Reactions between Calcium Oxide and Flue Gas Containing Sulfur Dioxide at Lower Temperatures

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An experimental study has been performed of the reactions occurring when the reactive particles of calcium oxide are exposed to sulfur dioxide bearing flue gas. Using a differential, fixed-bed reactor, kinetic measurements have been made in the temperature range of 170 and 580°C. A relatively simple correlation based on the amassed data has been proposed. This correlation allows the estimation of the reaction rate as a function of temperature, conversion of the solids and concentration of sulfur dioxide in the gas phase. The proposed rate law equation makes it possible to predict in a straightforward manner the rate of sorption which would be required to design the performance of a desulfurization unit.

Introduction

In-duct dry sorbent injection technology can provide low-cost options for the control of sulfur dioxide and other gaseous pollutants in existing waste incinerators and coal-fired plants (Yoon et al., 1988; Stouffer et al., 1989). Processes currently under active development involve injection of a reactive dry, calcium-based sorbent at lower temperatures—typically below 500°C—in the ductwork. Calcareous or dolomitic hydrated limes or quicklimes are essentially the only materials, the use of which can be economical in a once-through method. Pollutants are removed by the entrained sorbent particles in the duct and by passing through a sorbent bed in the particulate collector. Other mode of the gas-solid contact can be attained in a bubbling or circulating fluidized bed (for example, Hartman et al., 1983; Yates, 1983; Hartman et al., 1991). The reactivity of sorbent and efficient contact between gas and solid are among the major factors effecting the separation performance. The sorbent reactivity varies greatly with its specific features such as the chemical form (oxide, hydroxide), source or origin of parent material, and physical properties (such as crystallinity, porosity, specific surface area, and pore-size distribution).

In contrast to the high-temperature sulfation of calcium oxide at 850–950°C in an oxidizing atmosphere, the low-temperature sorption is very complex in its chemical nature. While calcium sulfate is the exclusive product of the high-temperature sulfation (Hartman and Coughlin, 1974, 1976; Dennis and Hayhurst, 1990; Dam-Johansen and Ostergaard, 1991), a host of reactions occur at the low-temperature sorption. Thermodynamic considerations suggest possible equilibrium constraints and competing reactions such as the carbonation and hydration of calcium oxide exposed to combustion gases. Recently, low-temperature studies were undertaken with the use of limestone (Klingspor et al., 1983, 1984) and calcium hydroxide (Irabien et al., 1990) at temperatures ranging from 40°C to 80°C. The authors are in agreement with the strong impact of the sorbent conversion on the rate of reaction. Trempel and Rochelle (1989) studied the reaction of calcium oxide and sulfur dioxide in the absence of water vapor and carbon dioxide.

The findings reported in this article form part of the results amassed in our comprehensive experimental study of the sulfation mechanisms, kinetics and modeling of dry desulfurizing reactors at practical conditions (Hartman et al., 1979, 1984, 1988; Trnka, 1987). This work is a sequel to our recent study (Hartman and Martinovský, 1991) dealing with heat changes and chemical equilibria of reactions, which are likely to occur when calcium oxide or magnesium oxide is exposed to the combustion gases at lower temperature. The present work is concerned only with the reactions of calcium oxide under well-defined oxidizing conditions.

The main goal of this work was to explore the sulfation of calcium oxide in the presence of oxygen, water vapor and carbon dioxide at different temperatures. The study was aimed at the reaction chemism, reaction kinetics and attainable con-

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versions of the solids. The amassed results can be useful to optimize the operating conditions and to model the low-temperature desulfurization processes.

Experimental Studies

The apparatus and experimental procedures were described before (Hartman and Coughlin, 1974, 1976), so only a brief outline is given here. An electrically heated, differential reactor with a fixed layer of particles was employed. The flue gas was generated by catalytic combustion of propane with an excess of air. The concentrations of sulfur dioxide and carbon dioxide in the gas phase were measured by introducing the filtered and dried sample into infrared gas analyzers. The concentration of oxygen was measured using an oxygen paramagnetic monitor. Gas chromatography analyses confirmed the complete combustion of propane. Sulfur dioxide was added from a cylinder to the gases leaving the combustor. The composition of the gas entering the reactor was 12.6% water, 10.1% carbon dioxide, 3.5% oxygen, 0.05–0.4% sulfur dioxide by volume, with the remainder consisting of nitrogen. In experiments with SO_2-bearing air, the entering air was humidified by bubbling through water at 45°C so that the content of water vapor amounted to approximately 2% by volume. The composition of the gas streams employed in this work is given in Table 1. The gas passed through a thin layer of particles at a superficial velocity of 2.5 m/s. The particles were dispersed on quartz gauze in a removable platinum basket. Such arrangements made it possible to measure the weight gain in the course of sorption. Small size of samples and the high superficial velocity of the gas stream ensured the differential course of reactions and eliminated safely the effect of external mass transfer.

Considerable effort was required by the chemical analyses of partially reacted sorbent particles. The chemical analyses were supplemented with X-ray analyses and TGA measurements in some experimental runs.

The amount of calcium in the samples was determined by complexiometric titration. The total sulfur was analyzed by the oxidation melting with a mixture of Na_2CO_3 and KNO_3. The amount of sulfate was then determined by subsequent titration with $Ba(ClO_4)$ solution in isopropyl alcohol using a mixture of thorin and methylene blue as indicator. The amount of sulfite was also analyzed by applying a method based on titration. The method includes reaction of sulfite with iodine in an acidic aqueous solution and titration of the iodine excess with sodium thiosulfate using starch as the indicator. Carbon dioxide fixed on solids was released by an addition of the hot solution of $HClO_4$. On cooling, the released carbon dioxide was absorbed into a solution of NaOH and determined by potentiometric titration. The amount of calcium hydroxide was estimated from the TGA measurements. Both reactor temperature and sulfur dioxide concentration were continuously recorded.

Table 1. Composition of Gas Streams*

	Concentration % by Vol.			
Gas stream	H_2O	CO_2	O_2	SO_2
Flue Gas	12.6	10.1	3.5	0.–0.4
Wet Air	2.0	0.02	20.7	0.3

*With the remainder consisting of nitrogen.

Table 2. Chemical Composition of Calcium Hydroxide

Constituent	% by Wt.
Magnesium	0.05
Sodium and Potassium	0.005
Iron	0.004
Sulfate	0.008
Calcium Hydroxide	96.8
Calcium Carbonate	3.2
Loss on Ignition at 500°C	23.5
Loss on Ignition at 850°C	24.9

Sample Preparation

Calcium hydroxide used in this study was obtained as Analyzed Reagent grade. The chemical specification is listed in Table 2, showing a purity of nearly 97%. Sedimentation analysis revealed that the size of the majority of the particles was approximately 5 μm. All the particles were smaller than 50 μm. X-ray analyses were made to investigate the structure of the calcium hydroxide. The results indicate that the hydrate form is fine-grained with possible defects in the lattice.

Calcium hydroxide in powder form was first mixed with some distilled water, and the paste was extruded through a coarse sieve. The formed extrudate was dried in a vacuum dryer, and then crushed, sieved and maintained in an airtight container. Every care was taken to prevent the carbonation of the hydroxide during the course of sample preparation.

Pore-size distribution of the hydrate sample was determined by measuring the volume of mercury penetrating the pore volume at increasing pressure. The resulting derivative curve shows a single peak at the radius of 170 nm. The specific pore volume, the radii of which ranged from 7.5 to 7,500 nm, was 0.44 cm^3/g. The handbook value for the density of calcium hydroxide ($\rho = 2.3$ g/cm^3), together with the specific pore volume, leads to the porosity of dried, noncalcined particles of calcium hydroxide of 0.50. We showed (Hartman et al., 1978) that, if the calcination process takes place at moderate temperatures such as around 850°C, shrinkage of the particles does not occur and the pore volume of the uncalcined particles is preserved during the thermal decomposition. Moreover, the porosity of the decomposed particles is increased further by calcination according to Eq. 8 in our work (Hartman et al., 1978) to a value as high as 0.7. Textural characteristics of both forms of the solids are presented in Table 3. To ensure the well-defined and reactive state of calcium oxide as the starting solid, the dried, extruded pellets were calcined at 450°C for 15 minutes in a separate furnace. The well-dried pellets were

Table 3. Physical Properties of the Solids

	Calcium Hydroxide (Dry, Extruded Pellet Pieces)	Calcine
Mean Particle Size, mm	0.565 (0.5–0.63)	0.565 (0.5–0.63)
Porosity	0.498	0.72
Mean pore size, nm	170	220

calcined in a moderate flow of nitrogen to drive off the released water vapor. A typical surface area of calcines amounted to 30 m^2/g. On calcination, the particles were immediately inserted into the reactor and the reaction was followed. Preliminary tests showed that the particle size was not significantly changed by the thermal decomposition. With respect to the purity of the parent material and the aforementioned treatment, it is apparent that the reactivity of calcium oxide employed in this work has not been significantly affected by sintering (Borgwardt, 1989; Borgwardt and Rochelle, 1990).

Calculation of Equilibrium

Conditions

Carbon dioxide, as well as water vapor, is present in flue gas in concentrations exceeding by almost two orders of magnitude the concentration of sulfur dioxide and can increase its fugacity in a definite range of temperatures (Erdös, 1962). Main reactions, which are likely to occur when a particle of calcium oxide is exposed to flue gas at lower temperatures, are listed in Table 4. In our recent work (Hartman and Martinovský, 1991), we studied the equilibria of the listed reactions. Using a standard thermochemical approach, the equilibrium constants or equilibrium partial pressures were expressed algebraically as functions of temperature. Further testing of these proposed equations has shown that the original, somewhat lengthy expressions can be simplified without loss in accuracy. Thus, the dissociation pressures of the compounds pertinent to the low-temperature fixation can be expressed as follows:

Calcium hydroxide

$$\ln P_{H_2O} = -\frac{13{,}151.1}{T} + 20.7912 \qquad (1)$$

Calcium carbonate

$$\ln P_{CO_2} = -\frac{20{,}256.7}{T} + 21.9146 \qquad (2)$$

Table 4. Possible Main and Accompanying Reactions in SO_2 Sorption by CaO from Flue Gas at Lower Temperatures

Reaction	No.	Heat of Reaction, ΔH^0_{298} (kJ/mol)	Expansion Ratio of Solid
$CaO(s) + SO_2(g) + 1/2\ O_2(g) = CaSO_4(s)$	I	500.57	3.08^{*} 2.72^{**}
$CaO(s) + SO_3(g) = CaSO_4(s)$	II	402.23	3.08^{*} 2.72^{**}
$CaO(s) + SO_2(g) = CaSO_3(s)$	III	223.74	†
$CaSO_3(s) + 1/2\ O_2(g) = CaSO_4(s)$	IV	276.83	†
$SO_2(g) + 1/2\ O_2(g) = SO_3(g)$	V	98.35	—
$CaO(s) + CO_2(g) = CaCO_3(s)$	VI	177.94	2.18
$CaO(s) + H_2O(g) = Ca(OH)_2(s)$	VII	109.28	1.96

*Hexagonal or triclinic modification of $CaSO_4$.
**Rhombic or monoclinic modification of $CaSO_4$.
†Not available.
Hydrates $CaSO_3 \cdot 2H_2O(s)$, $CaSO_4 \cdot 1/2\ H_2O(s)$ and $CaSO_4 \cdot 2H_2O(s)$ can be formed at sufficiently low temperatures.

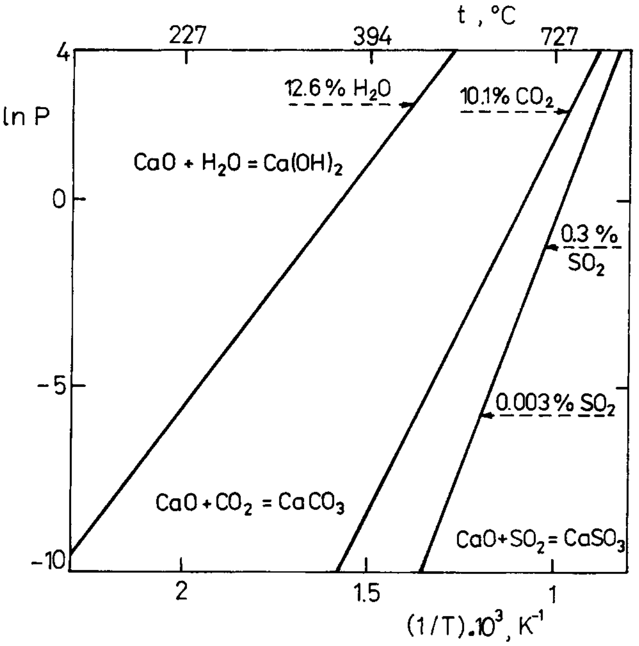

Figure 1. Computed dissociation pressures of calcium hydroxide (Eq. 1), calcium carbonate (Eq. 2), and calcium sulfite (Eq. 3).

Calcium sulfite

$$\ln P_{SO_2} = -\frac{26{,}441.1}{T} + 25.8454 \qquad (3)$$

Equations 1, 2 and 3 are presented in the graphical form in Figure 1. The above-mentioned relationships make it possible to outline ranges where the fixation of a given gaseous component is likely to occur. The equilibrium conditions predicted with the use of Eqs. 1, 2 and 3 for the gas streams employed are shown in Table 5 and Figure 1. These results suggest that, aside from sulfur dioxide, calcium oxide can also combine in flue gas with water vapor at temperatures below 450°C and with carbon dioxide below 760°C. The oxidation reactions, leading to thermally very stable calcium sulfate, are not considered here (see Hartman and Martinovský, 1991). Our experience indicates that, in a typical flue gas, less than one tenth of the overall amount of SO_x is present as sulfur trioxide. The concentration of SO_3 in our gas stream varied between 0.005 and 0.007% by vol.

One should realize that the conclusions reached are based on sound, but simplified, theoretical considerations. Never-

Table 5. Equilibrium Conditions in Flue Gas

Reaction	$CaO + H_2O = Ca(OH)_2$	$CaO + CO_2 = CaCO_3$	$CaO + SO_2 = CaSO_3$	
Gaseous component	H_2O	CO_2	SO_2	
Conc., % by Vol.	12.6	10.1	0.3	0.003
Partial Pres., kPa	12.77	10.23	0.304	0.00304
Temp., °C	448	761	705	563

theless, they spell out clearly the influence of temperature on the ability of calcium oxide to capture water vapor, carbon dioxide, and sulfur dioxide in flue gas.

Equilibrium vapor pressure of liquid water can be estimated with the aid of Eq. 4:

$$\ln P^*_{H_2O} = -\frac{5{,}041.68}{T} + 18.1304 \qquad (4)$$

which correlates the experimental data taken from the handbook by Perry and Chilton (1973) with good accuracy. The dew point of the generated combustion gas estimated with the aid of Eq. 4 amounts to 50.4°C.

The experimental program was divided into three sections:

(1) Experiments were performed to determine the effects of temperature (170–580°C) and elapsed time of reaction (5–120 min) upon the sorbent conversion. In separate experimental runs, the sorbent particles were exposed to three different gaseous streams: flue gas generated by combustion of propane with varied additions of sulfur dioxide (0.05–0.4% SO_2 by vol.), wet air (2% H_2O by vol.) with a metered addition of sulfur dioxide (0.3% SO_2 by vol.) and the above combustion gas without the addition of sulfur dioxide.

(2) The reacted particles were subjected to the chemical, X-ray and TGA analyses.

(3) The reaction rates were evaluated and correlated as functions of temperature, conversion and concentration of sulfur dioxide in the gas phase.

Results and Discussion

Sorption capacities

The results and discussion presented here refer to the experiments in which the particles of calcium oxide were maintained in efficient contact with the gas phase under conditions of interest for two hours. Experience shows that even the most reactive solids practically cease sorption at such selected conditions. Therefore, the values of weight gain and conversion reported below should be viewed as the maximum that can be attained.

Weight gain of the reacting particles is readily measurable with good accuracy. If the reaction chemistry is unequivocally clear, as it is, for example, at the high-temperature sulfation of calcium oxide (above 700°C), progress of reaction can be measured as weight gain of particles brought about by the reaction. Equilibrium considerations and Table 3 indicate that the weight gain measured cannot be attributed to any single chemical reaction at lower temperatures. It can only be viewed as the resultant of a number of thermodynamically feasible reactions. However, the weight of a particle or its specific gravity is the information much needed in the design of fluidized bed or transport-line contacting units for cleanup of flue gas.

The weight gain of solids exposed for two hours widely varies from 0.1 to approximately 1 in the dependence on temperature and the surrounding gas. As can be seen in Figure 2, the particles exposed to the flue gas with sulfur dioxide exhibit the largest weight gain over the whole range of temperatures. It should be noted that, except for the run at 585°C, the lowest weight gains were measured for fixation of sulfur dioxide from wet air. The relative position of the curves in Figure 2 suggests possible participation of carbon dioxide and water vapor in the process of sorption from flue gas. Replicate measurements indicated that experimental errors were always less than a few fractions of a percent. Therefore, a distinct minimum on curve 2 cannot be accepted as a likely result of experimental inaccuracies. Independent X-ray analysis of the particles reacted at 170°C revealed that a smaller amount of the demihydrate, $CaSO_4$, 1/2 H_2O was also formed. No demihydrate was detected in the samples reacted at temperatures above 170°C.

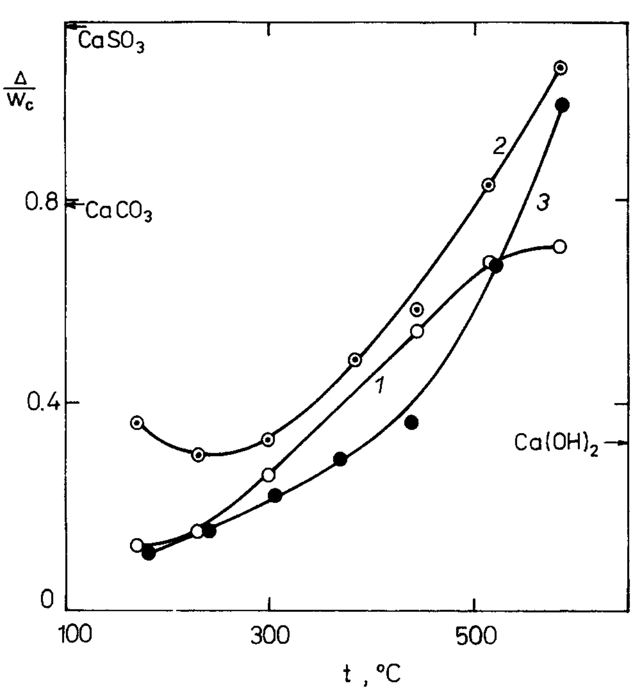

Figure 2. Weight gain of particles of calcium oxide exposed to different gaseous streams as a function of temperature.

Length of exposure, 2 h; particle size, 0.565 mm; curve 1, flue gas with no sulfur dioxide; curve 2, flue gas containing 0.3% SO_2 by vol.; curve 3, wet air containing 0.3% SO_2 and 2% H_2O by vol. The arrows show the weight gain when CaO is completely converted to $Ca(OH)_2$, $CaCO_3$, and $CaSO_3$, respectively.

It is a well-documented fact that the presence of water vapor plays an important role in the gas-solid reactions, particularly at lower temperatures. For example, Mareček et al. (1970) found the presence of water as a prerequisite to the rapid and complete course of the reaction between the active sodium carbonate and sulfur dioxide at 120–180°C. On the other hand, it should be noted that, working with the very reactive solids, these authors did not observe any further increase of the rate of reaction on further increasing the partial pressure of water vapor above a value of 0.67 kPa (0.66% H_2O by vol.). As mentioned in the preceding paragraphs, the flue gas and wet air employed in the experiments contained 12.6 and 2% H_2O by vol., respectively. It is believed that the presence of 2% H_2O by vol. in the wet air is a safe guarantee of the rapid fixation of sulfur dioxide from this gaseous environment.

Curve 1 in Figure 2 illustrates the considerable affinity of water vapor and carbon dioxide to calcium oxide. The relationship between conversion and weight gain is given by stoichiometry as:

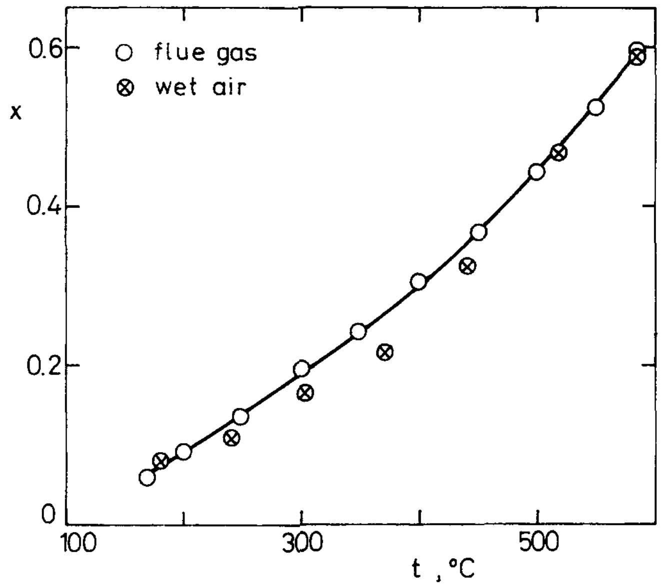

Figure 3. Overall conversion of calcium oxide to calcium sulfite and calcium sulfate attained at different temperatures.

In a two-hour exposure of calcium oxide to flue gas and wet air containing 0.3% SO_2 by vol.; particle size, 0.565 mm.

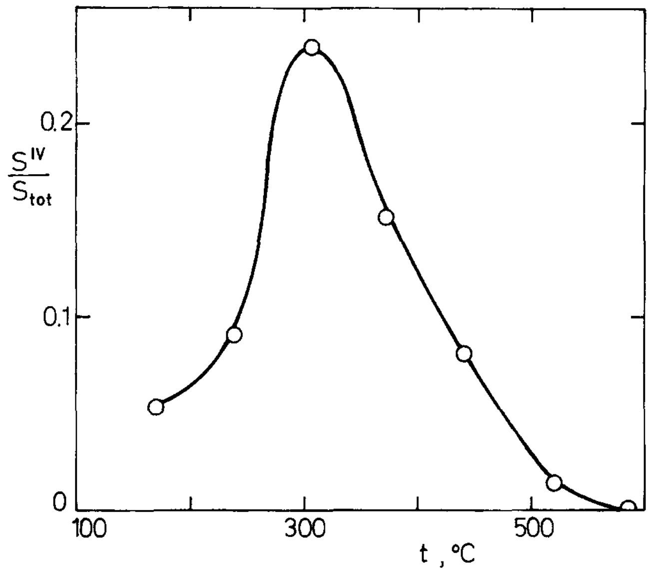

Figure 4. Fraction of total sulfur captured by calcium oxide in the form of calcium sulfite.

In a two-hour exposure to flue gas with 0.3% SO_2 by vol. at different temperatures; particle size, 0.565 mm.

$$x_i = k_i(\Delta/w_c) \qquad (5)$$

where $i \equiv SO_3$, SO_2, CO_2 and H_2O. The respective coefficients amount to $k_{SO_3} = 0.7004$, $k_{SO_2} = 0.8754$, $k_{CO_2} = 1.274$ and $k_{H_2O} = 3.113$. Using this elementary ciphers some unequivocal findings can be inferred from Figure 2. Even under most favorable conditions employed, calcium oxide was not completely converted to sulfite and/or sulfate. At temperatures above approximately 330°C, calcium hydroxide cannot exclusively be formed when calcium oxide is contacted with flue gas containing no sulfur dioxide.

In this work, we employ the concept of "sulfation" as a general term for the reactions between calcium oxide and sulfur dioxide in the flue gas or wet air. Figure 3 shows the total conversion of calcium oxide to calcium sulfite and calcium sulfate in a dependence upon temperature for the sorption from flue gas and wet air. From the experimental data it is clear that over the range examined, temperature was exerting the strong favorable influence on the conversions attained. The values of the conversion in Figure 3 were determined working with the samples that were contacted for two hours and then chemically analyzed for calcium and total sulfur. The differences in conversion attained during exposure either to the flue gas or to the wet air are only minor. Nevertheless, it may be worth noting the somewhat more pronounced convexity of the experimental dependence x vs. t for the fixation from the wet air.

With knowledge of both the amount of sulfite and total sulfur captured by calcium oxide, the degree of oxidation could be determined. Though very little soluble, calcium sulfite with its markedly reducing effects is undesirable product from the ecological point of view. As can be seen from Figure 4, the fraction of sulfite sulfur (S^{IV}) is a nonmonotonous function of temperature. The maximum relative quantity of calcium sulfite was found in a sample contacted at 300°C and amounted to 24%. A very low fraction of calcium sulfite was formed at 520°C. No calcium sulfite was detected in the solids that reacted at 585°C. The occurrence of the maximum on the experimental curve in Figure 4 is surprising, and unfortunately, we are unable to propose an adequate explanation of this phenomenon.

The acidity of sulfur dioxide is much more pronounced than that of carbon dioxide or water. It should be borne in mind, however, that the latter compounds are present in flue gas on a concentration level that is practically by two orders of magnitude higher than the concentrations of sulfur dioxide. Therefore, it is not *a priori* clear whether and to what extent the sulfation reactions are affected by possible carbonation and/or hydration. It should be noted that the equilibrium constraints for water vapor and carbon dioxide become evident at much lower temperatures than those for sulfur dioxide as illustrated in Figure 1.

In general, the presence of carbon dioxide as other acidic component tends to increase the fugacity of sulfur dioxide in the simultaneous reaction with a basic metal oxide. Thermodynamic considerations suggest that such effect depends upon the nature of the oxide: the higher basicity of the sorbent, the lesser effect can be observed. While in the system $MgO(s) - SO_2(g) - CO_2(g)$ the equilibrium pressure of sulfur dioxide is significantly increased by the presence of carbon dioxide, the corresponding effects are negligible in our system $CaO(s) - SO_2(g) - CO_2(g)$ (Erdös, 1962; Hartman and Svoboda, 1985). It should be noted that these discussions refer to the systems without oxygen. As we recently documented, the sulfates of the alkaline earth metals are thermally much more stable than sulfites (Hartman and Martinovský, 1992). It is also apparent that the thermodynamic considerations are particularly important when very low concentrations of sulfur dioxide are in question.

As the results in Figure 5 indicate, the sorption of sulfur dioxide from flue gas is accompanied by the simultaneous

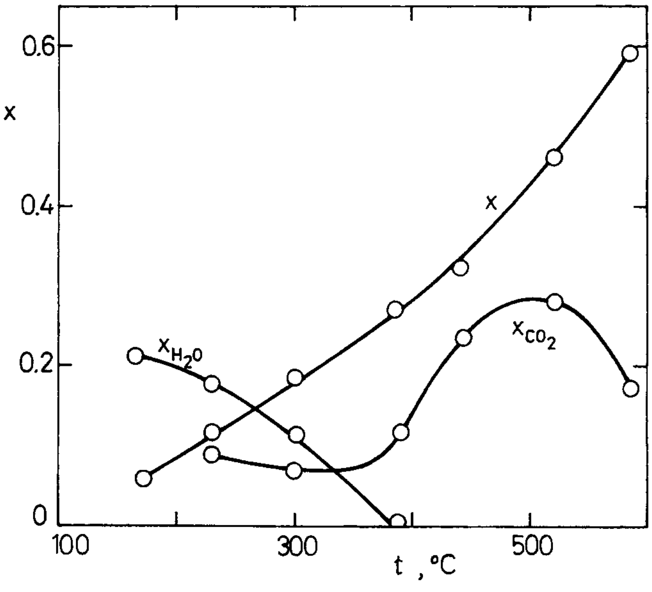

Figure 5. Extent of sulfation reactions, x, vs. simultaneous carbonation, x_{CO_2}, and hydration, x_{H_2O}, with calcium oxide exposed to flue gas at different temperatures.

Concentration of SO_2, 0.3% by vol.; particle size, 0.565 mm.

processes of carbonation and hydration. It shows that the extent of the hydration is even larger than that of sulfation at temperatures below approximately 250°C. The amount of water fixated decreases with temperature to zero at about 380°C. The dependence of the conversion to calcium carbonate on temperature is not so simple as it is in the case of calcium hydroxide. A maximum conversion to calcium carbonate of 28% was attained at 520°C. This dependence shows a marked decrease with further increase of temperature. The curves in Figure 5 also indicate that the overall utilization of calcium oxide (or the overall conversion to hydrate, carbonate, sulfite, and sulfate) increases with increasing temperature of sorption. The maximum total conversion attained at 580°C amounts to nearly 80%.

To examine a possible hindrance effect of sulfur dioxide on the simultaneous sorption of water vapor and carbon dioxide, the experimental data in Figure 5 were supplemented by measurements with the flue gas containing no sulfur dioxide. Results of these experiments are plotted in Figure 6. As can be seen from the comparison of Figures 5 and 6, there is virtually no difference between the amount of water sorbed from the plain flue gas and from that with sulfur dioxide. No water vapor combines with calcium oxide at temperatures above 440°C, which is in good agreement with the predicted equilibrium temperature in Table 5. Different from the water vapor, the sorption of carbon dioxide is significantly more rapid at temperatures above 250°C when sulfur dioxide is not present in the gas phase.

Rate of sorption

Series of experimental runs were performed to investigate the influence of the exposure time upon the overall conversion of calcium oxide to calcium sulfate and sulfite at different temperatures. All the measurements were carried out with the flue gas as well as with the wet air. The measured dependences of the conversion on the time of exposure and temperature are plotted in Figures 7 and 8. The experimental data and curves in these figures demonstrate a considerable effect of temperature on the course of the sorption. It is also evident from Figures 7 and 8 that the rate of reaction decreases rapidly as the exposure time continues and the conversion is increasing. Such features of the sulfation reaction was also found in our earlier study (Hartman and Coughlin, 1976) on the high-temperature reaction between sulfur dioxide and limestone.

To examine possible intraparticle diffusional effects, experiments were carried out with particles of different size: 0.28, 0.56 and 1.12 mm. The results showed that, for the largest particles, the conversions were only slightly lower than those obtained with the smaller particles. This finding suggests that, in contrast to dense limestones, the effect of intraparticle diffusion on the overall course of sulfation of porous particles of calcium oxide is not important. That is why the diffusional effect is not considered in a correlation treatment of data in the next section. Apparently, the reaction is slowed down by the retardation effect of the reaction products accumulating on the pore walls in the course of the sorption.

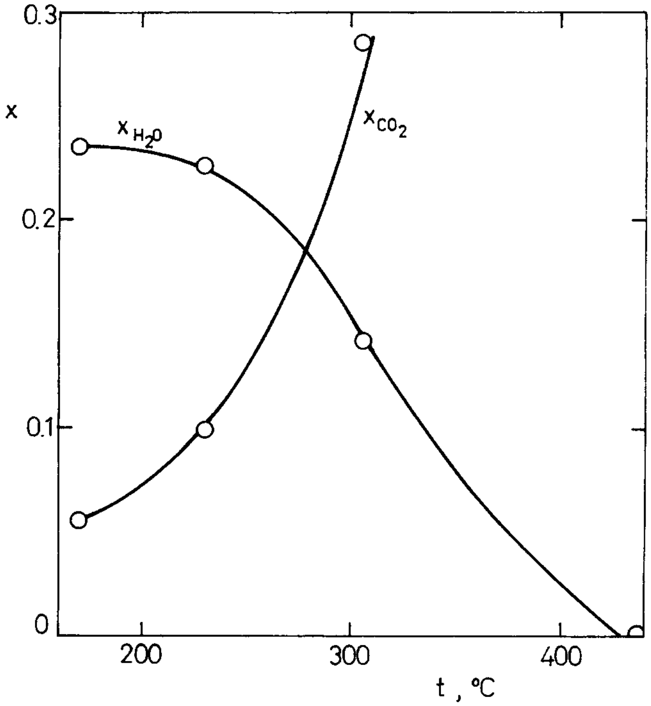

Figure 6. Simultaneous sorption of water vapor and carbon dioxide by calcium oxide from flue gas with no sulfur dioxide at different temperatures.

Particle size, 0.565 mm; length of exposure, 2 h.

Determination of rate expression

It follows from the preceding paragraphs that the rate of reaction is affected by a number of factors. Keeping in mind the wide span of temperatures and the complex reaction chemistry, it would not be realistic to think of a single rate-con-

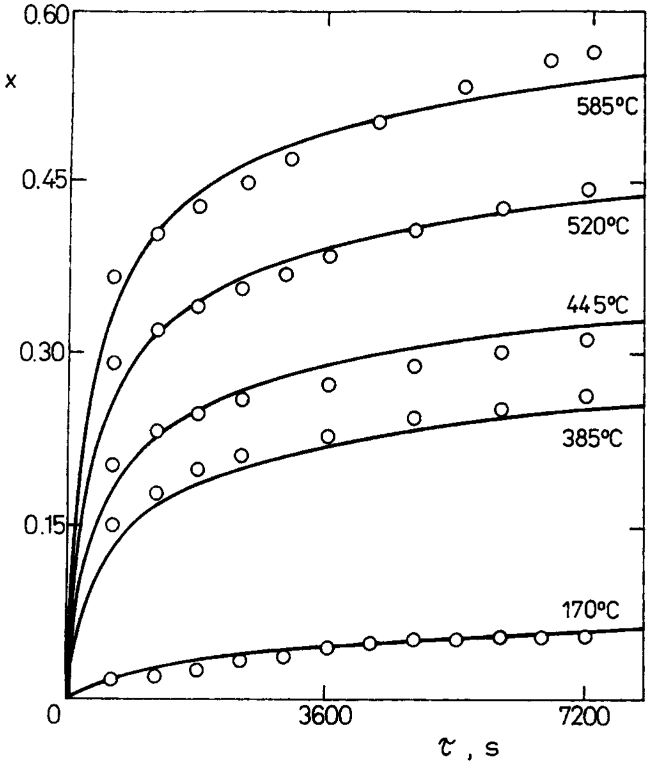

Figure 7. Overall conversion of calcium oxide to calcium sulfate and calcium sulfite as a function of the exposure time and temperature.

Concentration of SO_2, 0.3% by vol.; particle size, 0.565 mm; gas stream, flue gas; o, experimental data points measured at different temperatures. The solid lines show the predictions of Eqs. 6-11 for the respective temperatures.

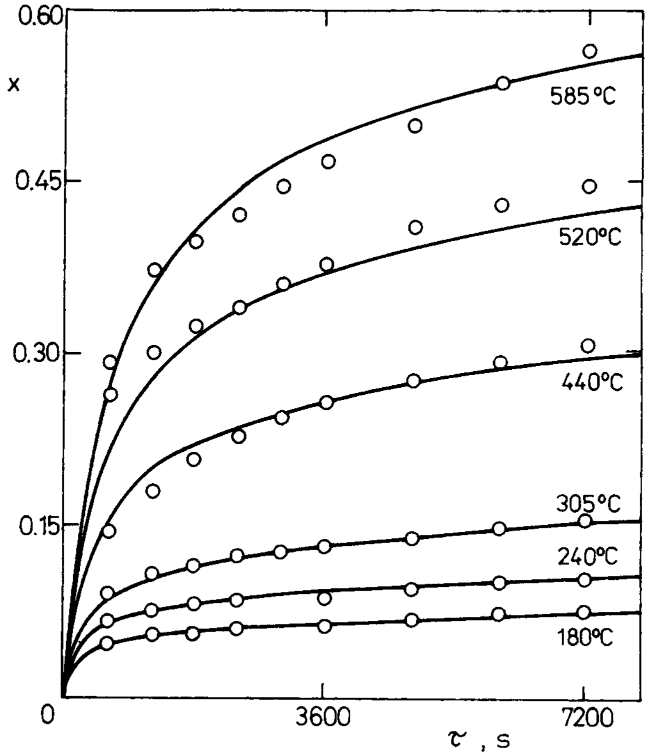

Figure 8. Overall conversion of calcium oxide to calcium sulfate and calcium sulfite as a function of the exposure time and temperature.

Concentration of SO_2, 0.3% by vol.; particle size, 0.565 mm; gas stream, wet air; o, experimental data points measured at different temperatures. The solid lines show the predictions of Eqs. 6-11 for the respective temperatures.

trolling step or process. Moreover, the relative importance of numerous factors can change in the course of the reaction. While the nucleation effects and the chemical step are undoubtedly important at lower temperatures, diffusional and sintering effects have certainly to be considered at higher temperatures. Having tested several procedures, the following approach was adopted. The intrinsic kinetics of gas-solid reactions can, in general, be described by an equation of the form:

$$r \equiv \frac{dx}{d\tau} = k(T)\, f(c)\, g(x,\tau) \qquad (6)$$

with the initial condition:

$$x=0 \quad \text{at} \quad \tau=0. \qquad (7)$$

The function $f(c)$ includes the effect of gaseous reactant concentration c. The function $g(x, \tau)$ accounts for the retarding effect of random nucleation and growth of nuclei, and describes the dependence on the fraction x of solid converted. Treatment of the initial rates of reaction deduced from the experiments with four different concentrations of sulfur dioxide in the gas phase (0.05-0.4% SO_2 by vol.) has led to the concentration function:

$$f(c) = c^{0.6}. \qquad (8)$$

The expressions for $k(T)$ and $g(x, \tau)$ are assumed to be in the forms as follows:

$$k(T) = A \exp[-E/(RT)] \qquad (9)$$

$$g(x,T) = (1-x)^{n(T)} \qquad (10)$$

where

$$n(T) = C \exp(-DT). \qquad (11)$$

The symbols A, E, C, and D represent by this time the unknown parameters. The available data are shown in Figures 7 and 8 as the sets of values $x(\tau)$ for 9-13 time points from an interval of 0-7,200 s at 5-6 temperature levels between 170 and 585°C.

The parameters for Eqs. 9 and 11 were sought to minimize the standard deviation between the experimental solid conversion and the conversion estimated from Eq. 6. Flexible polyhedron search, also called the simplex minimization, was employed as the optimization technique. For details on this search method, refer to, for example, a monograph of Himmelblau (1972). It should be noted that the fitted function, $x(\tau, T)$, is not given by an analytical solution, but it is a solution of a differential equation. Consequently, each evaluation of the objective function at a given point involves a numerical

Table 6. Fitted Parameters in the Correlation Embodied in Eqs. 6-11

Parameter	Flue Gas	Wet Air
A	$0.35614\cdot10^{2}$	$0.62952\cdot10^{-1}$
E	$0.36833\cdot10^{5}$	$0.11616\cdot10^{4}$
C	$0.24375\cdot10^{3}$	$0.1507\cdot10^{4}$
D	$0.39936\cdot10^{-2}$	$0.65168\cdot10^{-2}$
Range of Std. Dev., s	0.0056-0.0171	0.0026-0.0189

solution of the corresponding differential equation. The fitting is carried out with respect to two independent variables: time and temperature of exposure. The fitting took place separately with the data for the respective gas streams ($c = 0.003$) over all time points and temperature profiles.

The model equation was rewritten into the form:

$$\frac{dx}{d\tau} = F(T)(1-x)^{n(T)} \tag{12}$$

where

$$F(T) = Af(c)\exp[-E/(RT)] \tag{13}$$

and $n(T)$ is given by Eq. 11.

The values $F_i = F(T_i)$ and $n_i = n(T_i)$ were evaluated with the aid of fitting only over the time points at the respective levels of temperature. Then, the search was pursued for all four parameters A, E, C, and D as a four-dimensional fitting over all time points and temperature profiles: an initial guess of the values of A, E, C, and D was made with the aid of the values $F(T)$ and $n(T)$ given by Eqs. 11 and 13 at the lowest and the highest temperature.

Replicate fittings were also carried out starting with different initial guesses of the sought parameters. Using the parameter values moderately deviated from the final ones, the optimization procedure arrived safely at the original values. The values of the fitted parameters are given in Table 6. One should realize that the model parameters shown in this table are related to the reaction rate ($dx/d\tau$) and not to the conversion (x). It is apparent that the time derivatives can be very different even though the conversions (integral quantities) are similar.

Figures 7 and 8 show reasonably good agreement between the computed conversions and the experimental values. Table 6 also gives standard deviations of the final correlation. As can be seen, the correlation embodied in Eqs. 6-11 fits the experimental data with good accuracy. Of course, the correlation developed here has the usual limitations and should be applied with caution outside the experimental conditions for which it was deduced.

The proposed reaction rate equations can directly be incorporated into various models of the gas-solid reactors for removal of sulfur dioxide from flue gas (for example, Hartman et al., 1979, 1983, 1984, 1988, 1991). Such models may serve as a rational basis for the conceptual design of a suitable contacting apparatus.

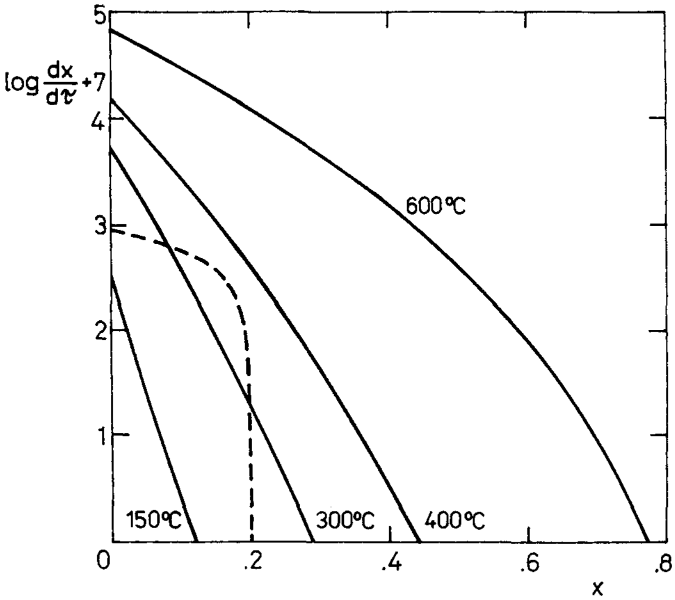

Figure 9. Reaction rates predicted by correlation 6 developed in this work.

Concentration of sulfur dioxide, 0.3% by vol.; gas stream, flue gas. The dashed line shows the values predicted by the expression proposed by Irabien et al. (1990) for the reaction of SO_2 with $Ca(OH)_2$ at 54°C.

For illustration, rates of sorption have been computed for different conversions and temperatures. The results plotted in Figure 9 show that the capability of the sorbent to remove sulfur dioxide from the gas phase decreases considerably with increasing conversion. The rates of sulfation in the flue gas and in the wet air are not very different. As can be seen in Figure 10, their ratio varies with temperature and conversion. From these results it can be inferred that a potential hindrance effect of carbon dioxide on the sorption of sulfur dioxide is

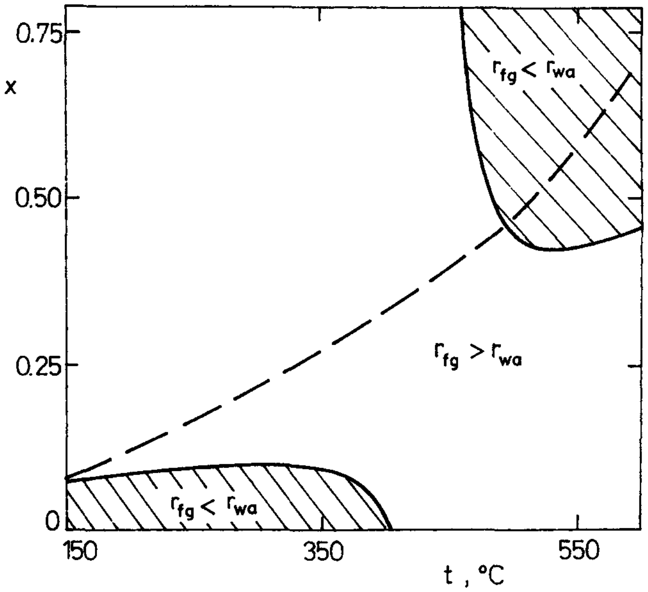

Figure 10. Mapping of the ratio of the rates of sulfur dioxide sorption from the flue gas and from the wet air.

The solid lines show situations in which the two rates are equal. The dashed line marks the range of experimental work.

rather weak, if any. It may occur at 150–400°C when the conversion is low and at 450–580°C when the conversion attains medium or higher values.

Recently, Irabien et al. (1990) reported experimental results on the low-temperature sulfation reaction obtained in an integral, fixed-bed reactor. They worked with fine particles of calcium hydroxide (0.010–0.060 mm) at 54°C and simulated flue gas (0.1–0.6% SO_2, 2% O_2, 12% CO_2 and 12% H_2O by vol.). The authors evaluated the rates of sorption from the breakthrough curves of their reactor and correlated them with the concentration of sulfur dioxide and conversion of the sorbent.

The results of Irabien et al. (1990) are also plotted in Figure 9 with the predictions of Eq. 6. Although such comparison can only be taken as very approximate, the sulfation rates reported by Irabien et al. are higher than the predictions of Eq. 6. We believe that this fact can be linked to a favorable effect of water on the sorption and reaction of sulfur dioxide. It follows from Eq. 4 that the dew point amounts to approximately 49.5°C, which is very near the operating temperature (54°C). At such close proximity of the dew point when the relative pressure of water vapor attains a value of 0.8, water vapor is intensively sorbed. Under such conditions, the presence of the liquid phase on the solid surface, particularly in the pores, is quite likely which would considerably increase the rate of sorption. Such phenomena would deserve a closer exploration by experiment.

Conclusions

A number of the chemical reactions occur simultaneously when calcium oxide is exposed to a typical, sulfur dioxide bearing flue gas at temperatures between 170 and 580°C. Water vapor is preferentially sorbed at temperatures below 230–250°C. Its amount combined with calcium oxide decreases with increasing temperature to zero at 380°C. The carbonation reaction is significant over the entire range of temperature. It shows a maximum extent at approximately 500°C with a rapid decrease thereafter.

Overall capacity of calcium oxide to react with sulfur dioxide augments monotonously with increasing temperature. Although an excess of oxygen is present in the reacting gas, a mixture of calcium sulfate and calcium sulfite is generally formed. A small amount of the demihydrate $CaSO_4 \cdot 1/2\ H_2O$ is also produced when the sorption takes place at temperatures lower than 170°C. Calcium sulfate is exclusively formed at 580°C.

The maximum overall conversions to calcium sulfate and calcium sulfite, attained after a two-hour exposure, vary with temperature from about 8% at 170°C to 60% at 580°C. A potential hindrance effect of carbon dioxide on the sulfur dioxide sorption is practically negligible, though the concentration of CO_2 in flue gas is almost two orders of magnitude higher than that of SO_2.

An effect of the solids conversion and concentration of sulfur dioxide in the gas phase on the overall sulfation rate of calcium oxide at different temperatures can be described by a simple, rather empirical expression. Flexible polyhedron search has proven to be a reliable optimization technique in the four-dimensional, nonlinear fitting of the experimental data.

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Notation

A = effective frequency factor, fitted parameter, 1/s
c = volume fraction of sulfur dioxide in gas phase
C = fitted parameter
D = fitted parameter, 1/K
E = effective activation energy, fitted parameter, J/mol·K
$f(c)$ = concentration function in Eq. 6
$F(T)$ = function given by Eq. 13
$g(x, T)$ = conversion function in Eq. 6
$k(T)$ = effective rate constant of reaction, 1/s
P_{CO_2} = dissociation pressure of calcium carbonate, kPa
P_{H_2O} = dissociation pressure of calcium hydroxide, kPa
$P^*_{H_2O}$ = equilibrium vapor pressure of liquid water, kPa
P_{SO_2} = dissociation pressure of calcium sulfite, kPa
r = reaction rate, 1/s
r_{fg} = reaction rate in flue gas, 1/s
r_{wa} = reaction rate in wet air, 1/s
R = gas-law constant = 8.3144 J/mol·K
$s = \left[\sum_{j=1}^{m} (x_j - \hat{x}_j)^2 / m \right]^{1/2}$ = standard deviation
t = temperature, °C
T = temperature, K
x = overall conversion of calcium oxide to calcium sulfate and calcium sulfite, (mol SO_3 + mol SO_2)/mol CaO
$\hat{x}$ = least-square estimate of overall conversion of calcium oxide
x_{CO_2} = fractional conversion of calcium oxide to calcium carbonate
x_{H_2O} = fractional conversion of calcium oxide to calcium hydroxide
w_c = weight of calcium oxide, g

Greek letters

Δ = weight gain, g
ρ_s = density of solid phase, mol/cm^3
τ = exposure time, s

Other symbols

ln = base e or natural logarithm
log = base ten or Briggsian logarithm

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