction rates and increased capacities. The rate decays exponentially as sulfation proceeds until the pores are filled with reaction product. The high reaction rates achieved in the limestone injection process apparently result from the large active surface area existing for short periods immediately after the dissociation of CaCO_3 .

Hartman and Coughlin (1974) developed a simple structural model in order to correlate their experimental results for the reaction of porous limestone particles with SO_2 gas. The model incorporates parameters such as porosity, true density, CaCO_3 content of the natural rock, and the rate of conversion to sulfate. Comparison between the model and the experimental results indicates that the reaction is strongly influenced by the reduction in porosity caused by sulfation. Both reaction rate and porosity become very small at conversions of $\sim 50\%$. The pore-size distributions of calcines and sulfated samples are remarkably different. Pores with radii $>0.4 \mu\text{m}$ are probably responsible for high SO_2 capacity in limestone. Incomplete conversion of CaO results from the strong diffusional resistance in the interior of the particles owing to the reduction in porosity as the reaction proceeds.

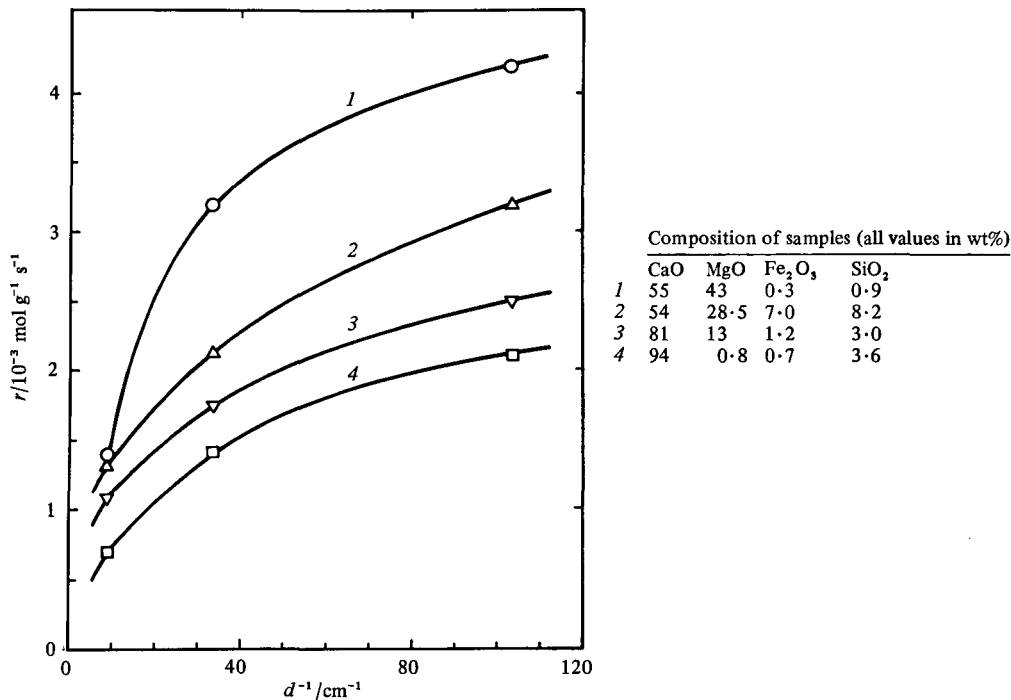


Figure 2. Reaction rate, r , of different calcines with SO_2 versus reciprocal particle diameter, d^{-1} . After Borgwardt (1970).

3.3.3 Effect of SO_2 concentration and the order of the sulfation reaction. The effect of SO_2 concentration on the rate of sulfation was studied by Borgwardt (1970). The SO_2 concentration was varied between 60 and 6000 ppm. The rate was measured for a CaO conversion of 10.5% in 1.2 mm stone particles reacted at 870°C . The straight line fitted to the logarithmic rate data yields a slope of one (figure 3), thus the reaction appears to be of first order with respect to SO_2 concentration.

3.3.4 Reaction rate and CaO consumption. The reaction rate decreases rapidly with increasing conversion; this can be described by an exponential relationship between the frequency factor, A , and the sulfate loading. The rate constant per unit volume of solid, k_v , is thus a function of temperature and sulfate loading, and can be described by the Arrhenius equation:

$$k_v = A \exp\left(-\frac{E}{RT}\right). \quad (5)$$

The activation energy, E , was found to be dependent upon the type of stone, with values in the range 34–76 kJ mol⁻¹ (Borgwardt 1970). CaO consumption ranged from 4.5% for particle sizes >150 μm to 42.5% for 75 μm particles. The additive efficiency is defined as the weight of sulfur removed relative to the weight of additive input (Whitten and Hagstrom 1970).

Borgwardt and Harvey (1972) also reported that CaO consumption increased by a factor of two when the particle size was reduced from 1.3 to 0.25 mm, and increased again by a factor of three when particle size was reduced from 0.25 to 0.096 mm.

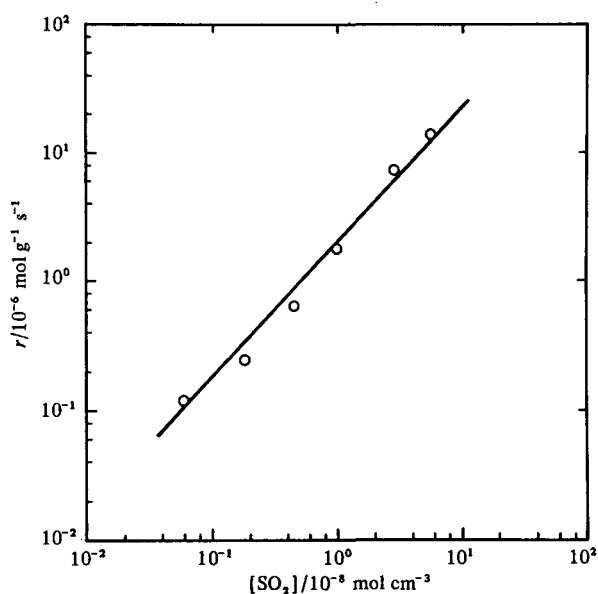


Figure 3. Reaction rate, r , of a dolomitic calcine (sample 1, figure 2) as a function of SO₂ concentration. After Borgwardt (1970).

4 Mechanism of the sulfation reaction

4.1 The grain model

According to this model, a limestone particle is considered to be a porous particle comprising spherical grains of uniform size separated by pores through which the reacting gases diffuse. As the reaction proceeds, a shell of reaction product is formed on the surface of the grains. In their approach, Pigford and Sliger (1973) assumed that the reaction rate is governed either by the diffusion of SO₂ through the pores or by its diffusion through the developing shells of the reaction product. This model was tested on the data of Coutant et al (1971) and of Borgwardt (1970). Contrary to the assumptions of Pigford and Sliger, the experimental findings of Wen and Ishida (1973) showed that at low temperatures (590–680 °C) the overall rate was controlled by the chemical reaction taking place on the grains of CaO. Borgwardt (1970) concluded that the diffusional resistance developed in the particle interior becomes limiting only after the conversion reaches values >20%. In order to obtain a better understanding of the intricate reaction between limestone particles and SO₂ in the light of the grain theory, Hartman and Coughlin (1976) have developed a mathematical model incorporating the effect of the chemical reaction step therein, as suggested by Shen and Smith (1965). Good agreement has been obtained between the predictions of this model and the experimental results.

4.2 *The shell model*

Falkenberry and Slack (1969), Harrington et al (1968), and Jonke (1972) have explained the mechanism of the lime-sulfation reaction on the basis of a shell-formation model. According to this model, a product shell is produced on the surface of the particles during the preliminary stage of sulfation, making unreacted material located within the particle inaccessible for further reaction. According to Falkenberry and Slack (1969), the sulfation reaction, which is slow compared to the calcination reaction, proceeds in two stages: the first is chemical in nature, with a rate proportional to the reciprocal of the average particle diameter and to a porosity parameter; the second involves diffusion of SO_2 through the shell formed in the first stage, and is quite slow. Jonke (1972) proposed that sulfation proceeds essentially via the shell-formation step, and is enhanced by localized reducing conditions in the dense phase of the fluid bed. Electron-microprobe examination of sulfated lime particles taken from elutriated solids and from (reducing atmosphere) combustor beds showed varied sulfur distributions. For some particles taken from the combustor bed, distribution of sulfur across the particle diameter was almost uniform; and for the others, there was deep sulfur penetration. This supported the hypothesis that local reducing conditions existing during combustion promote the penetration of SO_2 into the lime particles.

A mathematical model of the CaO-SO_2 reaction in a fluidized-bed combustor was given by Bethell et al (1973). This model was found to be suitable for dolomite and reactive limestone. Chen and Saxena (1977) have also developed a model for the combustion of coal in fluidized beds, with sulfur emission control by limestone or dolomite.

5 Compact limestone desulfurization process (regeneration of sulfur acceptor)

Because of the poor conversion efficiency of the lime-sulfation reaction (even if additives are used), large quantities of limestone are required to achieve low SO_2 emission from the combustion of high-sulfur coal. In order to reduce sorbent feed rates and minimize the amount of sulfated material which must be discarded, preliminary investigations have been made of a compact limestone desulfurization process in which CaSO_4 is regenerated to CaO and SO_2 by reductive decomposition in a high-temperature fluidized bed.

Vogel (1978) reported a regeneration process in which CaSO_4 is heated in a fluidized bed to $\sim 1100^\circ\text{C}$ in the presence of reductant gases. Reductive decomposition reaction rates are rapid—less than ten minutes is required for effective regeneration. The products are CaO , which is reused in the combustion step, and a gas containing SO_2 at concentrations $\sim 10\%$, which can be processed for its sulfur content. Stones were cycled batchwise between the combustor and regenerator in order to demonstrate that reactivity of the stone can be sufficiently maintained. In comparison with the once-through Ca/S ratio of ~ 0.93 for 75% sulfur retention, an estimated saving of 78% of the fresh limestone capacity has been obtained in a cyclic process.

A process is being developed (Ruth 1978) for continuously regenerating sulfated limestone sorbent (CaSO_4) to CaO and SO_2 by reaction with a reducing gas at

1100°C and 7-10 bar in a fluidized bed. In preliminary experiments, batches of sulfated sorbent were regenerated and up to 3.7 mol% SO_2 was produced. Reduction of CaSO_4 to CaO was nearly complete. Compared with a system without regeneration, make-up sorbent requirements were reduced by at least a factor of four.'

6 Authors' investigations

Weisweiler and Kohler (1981) studied the effectiveness of limestone for desulfurization of flue gases in an electrically heated fluidized-bed reactor of ceramic material, 36.5 mm in internal diameter. They investigated the dependence of desulfurization effectiveness

on parameters including temperature, grain size, bed height, gas velocity, residence time, concentration of SO_2 , and extent of calcination. The degree of conversion of limestone to CaSO_4 and the quantity of desulfurization achieved were both measured.

The results of these experiments confirm the dependence of the effectiveness of the process on temperature and the increase of reactivity on calcination, in agreement with the findings of other authors. The optimal temperature was found to be in the range 750-850 °C. A static bed-height of only 2 cm unreacted limestone was sufficient to achieve complete desulfurization of an air- SO_2 mixture containing 5000 ppm SO_2 at a gas velocity of up to 1 m s⁻¹. Under these conditions, the average residence time is only 0.04 s for the fluid at the highest gas velocity. Above 5000 ppm, the SO_2 concentration had no effect on the capacity. However, below this concentration, the capacity decreases with decreasing SO_2 concentration. The maximum degree of conversion of untreated limestone to CaSO_4 is ~40%, and that of calcined limestone is up to 50%, depending upon the source and particle size of the material. The low conversion efficiency is a major drawback of the process.

The reactivity of limestone is dependent upon the particle size. The capacity increases strongly with decreasing particle diameter, although measurements of porosity by the mercury-penetration method showed no change in volume and surface area of the pores. For example, at 770 °C the conversion was 35% for particles of mean size 300 μm ; it was only 18% for particles of mean size 900 μm . Calcination increases the volume of the pores by a factor as high as 20, but the corresponding increases in capacity are only 35-41% for 300 μm particles and 18-23% for 900 μm particles.

Measurements of the local sulfur distribution in single grains by an electron-microprobe analyzer, combined with measurements of the porosity, showed the formation of a bulky layer of calcium sulphate during the reaction of SO_2 with lime or limestone. This layer occludes the pores of the material and causes blocking of much of the inner surface from reaction. In a typical case at a conversion of 17% of the limestone, the pore volume was only 20% of the original value for unreacted stone. The pore-size distribution showed that the small pores (with radii <100 μm) are primarily occluded. Most of these pores of radii <100 μm size are just those formed during calcination. This could explain the fairly low increase of the capacity of calcined limestone compared with that of natural rock. The investigations showed that the inhibition of the reaction arises mainly from transport effects.

These investigations have confirmed the advantages of using limestone with larger pores, of calcining the limestone to increase the pore volume, and of utilizing fine-particle stones for desulfurization. The investigations are being continued with regard to the activation of the stone by doping with suitable additives in order to improve the capacity of the material.

7 Sulfation reactivity of lime and related phenomena—present status and proposed work

Notwithstanding the large amount of work that has been done, there is as yet no clear understanding as to why limestones vary so much in reactivity. Porosity after calcination has been established as an important consideration, but no good correlation of such porosity with the characteristics of the original limestone has been established. Moreover, no well-defined correlation has been found between differences in reactivity and differences in chemical composition. Differences in the reactivities of naturally occurring materials may be attributable to variable physical properties. At present, this point is supported more by logic than by experimental data. Extensive study of the physical characteristics of stones before and after calcination is required.

The present lack of understanding of the sulfation mechanism has led to difficulties in improving the reaction conditions with a view to increasing the desulfurization efficiency. Some examples of possible improvements follow.

- (i) Because the reaction apparently is not rate-limited and the formation of a surface shell may inhibit complete utilization of the sorbents, a successful process will have to make use of very finely divided material or provide some mechanism for removing the product shell—by incorporating an attrition-promoting reactor, for example,
- (ii) One factor believed to affect adversely the efficiency of the process is the short time available in the effective temperature zone. Increasing the retention time should help in this, but the situation is complicated by the possibility that formation of a reaction-product shell on the surface may block off the particle interior. This leads to the question as to how effectively the calcined particles and SO₂ molecules are brought together: An effective practicable method of increasing the degree of mixing between the two reactants must be devised.
- (iii) Although present results are based on observations made over a limited temperature range, they suggest the possibility of an optimum reaction temperature that is characteristic of the sorbent material. From the point of view of process optimization, this temperature should be determined for each material.
- (iv) Large amounts of CaSO₄ are produced as a result of the lime-sulfation reaction. This has posed an extremely important disposal problem in industrially advanced countries such as Japan (Ohtsuka and Ishihara 1978). New technology is to be developed for its effective utilization.
- (v) The mechanism of fluidized-bed combustion of sulfurous coal together with limestone has not been fully determined. Available information on combustion in the so-called 'shallow fluidized bed', which is considered to be the only process suitable for the purpose, is also scanty (Chakrabarty and Howard, 1978).

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