

SULPHUR DIOXIDE REACTIVITY OF COMMERCIAL LIMESTONES

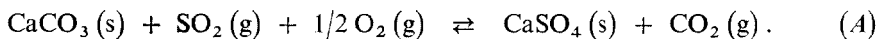
M. HARTMAN

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague - Suchbát*

Received July 4th, 1974

A differential reactor with a fixed bed of limestone particles was used to measure their conversion to calcium sulphate in flue gas containing sulphur dioxide. The flue gas fed to the reactor was generated by combustion of propane and metered addition of SO₂. The conversions of nine naturally occurring limestones were studied in terms of exposure time, particle size and temperature. The conversions of commercial high-grade limestones attained under the favourable experimental conditions are generally low and range from 19 to 41%. The differences in conversion can be related neither to differences in chemical composition nor to the porosity of the calcined limestones. Temperature and particle size have a moderate effect on conversion. Electron microprobe analysis shows that sulphur, present as sulphate, is uniformly distributed within particles reacted under the favourable conditions. The cause of the low conversion of calcium oxide to sulphate seems to be the strong diffusional resistance developed in the interior of particles during the course of the reaction.

Massive efforts are being made in many countries to develop efficient and commercially feasible processes for controlling atmospheric pollution by sulphur dioxide in power plant flue gas. There has been considerable interest in dry, high temperature processes¹, such as the reaction between limestone and sulphur dioxide in flue gas at high temperature and in the presence of excess of oxygen as follows²:



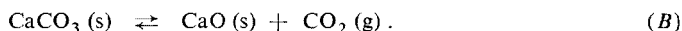
Contact between solid and gas can be readily attained by injecting finely powdered limestone into the boiler combustion chamber^{3,4}, by passing combustion gases through a fluidized bed of limestone or by burning fuel within such a bed⁵.

A major obstacle to the commercial feasibility of dry limestone processes is the important fact that limestone reacts only partially^{6,7}.

The purpose of the investigation reported in this paper is to determine the effect of parameters such as the time of exposure of solids to SO₂, temperature and particle size on conversion of naturally occurring limestones to calcium sulphate. The experiments were performed with respect to operating conditions for fluidized beds of practical interest.

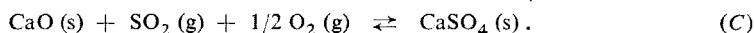
Chemical Equilibrium

The heterogenous reaction (*A*) of solid calcium carbonate with gaseous sulphur dioxide and oxygen, can be accompanied by or involve the prior calcination of calcium carbonate:



Reaction is strongly endothermic with the heat of reaction as large as 42.6 ± 0.2 kcal/mol⁸. Carbon dioxide present in flue gas lowers the driving force of thermal decomposition of limestone. As follows from the equilibrium data⁹, for flue gas containing 10% CO₂, the decomposition of limestone starts at 750°C. The rate of calcination accelerates rapidly as the temperature is elevated above the dissociation point. The thermal decomposition of calcium carbonate is controlled by the rate at which heat is transferred to a reaction zone and by the rate at which carbon dioxide is transferred away from this zone^{10,11}. When calcination temperature is increased above 1200°C considerable shrinkage of limestone particles occurs and calcium oxide formed is less reactive¹². It is generally recognized that conditions under which limestones are calcined play an important role in developing a reactive lime.

Reaction (*B*) is usually fast at high temperature and the results reported below suggest that the overall reaction (*A*) may proceed, to some extent, by reaction (*B*) followed by reaction (*C*):

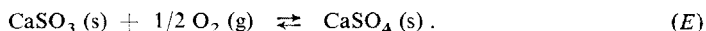
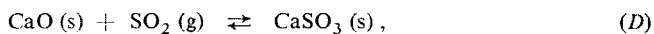


The data on thermodynamics of this reaction were gathered by Reid¹³. The equilibrium concentrations of sulphur dioxide in the flue gas containing 3% O₂ calculated from standard free-energy changes at selected temperature are shown in Fig. 1. It follows from the curve in Fig. 1 that the equilibrium conditions are favourable over the relatively wide range of temperatures. If concentrations of SO₂ and O₂ are assumed to be equal to 0.3 and 3.0% respectively, it should still be possible to remove practically all SO₂ present in the flue gas at 1070°C. It can be seen that at temperatures above 1170°C, the driving force for reaction of CaO with SO₂ will be decreased considerably by virtue of the increased instability of sulphate. The equilibrium may be shifted by silica, alumina and iron oxide¹⁴ present in limestone and in ash released during combustion. These oxides combine with calcium oxide at elevated temperatures.

Reaction Mechanism

The reaction between calcium carbonate and sulphur dioxide is thermodynamically feasible but its rate is too low¹³. According to Ingraham and Marier¹⁵ sulphur dioxide does not displace carbon dioxide from limestone at temperatures below its calcination point. At temperatures above 850°C small particles of limestone calcine rapidly and the reaction with CaO is more important than that with CaCO₃.

Using an infrared spectroscopic technique, Ferguson and Rissmann¹⁶ investigated the sorption of SO₂ from the simulated flue gas on the surface of CaO. Based on their experimental results they suggested the following mechanistic sequence of reactions (*D*) and (*E*):



In the first phase, chemisorption of sulphur dioxide takes place. In the second phase, sulphite formed is converted to sulphate. The rate data for reactions (D) and (E) show that at temperature above 500°C, oxidation proceeds faster than chemisorption. This finding is in agreement with the fact that at temperatures above 800°C, calcium sulphate is the exclusive sulphation product^{15,17}.

If oxygen is absent in the flue gas considerable amounts of sulphite, sulphide and elemental sulphur are formed¹⁸.

Reaction Rate

Variables, which have effect on the rate of reaction, fall into three groups: 1) The characteristics of calcium oxide: type of limestone rock, conversion to sulphate, particle size, physical parameters of the particles such as the surface area, porosity and pore size, and chemical composition of the particles. 2) The chemical composition of the gas phase: concentration of SO₂, O₂, H₂O and CO₂. 3) The operating variables: temperature, pressure, velocity of the gas phase.

The wide variation in SO₂ reactivity of different naturally occurring limestones was found. In Potter's experiments⁷, in which eighty-six carbonate rock samples reacted with sulphur dioxide in flue gas, the sulphate loading at which the stones had practically ceased reacting varied between 0.05 and 0.85 g SO₃/g calcine. Studies of Borgwardt and Harvey^{17,19} demonstrated that the initial rate of reaction is proportional to the amount of surface area of the lime particles. These studies also suggested the considerable effect of physical properties of the calcines on their reactivity. Borgwardt's data¹⁷ indicate that in its initial stages reaction (C) is of first order with respect to the concentration of SO₂ in the gas phase. The effect of water vapour on the course of reaction is not completely clear. Hatfield¹⁸ reports that the presence of water vapour in the flue gas promotes the reaction slightly. Murthi and coworkers¹² found that the reactivity of lime particles

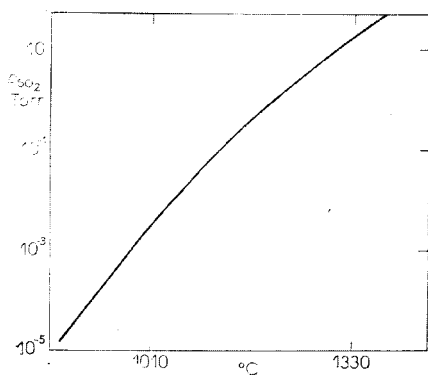


FIG. 1
Calculated Equilibrium Pressure of SO₂ in
Flue Gas in Contact with CaO

$$P_{O_2} = 22.8 \text{ Torr.}$$

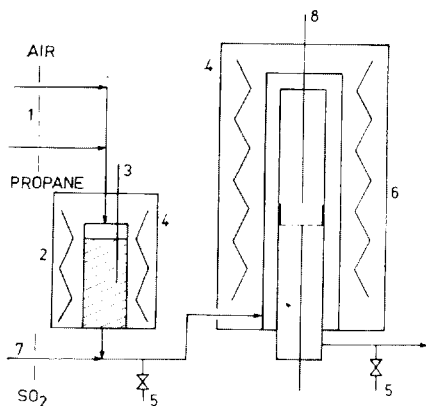
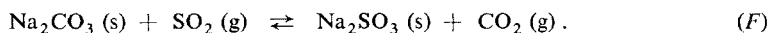


FIG. 2
Schematic Diagram of the Apparatus
1 Rotameter, 2 combustor, 3, 8 thermo-
couples, 4 heating spiral, 5 valve, 6 differential
reactor, 7 capillary flowmeter.

was substantially reduced in the presence of water vapour. Investigating a similar reaction:



Erdős and coworkers^{20,21} concluded that the presence of water vapour in the gas is necessary for a rapid course of this reaction. The rate of reaction was sensitive to temperature within the range of temperatures 650–980°C in Borgwardt's measurements¹⁷. At the temperatures above 1000°C the reaction rates were decreasing with temperature. A higher rate of sulphation was reported by O'Neill and coworkers²² at the elevated operating pressure.

EXPERIMENTAL

The apparatus, including a differential reactor used for the kinetic studies, is shown schematically in Fig. 2. The flue gas fed to the reactor was generated by combustion of propane with a moderate excess of air. To insure complete combustion the combustion tube (46 mm i.d.), was packed to a depth of 15 cm with spheres of alumina impregnated with cobalt oxide. Sulphur dioxide was added from a cylinder to the gases leaving the combustor. The composition of the gas entering the differential reactor was 12.6% H₂O, 10.1% CO₂, 3.5% O₂, 0.29% SO₂ by volume, with the balance consisting of N₂.

The concentration of SO₂ in the gas was determined by absorption in diluted H₂O₂ solution and titrating the sulphuric acid thereby formed with 0.1M-KOH solution.

The combustion gases passed through an annular preheat section 100 cm long and 4.6 cm in diameter and then contacted the limestone in the inner tube which was 18 mm i.d. The limestone

TABLE I
Chemical Composition of Limestones

Limestone		Limestone analysis (% by weight)					weight loss on ignition at 1000°C	Porosity of calcines (calcined at 850°C)
		CaO	MgO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃		
Černý důl	CD	54.6	0.42	1.00	0.15	0.11	43.2	0.485
Čížkovice	CI	42.4	0.63	15.01	3.57	1.40	35.5	0.524
Lánov	LA	32.8	18.84	1.09	0.29	0.24	45.9	
Měrotín	ME	54.9	0.06	0.35	0.12	0.20	43.3	0.501
Mokrá	MO	54.9	0.42	0.27	0.09	0.11	43.6	0.529
PrachoviceI.	PI	53.4	1.26	0.53	0.31	0.24	43.5	0.505
PrachoviceII.	P2	53.0	1.88	0.41	0.20	0.20	43.7	0.512
Štramberk	ST	53.6	0.73	2.15	0.54	0.47	42.6	0.521
Vitošov	VI	55.0	0.21	0.29	0.10	0.08	43.4	0.517

particles were uniformly dispersed on quartz gauze in a removable cup, the bottom of which was perforated to permit the flue gases to flow through.

To insure that the measured reaction rates were not influenced by mass transfer to the surface of solid a high flow rate of gas was used in each experiment. The superficial velocity in the inner tube of the reactor was 2.5 m/s at 850°C and very small changes in gas composition (to approximate a "differential-reactor") were realized by using small samples (about 50 mg) of dried, uncalcined limestone. Larger samples were used for a porosity study during which the rate of reaction was not determined.

The reactor was heated using a Kanthal A 1 resistance wire. Temperature in the reactor was measured by a calibrated PtRh-Pt thermocouple located 1 cm above the sample cup. Temperature was maintained constant within a few centigrade degrees.

Samples exposed to the flue gas in the reactor were analyzed for sulphate by first dissolving them in distilled water in contact with an excess of cation exchange resin. The amount of sulphate was determined by titration of the filtrate with 0.005M-Ba(ClO₄)₂ solution in 80% 2-propanol using a mixture of thiorin and methylene blue as indicator.

Porosities of the limestone samples were determined by helium and mercury displacement. Pore size distributions were determined by measuring the volume of mercury penetrating the pore volume at increasing pressure.

Nine different limestones from various quarries located in Bohemia and Moravia were used in this study, the chemical composition of which are shown in Table I. The hand-picked samples were crushed and sieved and the fractions of particles within size ranges 0.25–0.32 mm ($\bar{D}_p = 0.285$ mm), 0.50–0.63 mm ($\bar{D}_p = 0.565$ mm), and 1.00–1.25 mm ($\bar{D}_p = 1.12$ mm), were investigated in this study.

RESULTS

Exposure time. In the preliminary experiments the rate of simple calcination, reaction (B), of the limestone VI was measured as weight loss. The limestone particles of mean size $\bar{D}_p = 0.565$ mm were exposed to the flue gas containing no sulphur dioxide at 850°C. In Fig. 3 are plotted the results of these calcination experiments. The data shown in this figure were obtained with the different samples of weight 50.0 ± 0.1 mg.

The great initial weight loss of the samples indicates that the particles are heated and decomposed very rapidly. After two minutes exposure the weight of the samples remains practically unchanged. Weight loss on calcination attained is 41.4%. This value is somewhat lower than that in Table I.

If sulphur dioxide is present in the flue gas, weight of the samples also decreases rapidly at first, but after two minutes of exposure it starts to increase. As shown in Fig. 3, dependence of the weight of samples on the exposure duration exhibits a distinct minimum at about two minutes. This results from the fact that calcination and sulphation of the particles take place simultaneously and at different rates.

It is obvious from the curves in Figs 3 and 4 that the sulphation reaction is very rapid in its initial stage. As the exposure time continues, however, the rate of reaction decreases rapidly. After about 10–11 minutes of exposure about 31% of the total amount of calcium oxide in the particles was converted to sulphate with rather

slow conversion thereafter. After 30 minutes, for example, a conversion of only 35% was attained.

Because of differences in experimental conditions only a rough comparison can be made with the results of Borgwardt¹⁷ and Murthi and coworkers¹². Under comparable circumstances Murthi estimated an initial rate that was about ten times lower than that determined by Borgwardt. The initial reaction rate of limestone VI reported here lies between the values given by these authors.

The conversions of the particles exposed to the flue gas for very long times were also measured. After exposure for two hours to the flue gas only slight further increase of the conversion could be seen. The maximum conversion of calcium oxide obtained at an exposure time of eight hours was 42.5%. Practically no increase of the conversion can be expected with further prolongation of the exposure time.

Temperature. Using the particles of mean size $\bar{D}_p = 0.565$ mm, the effect of temperature on the conversion was investigated. The conversions of calcium oxide were determined after the exposures for 30 and 120 minutes to the flue gas at 800, 850 and 900°C. At these temperatures the rate of simple calcination was also measured.

The results for limestone VI are shown in Fig. 5. It is interesting that even at 800°C the particles of limestone were completely calcined. As the temperature was increased from 800°C to 900°C the conversion rose from 30 to 36.6% at the exposure time of 30 minutes. The conversion of samples exposed to the flue gas for 120 minutes increased from 37.1 to 41.7%.

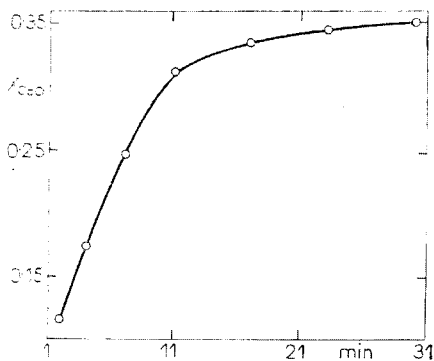


FIG. 3
Calcination 1 and Sulphation 2 Curves of Limestone VI

Temperature 850°C, particle size 0.565 mm, concentration of SO₂ 0.29% by vol. (curve 2).

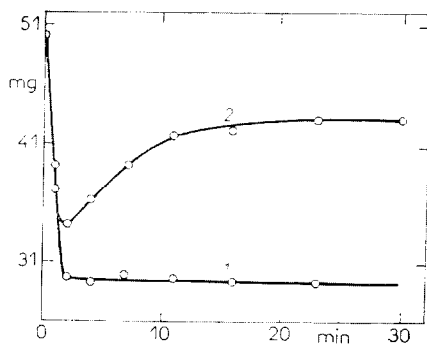


FIG. 4
Dependence of the Conversion of Calcium Oxide to Sulphate on the Exposure Time
Temperature 850°C, particle size 0.565 mm, concentration of SO₂ 0.29% by vol.

The results indicate that the effect of temperature is not a strong one and is diminishing as the conversion increases. A somewhat weaker dependence on temperature suggests that the rate of diffusion in the interior of the particles has a considerable effect on the progress of reaction.

Particle size. The fractions of particles within size ranges 0.25–0.32 mm ($\bar{D}_p = 0.285$ mm), 0.50–0.63 mm ($\bar{D}_p = 0.565$ mm) and 1.00–1.25 mm ($\bar{D}_p = 1.12$ mm) were used to determine dependence of the conversion on the particle size at 850°C.

As seen in Fig. 6 conversions of the large particles are low. The conversions attained after the exposures for 30 and 120 minutes to the flue gas are equal to 18.4 and 23.1% respectively. Reducing the particle size by half the conversion increases by the factor of 1.6. Further particle-halving increases the conversion by the factor of 1.2. It is interesting to note that the changes in conversion are practically identical for both exposure times.

Higher conversions can be attained with smaller particles, however, the dependence of conversion on particle size is somewhat weaker for the small particles. In Borgwardt's work¹⁷ the reaction rate was essentially independent of particle size for $\bar{D}_p < 0.5$ mm.

Conversions of different limestones. Ten different commercial limestones from various quarries located in Bohemia and Moravia were selected for this study. One

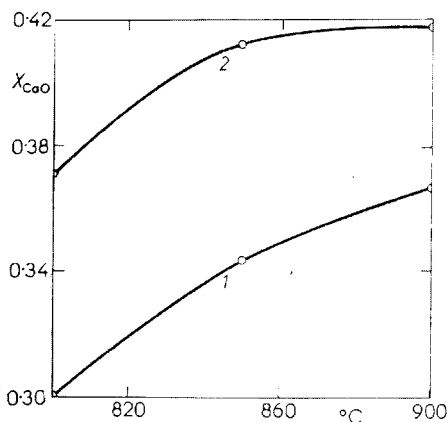


FIG. 5

Dependence of the Conversion of Calcium Oxide to Sulphate on the Temperature

Particle size 0.565 mm, concentration of SO₂ 0.29% by vol., exposure time 30 min 1, 120 min 2.

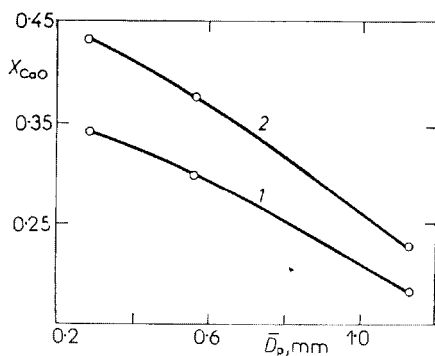


FIG. 6

Dependence of the Conversion of Calcium Oxide to Sulphate on the Particle Size

Limestone ST, temperature 850°C, concentration of SO₂ 0.29% by vol., exposure time 30 min 1, 120 min 2.

of the samples (Čertovy Schody) was found to decrepitate severely upon heating and, therefore, it was not used in the work.

Conversions of the samples from nine different quarries with 0.565 mm particles exposed at 850°C for 30 minutes to the flue gas containing 0.29% SO₂ are shown in Table II. The attained conversions are generally low and range from 0.19 to 0.44. Only two of the limestones, the CaO content of which is considerably lower than that of the others, show the conversions higher than 0.4.

TABLE II
Conversions of the Limestones

Temperature 850°C, particle size 0.565 mm, concentration of SO₂ 0.29% by vol., duration of exposure 30 min.

Limestone	Conversion, mol SO ₃ /mol CaO	Specific consumption of limestone, g limestone/g SO ₂
CD	0.230	6.96
CI	0.437	4.72
LA	0.440	6.06
ME	0.308	5.16
MO	0.240	6.65
P1	0.194	8.47
P2	0.267	6.18
ST	0.292	5.59
VI	0.347	4.58

The chemical composition does not explain the wide variation in conversion of the limestones. The considerable differences in conversions can be related neither to the porosity of the calcined limestones. The porosities of the fully calcined limestones shown in Table I are close to 0.5 cm³/cm³ and do not differ much among themselves. Pore-size distribution measurement revealed that the calcine of limestone VI, which showed a substantially higher capacity to react with SO₂ than did limestone P1, comprised a considerable volume of pores with the radii larger than 4000 Å. It is of interest that pores of this size were scarce in calcine P1.

The broadening of X-ray diffraction powder lines was used in determining the crystallite size of the limestones. No differences in the crystallite size were detected and hence the conversion cannot be simply related to the crystallite size of the particular limestone. In their kinetic study of reaction between the solid sodium carbonate and the gaseous sulphur dioxide Bareš and coworkers²³ found that the reactivity

of the sodium carbonate greatly varied with the method of its preparation. Apparently, the genesis of the limestones can play a major role in developing their reactivity.

For comparing sorption capacities of the limestones with different content of CaO, it is more convenient to use the specific consumption of limestone as a parameter rather than the conversion. The specific consumptions of the limestones determined from their conversions and their contents of CaO are shown in Table II. These results indicate that for removal of 1 g of SO₂ from the flue gas, the amounts of limestone ranging from 4.58 to 8.47 g are required.

Distribution of sulphur in the interior of particles. By means of the electron microprobe the sulphur distribution within individual reacted particles was determined. These analyses show that when favourable conditions such as long exposure time, high concentration of sulphur dioxide are applied, the sulphation proceeds throughout the whole interior of the particles. The sulphate content in the 1.12 mm particles of limestone P1 exposed at 850°C for 2 h to the flue gas containing 0.29% SO₂ is the same in the centre as on the outer edge. Despite the uniform distribution of sulphate the total conversion of particles remained low. This fact shows that solid in the pore walls contains unreacted calcium oxide. Using pelletized particles of calcium oxide Wen and Ishida²⁴ came to the same conclusion. The presence of unreacted calcium oxide in solid of the pore walls (or in the interior of the grains) suggests that the grain model used by Pigford and Sliger²⁵ for the analysis of sulfation reaction is physically well-founded.

DISCUSSION

The conversions of limestone attained in this work are generally low. It is assumed in the literature^{4,7} that the cause of the low attainable conversions is formation of a non-porous product layer on the surface of particles which does not allow the reacting gases to penetrate to the unreacted core. However, the electron microprobe analysis and pore distribution measurements have not confirmed the existence of such a layer. The results demonstrate that sulphur, present as sulphate, is uniformly distributed within individual particles reacted under favourable conditions. This fact indicates that the reaction takes place throughout the whole particle volume. The experiments reveal that the porosity of particles decreases as the sulphation proceeds but the sulphated particles always show some porosity.

Based on the differences in molar volumes of the individual components a possible explanation of the low attainable conversions of limestone is suggested.

It is assumed that the reacted particle retains its original gross external volume. Microscopic examination of samples of raw limestones, calcines and sulphated particles confirmed this assumption. Considering 1 gmol of non-porous calcium carbonate which is at first completely calcined and then reaction (C) proceeds, we can

write for the volume of solid phase:

$$(1 - e) V_{CC} = V_{CS}X + C_{CO}(1 - X). \quad (1)$$

From this equation the porosity e can be expressed

$$e = 1 - \frac{V_{CO} + X(V_{CS} - V_{CO})}{V_{CC}}, \quad (2)$$

where e is porosity of particle, V_{CC} molar volume of calcium carbonate, V_{CO} molar volume of calcium oxide, V_{CS} molar volume of calcium sulphate, X conversion of calcium oxide to sulphate. Numerical values for the molar volumes of calcium carbonate, calcium oxide and calcium sulphate reported in the literature²⁶ are as follows:

$$V_{CC} = 36.9 \text{ cm}^3/\text{mol}, \quad V_{CO} = 16.9 \text{ cm}^3/\text{mol}, \quad V_{CS} = 52.2 \text{ cm}^3/\text{mol}.$$

Incorporating these values in Eq. (2) it can be seen that sulphation (reaction (C)) causes large decreases in porosity, which has also been verified by experiment²⁷. On a molar basis, the pore volume consumed as CaSO_4 is formed by reaction (C) is greater than the pore volume developed by calcination reaction (B). This analysis, therefore, suggests that owing to decrease in porosity considerable diffusional resistances can develop within limestone particles during exposure to SO_2 -containing flue gases; as a result, incomplete conversion to CaSO_4 is likely.

The idea that the reaction rate is controlled by diffusion is supported by the fact that the reaction proceeds very slowly at long exposure times. Moreover, the conversion does not vary with temperature as much as would be expected from typical chemical reactions.

Incomplete conversion can be possibly explained by the diffusional resistance of the reaction product accumulating on the walls of pores. The reaction starts on the fresh surface of the pore walls at high rate. The reaction product accumulates on the pore walls in the interior of particles and the diffusional resistance increases rapidly as the reaction proceeds. The volume of calcium sulphate grows and the porosity of the particle decreases. After some elapsed time the diffusional resistance is so large that SO_2 can no longer reach the active CaO . Although the particle can still show some porosity at this stage and SO_2 can penetrate its interior, the reaction effectively ceases for practical purposes.

CONCLUSION

The sulphation reaction is very rapid in its initial stage. However, as the exposure time continues, and the conversion to sulphate increases, the rate of reaction decreases rapidly.

The conversions of samples of seven commercial high-grade limestones attained under the favourable experimental conditions are low and range from 19 to 41%. The differences in conversion cannot be related to differences in chemical composition of the samples. Considerably different conversions of the limestones can be explained neither on the basis of the varying porosity nor the different crystallite size of the particular limestone. The genesis of the limestones seems to play an important role in developing their reactivity.

Particle size and temperature have a moderate effect on the conversion. Under the favourable experimental conditions of reaction less than a half of calcium oxide in the most reactive sample was actually converted to sulphate in the experiments.

Electron microprobe data indicate that the sulphation reaction takes place throughout the whole volume of reacting particles under the favourable conditions.

The results suggest that the cause of the low conversions of calcium oxide to sulphate is the strong diffusional resistance developed in the interior of reacting particles at the advanced stage of the reaction.

REFERENCES

1. Hartman M., Polek J. R., Coughlin R. W.: Chem. Eng. Symp. Ser. 67, 7 (1971).
2. Potter A. E., Harrington R. E., Spaite P. W.: Air Eng. 10, 22 (1968).
3. Wickert K.: Mitt. Ver. Grosskesselbesitzer 83, 74 (1963).
4. Coutant R. W., Simon R., Campbell B., Barrett R. E.: *Investigation of the Reactivity of Limestone and Dolomite for Capturing SO₂ from Flue Gas*. Battelle Columbus Laboratories, Columbus, Ohio 1971.
5. Zielke C. W., Lebowitz H. E., Struck R. T., Gorin E.: Air Pollut. Control. Assoc. J. 20, 164 (1970).
6. van Heek K. H., Jüntgen H.: *Proc. 4th Dry Limestone Injection Processes Symp.*, Gilbertsville, Kentucky 1970.
7. Potter A. E.: Am. Ceram. Soc. Bull. 48, 855 (1969).
8. Šplíchal J., Škramovský S., Goll J.: This Journal 9, 302 (1937).
9. Johnston J. J.: Am. Chem. Soc. 32, 938 (1910).
10. Hills A. W. D.: Chem. Eng. Sci. 23, 297 (1968).
11. Campbell F. R., Hills A. W. D., Paulin A.: Chem. Eng. Sci. 25, 929 (1970).
12. Murthi K. S., Harrison D., Chan R. K.: Environ. Sci. Technol. 5, 776 (1971).
13. Reid W. T.: Eng. Power J., Trans. ASME, Ser. A 92, 11 (1970).
14. Segawa K.: Japan. Ceram. Assoc. J. 57, 97 (1949).
15. Ingraham T. R., Marier P.: Air Pollut. Control. Assoc. J. 21, 347 (1971).
16. Ferguson O. L., Rissmann E. F.: *Proc. 4th Dry Limestone Injection Process Symp.*, Gilbertsville, Kentucky 1970.
17. Borgwardt R. H.: Environ. Sci. Technol. 4, 59 (1970).

18. Hatfield J. D.: *Proc. 4th Dry Limestone Injection Process Symp.*, Gilbertsville, Kentucky 1970.
19. Borgwardt R. H., Harvey R. D.: *Environ. Sci. Technol.*, 6, 350 (1972).
20. Erdős E., Bareš J.: *5th International Symp. on the Reactivity of Solids* (G. M. Schwab, Ed.), p. 676. Elsevier, Amsterdam 1965.
21. Mareček J., Mocek K., Erdős E.: *This Journal* 35, 154 (1970).
22. O'Neill E. P., Keairns D. L., Kittle W. F.: *3rd Int. Conference on Fluidized Bed Combustion*, Hueston Woods, Ohio 1972.
23. Bareš J., Mareček J., Mocek K., Erdős E.: *This Journal* 35, 1628 (1970).
24. Wen C. Y., Ishida M.: *Environ. Sci. Technol.* 7, 703 (1973).
25. Pigford R. L., Sliger G.: *Ind. Eng. Chem. Proc. Des. Develop.* 12, 85 (1973).
26. Weast R. C.: *Handbook of Chemistry and Physics*, 49th Ed. The Chemical Rubber Co., Cleveland, Ohio 1968.
27. Hartman M., Coughlin R. W.: *Ind. Eng. Chem. Proc. Des. Develop.*, in press.

Translated by M. Rylek.