Calcium Silicates: A New Class of Highly Regenerative Sorbents for Hot Gas Desulfurization

A study has been conducted on the utilization of calcium silicates and the silica supported lime as regenerative sorbents for desulfurization of hot combustion gases. Except for γ-Ca_2SiO_4 and Ca_3SiO_5, all the calcium silicates and the silica supported calcium oxide are equally or more reactive than calcium oxide, and the regeneration rates of these sorbents are substantially higher than that of calcium oxide. There was no tendency of decaying of the reactivity after eight cycles of sorption and regeneration.

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SCOPE

Desulfurization of hot combustion gases is a major step in obtaining clean energy from coal in many important processes. Fluidized-bed combustion, lime injection, and flue gas desulfurization are some of the examples. In these processes, limestone has been used as a sorbent which forms primarily calcium sulfate at a temperature above 700°C. Regeneration of the sorbent has been a difficult problem because of the high chemical stability of the sulfate. Yet regeneration is desirable from the points of view of conservation, cost, and ecology. As a result, a considerable amount of research effort has been expended in developing alternate sorbents which were to be regenerative as well as reactive to sulfur dioxide.

Thermodynamic and kinetic screenings have been made of fifty three single and binary metallic oxides which include aluminates, ferrates, carbonates, and titanates. Barium titanate and calcium aluminate were among the final winners. On the other hand, alkalized alumina and the alumina supported lime have shown promise. The class of silicates, by which we include the silica supported lime and alkalized silica, had not been considered. The present study encompassed a thermodynamic and a kinetic investigation of the calcium silicates and the silica supported lime. Thermogravimetry, porosimetry, X-ray diffraction, IR spectrometry, etc., were the experimental techniques employed in the kinetic study.

CONCLUSIONS AND SIGNIFICANCE

Thermodynamic calculations showed that all the calcium silicates, that is, $CaSiO_3$, Ca_2SiO_4, and Ca_3SiO_5, are capable of sorption of sulfur dioxide from coal combustion gases to meet the standard emissions of 0.2 lb S/10^6 Btu (8.62×10^{-11} kg S/J) at below 900°C.

The temperature limits for the di and tricalcium silicates are higher than 900°C. The silicates are thermodynamically more regenerative from their sulfated states than calcium oxide.

Kinetic studies were performed on sulfation and regeneration of two $CaSiO_3$ samples, two β-Ca_2SiO_4 samples, a γ-Ca_2SiO_4 and a Ca_3SiO_5 sample. Except for the last two samples, the silicates showed higher overall rates and, more important, higher capacities for sulfation, as compared with calcium oxide on a molar basis.

The rates of regeneration of the silicates were much higher than that of calcium oxide. More specifically, the rate of thermal decomposition of the sulfated mono and dicalcium silicates were about fifteen times higher than that of the calcium sulfate, which indicated the relative bond strengths between sulfur trioxide and the sorbents.

X-ray diffraction and infrared analyses of the reaction products showed that silica and SO_4 are both chemically bonded to calcium in the sulfated $CaSiO_3$, silica is not chemically bonded to calcium sulfate in the sulfated Ca_2SiO_4, and the crystalline structures of both $CaSiO_3$ and Ca_2SiO_4 are restored upon regeneration of the sulfated silicates.

Sulfation rates of $CaSiO_3$ and Ca_2SiO_4 are first order with respect to sulfur dioxide only for $P_{SO_2} < 3\,000$ ppm of 101.3 KPa (1 atm). The activation energies for sulfation are, in the increasing order of the amount of silica, 1.55×10^4 J (3.7 kcal) (calcium oxide), 2.26×10^4 J (5.4 kcal) (Ca_2SiO_4) and 2.89×10^4 J (6.9 kcal) ($CaSiO_3$).

Rates of sulfation and regeneration were measured of the silica supported calcium oxide. Calcium oxide was precipitated on a high surface area granular silica from aqueous solutions of calcium salts followed by a heat treatment. With a heat treatment at 1075°C, β-$CaSiO_3$ was formed on the surface. The sulfation rate and the sulfur dioxide capacity of this sample were higher than lime, and the regeneration rate was about fifteen times higher than lime. Compared with the aluminum oxide supported calcium oxide, which were actually calcium aluminates on on the surface of aluminum oxide, the sulfation rates were about the same, but the regeneration rates were definitely higher for the silica supported sample.

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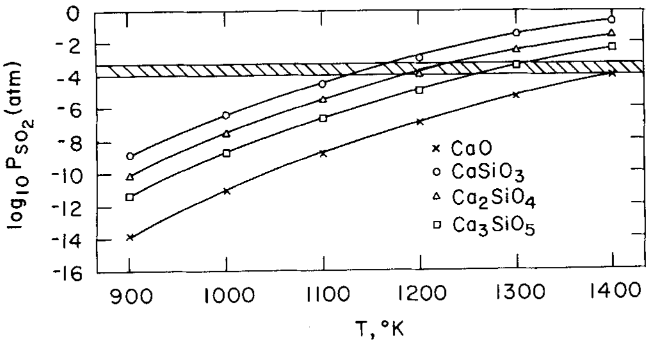

Figure 1. Equilibrium partial pressures of SO_2 for the reaction, $Ca_xSiO_{x+2} + x(SO_2 + 1/2\ O_2) \rightarrow xCaSO_4 + SiO_2$, with $P_{O_2} = 0.05$ atm.

Desulfurization of hot combustion gases is of vital importance for efficient utilization of coal in the advanced processes for power generation. In direct combustion processes, sulfur oxides are among the primary air pollutants, and great efforts have been expended in developing technologies for their abatement. These technologies involve mainly fluidized-bed combustion (FBC) and various types of scrubbers for flue gas desulfurization (FGD). FBC concerns combustion of coal with limestone particles as the bed material and has received increasing attention as a promising and versatile tecnology for clean power generation. In developing the technologies for FBC and FGD, a search for sorbents more effective than limestone, especially ones which are economically regenerative, has been a challenging task. For this purpose, a thermodynamic screening of fifty three single and binary metallic oxides has been performed by Lowell and Parsons (1975). The sorbents being screened included oxides, carbonates, aluminates, ferrates, and titanates. It was concluded that some eighteen compounds were feasible thermodynamically as regenerable sorbents. A later kinetic screening study by Ruth and Varga (1977) concluded that among the above thermodynamically screened sorbents, barium titanate ($BaTiO_3$) and a calcium aluminate cement ($CaAl_2O_4$ containing iron, silicon, and titanium oxides) were the most reactive sorbents for sulfur dioxide absorption and regeneration.

Various sorbent alternatives to lime have been used with success and information on the sorbents are well documented (Slack, 1975). With particular relevance to this work are the alkalized alumina and the alumina supported sorbents. The Bureau of Mines and Gulf first demonstrated the potential of the alumina supported oxides of alkali and alkaline earth metals as active sorbents for sulfur dioxide in flue gas at temperatures higher than 300°C (Bienstock et al., 1964, cited in Vogel et al., 1974). Investigations were made more recently on the use of the alumina supported calcium oxide as a regenerative sorbent for FBC. Workers at Argonne National Laboratory and Dow Chemical studied the sorption and regeneration rates of calcium oxide supported on a high temperature treated, high surface area α aluminum oxide (Snyder et al., 1976). In this work, calcium aluminates were actually formed on the support upon heat treatment which was part of their procedure for precipitating calcium oxide. Favorable kinetics were obtained in sulfation at 900°C and regeneration at higher temperatures. In the meantime, kinetic studies with calcium aluminates concluded that calcium aluminates are more reactive than the commercial calcium oxide in sorption of sulfur dioxide and that aluminum oxide can lower the decomposition temperature of calcium sulfate by forming calcium aluminates (Okutani et al., 1975). On the question of regeneration, it has been known that various metallic oxides and salts can catalyze the reaction. The promotion of thermal decomposition of calcium sulfate by various oxides, for example, silica, ferric oxide, titanium dioxide, aluminum oxide, manganous oxide, manganite, chromic oxide, and salts was reviewed by Colussi and Longo (1974).

Despite the fine efforts in the search for new, regenerative sorbents for sulfur dioxide, silicates have been heretofore altogether overlooked. Methods of commercial production of calcium silicates have been known to man since ancient times, as witnessed by the use of the calcareous cements in the Egyptian pyramids (Lea, 1970). In this paper, we present the results of a systematic study of the use of calcium silicates as regenerative sorbents for sulfur dioxide. Furthermore, although aluminum oxide has been used as a support for sorbent for its high surface area, silica has not been used. Because high surface area, heat resistant silica are commercially available, and they cost less than the α aluminum oxide, we also made an investigation on the silica-supported calcium oxide as a regenerative sorbent for sulfur dioxide.

THERMODYNAMIC CONSIDERATIONS

We shall first consider the thermodynamic feasibilities of the calcium silicates for sulfur dioxide sorption. Equilibrium calculations have been made for the following reactions:

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

$$CaSiO_3 + SO_2 + 1/2\ O_2 \rightarrow CaSO_4 + SiO_2 \qquad (2)$$

$$Ca_2SiO_4 + 2SO_2 + O_2 \rightarrow 2CaSO_4 + SiO_2 \qquad (3)$$

$$Ca_3SiO_5 + 3SO_2 + 3/2\ O_2 \rightarrow 3CaSO_4 + SiO_2 \qquad (4)$$

It is assumed that in the reaction products, silica is not bonded to calcium sulfate because thermochemical information on the bonded compounds, that is, (calcium sulfate)$_x$ · silica, is not available. However, this assumption represents the least favorable conditions, for any chemical bonds formed between silica and calcium sulfate will increase the free energy of formation of the reaction product (hence more negative) and will shift the reaction further to the right-hand side. In fact, as will be described later, x-ray diffraction and IR data indicated that the sulfate and silica were chemically bonded in the product of reaction (2).

The equilibrium partial pressures of sulfur dioxide, P_{SO_2}, for these four reactions in the temperature range 900° to 1 400°K are shown in Figure 1. The partial pressure of oxygen, P_{O_2}, was assumed to be 0.05 atm which corresponds to 20% excess air. The hatched area on Figure 1 indicates a stationary source standard of 0.2 lb S/10^6 Btu (8.62×10^{-11} kg S/J) for burning wide variety of American bituminous coals. It is seen that all the silicates are thermodynamically capable of sorption of sulfur dioxide in combustion gases. The poorest sorbent, thermodynamically, is monocalcium silicate which cannot be sulfated at the P_{SO_2} level corresponding to the above standard at temperatures higher than about 900°C.

Thermodynamic feasibilities of regeneration of the sulfated silicates shall now be discussed. Using monocalcium silicate and the reductant carbon monoxide as a set of examples, we consider the following reactions:

$$CaSO_4 + SiO_2 + CO \rightarrow CaSiO_3 + SO_2 + CO_2 \qquad (5)$$

$$CaSO_4 \cdot SiO_2 + CO \rightarrow CaSiO_3 + SO_2 + CO_2 \qquad (6)$$

$$CaSO_4 + SiO_2 + CO \rightarrow CaO + SiO_2 + SO_2 + CO_2 \quad (7)$$

Reaction (7) is thermodynamically identical with the regeneration of a lime sorbent. Reactions (5) and (6) represent the regeneration of the silicate.

Comparing reactions (5) and (7), because the free energy of formation of $CaSiO_3$ is more negative than that of $CaO + SiO_2$, reaction (5) is a more favorable reaction. A similar comparison between reactions (5) and (6) shows that (5) is more favorable than (6). A direct comparison between reactions (6) and (7) can not be made because the free energy of formation of calcium sulfate · silica is not known. However, chemical bond theories dictate that the bond to an atom weakens when other bonds are formed to the same atom. The atom in question here is calcium. This actually belongs to the area of molecular addition compounds. Several examples were given as an evidence of this principle (Sanderson, 1976). Based on this principle, the bond between sulfur trioxide and calcium should be weaker in calcium sulfate · silica than in calcium sulfate alone, and, therefore, reaction (6) is more feasible than reaction (7). To summarize, the thermodynamic feasibilities of the three regeneration reactions follow in the sequence

$$\text{Reaction 5} > \text{Reaction 6} > \text{Reaction 7} \quad (8)$$

Calcium silicates are, therefore, more regenerative thermodynamically than lime from their sulfated compounds.

EXPERIMENTAL

Rate Measurement

The rates of sulfation and regeneration were measured gravimetrically. The detailed procedures of measurement and calculation have been described elsewhere (Yang et al., 1975). A Mettler TA-1 thermoanalyzer was used for regeneration rate measurements, and a DuPont 951 thermoanalyzer was used for the sulfation rate measurements.

Formation of Silicates

The following materials were used in the experiments:

1. Monocalcium silicate: an analytical reagent grade sample from Research Organic/Inorganic Company (N.J.), an analytical reagent grade sample for Atomergic Company (N. Y.), and a commercial insulation material manufactured by Fibreboard Corporation (Colo.).
2. Dicalcium silicate: a low temperature β form sample (1 080°C) prepared by Portland Cement Association (Illinois), a low temperature β form sample (~1 000°C) prepared by Professor D. M. Roy of Pennsylvania State University, using her Evaporative Decomposition of Solution (EDS) technique, and a γ form prepared at 1 454°C without a stabilizer by Portland Cement Association.
3. Tricalcium silicate: a triclinic form sample prepared at 1 620°C by Portland Cement Association.

Brief procedures of preparation of the samples will be described except for the two monocalcium silicate samples from ROC and Atomergic.

The Fibreboard $CaSiO_3$ was formed in the following procedures: lime was mixed with a diatomaceous earth and a small amount of proprietary liquid siliceous promoter, heated at 93.3°C to form a gel, followed by heating in a steam autoclave at 204.4°C where $CaSiO_3 \cdot H_2O$ was formed and the hydrate was evaporated at 204.4°C. The sample was quite pure in $CaSiO_3$. The greatest impurity was sodium which was 0.2% by weight.

The PCA β-Ca_2SiO_4 sample was formed by repetitive firing at near 1 080°C in a furnace of a mixture of fine powders of 2 calcium oxide and silica with less than 0.1% by weight of potassium oxide as a stabilizer. X-ray diffraction analysis showed that the sample contains ~90% β form, 8% α'form, and 2% free calcium oxide.

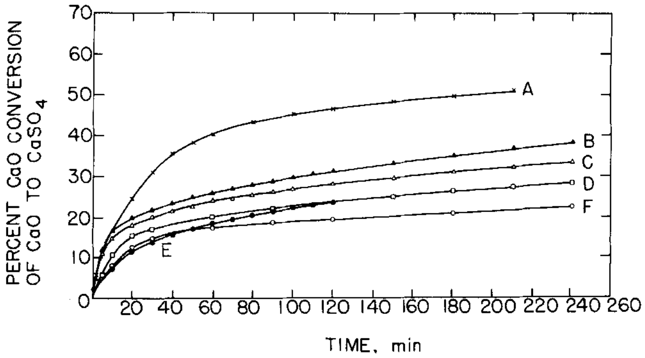

Figure 2. Sulfation rates of monocalcium silicate and lime with gas containing 0.25% SO_2, 5% O_2 in N_2 at 900°C.

A (×)	=	**commercial $CaSiO_3$ insulation powder (Fibreboard Corp.)**
B (▲)	=	**reagent grade $CaSiO_3$ (ROC/RIC 99.75%, 325/400 mesh), with 5% steam**
C (△)	=	**same as in B without steam**
D (□)	=	**reagent grade $CaSiO_3$ (ROC/RIC 99.75%, 325/400 mesh)**
E (●)	=	**reagent grade CaO (Mallinckrodt, 325/400 mesh)**
F (○)	=	**calcined Greer lime (16/20 mesh).**

The EDS β-Ca_2SiO_4 was formed by atomizing a solution of calcium nitrate and Ludox (DuPont trade name of a colloidal silica) in a hot zone of a furnace at 1 000°C. The β-Ca_2SiO_4 sample was formed in a very short time and was of a size of about 1×10^{-6} m in diameter.

The γ-Ca_2SiO_4 sample was formed by heating a stoichiometric mixture of fine powder of calcium oxide and silica at 1 454°C in a furnace for about 5 hr.

The triclinic Ca_3SiO_5 was formed by PCA at 1 620°C without the addition of a stabilizer.

Further chemical and physical characterizations of the samples will be given along discussion of the experimental results.

Gases and chemicals used were all of prepurified and reagent grades. The limestone sample was procured from Greer Limestone Company (W. Va.) and is referred as Greer limestone. The chemical analysis of the stone was as the following: silica = 8 to 13%, aluminum oxide = 2.5 to 4%, ferric oxide = 0.1 to 1%, calcium carbonate = 72 to 80%, magnesium carbonate = 3.5 to 5.0%, and sulfur = 0.2 to 0.4%.

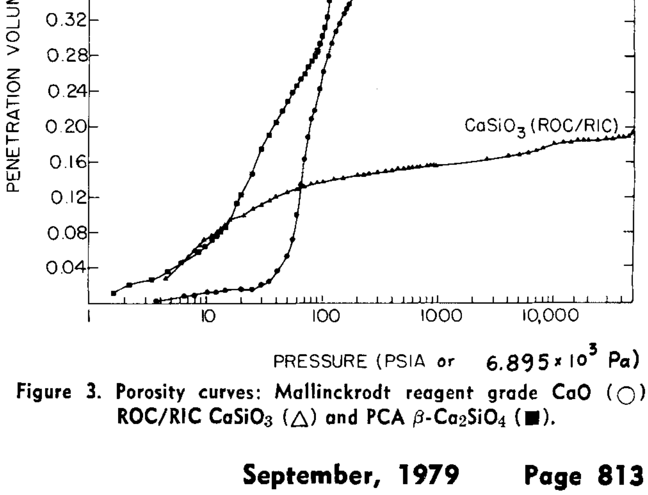

Figure 3. Porosity curves: Mallinckrodt reagent grade CaO (○), ROC/RIC $CaSiO_3$ (△) and PCA β-Ca_2SiO_4 (■).

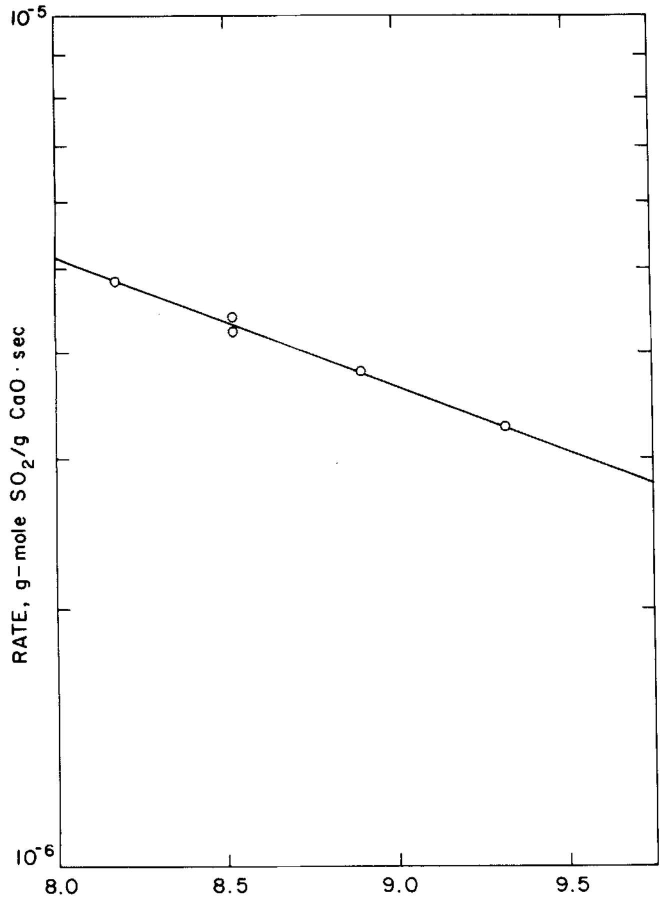

Figure 4. Effect of temperature on sulfation of reagent grade $CaSiO_3$ (ROC/RIC, 99.75%, 325/400 mesh) with 0.25% SO_2 and 5% O_2 in N_2.

RESULTS AND DISCUSSION

Rates of Sulfation and Regeneration of $CaSiO_3$

Rates of sulfation of two $CaSiO_3$ samples are compared in terms of X-t curves with those of calcium oxide samples in Figure 2. The reaction conditions were similar to those encountered in fluidized-bed combustion. The rate curves cannot be discussed meaningfully without considering the pore structures of the sorbents. The pore *distribution* curves were, therefore, measured with a Micrometrics mercury porosimeter (Figure 3). The porosity curves of the Greer lime and the Fibreboard $CaSiO_3$ were not included in Figure 3 but will be described here. The Greer lime gave a penetration volume of 4×10^{-4} m^3/kg with the pore size centered in the range of 0.1 to 10^{-6} m (Yang and Shen, 1978). The Fibreboard sample had a bimodal pore distribution with one peak at 5×10^{-6} m and another at 5×10^{-7} m and a total pore volume of about 1×10^{-3} m^3/kg.

The capacity of the sorbent as well as the reactivity are the crucial factors in determining the performance of a fluidized-bed combustor, for example, the sulfur retention efficiency and the lime requirement or the calcium/sulfur ratio. The capacity normally is indicated in the rate curve by the conversion of the sorbent where the rate decays substantially. The results in Figure 2 showed primarily that the monocalcium silicates were more reactive and had higher capacities for sulfur dioxide than calcium oxide. An interesting and fair comparison may be made between curves C and E. The pore sizes of the two samples were both large, 1×10^{-6} m, whereas the total pore volume of calcium oxide was about 2.5 times greater than that of $CaSiO_3$. The rate of the $CaSiO_3$ was consistently higher than that of calcium oxide. Limitation of the capacity of lime for sulfation is basically caused by the expansion of the crystal structure from calcium oxide to calcium sulfate, and hence the closing of the fine pores. Inasmuch as the sizes of the unit cells of the calcium silicates are considerably larger than that of calcium oxide, it is reasonable to speculate that the crystal size expansion upon sulfation is smaller with the silicates than with calcium oxide. Based on the same chemical reactivity and pore structure, the silicates should be more capable of absorption of sulfur dioxide. Further information in this area is being gathered in our laboratory.

A rate increase by water vapor was observed with the silicate sorbent. This effect has also been seen with the lime sorbent (Yang et al., 1975).

To evaluate the chemical kinetic parameters of the sulfation reaction of $CaSiO_3$, we used the initial rate approach (Yang et al., 1975). The surface chemical rate is approximated by the initial rate. The initial rate can be obtained from the slope of the rate curve, as shown in Figure 2, at the origin. The rates will be compared for various silicates. The activation energy and the reaction order with respect to sulfur dioxide were determined for the sulfation reaction with the fine size reagent grade $CaSiO_3$. The temperature dependence is shown in Figure 4, which yielded an activation energy of 2.89×10^4 J. The rate dependence on the partial pressure of sulfur dioxide, P_{SO_2}, is shown on a log-log plot in Figure 5. This plot did not yield a straight line. Very intriguingly, the shape of the curve was similar to that with calcium oxide (Yang et al., 1978*b*). The sulfation reaction of lime has been regarded as a first-order reaction with respect to sulfur dioxide after the work by Borgwardt and Harvey (1972). Careful measurements in our laboratory have shown that this is true only when the sulfur dioxide concentration is small. For lime sorbents, the limit for the first-order dependence is about 1 000 ppm at 1 atm. For $CaSiO_3$, the limit is about 3 000 ppm at 1 atm. The chemical rate does not increase appreciably with P_{SO_2} in the range of an order of magnitude higher than these limits. The reactions become first order as P_{SO_2} further increases. A Langmuir type of rate expression can only account for the rate dependence in the first two regimes, that is, the lower P_{SO_2} regimes. A more complex mechanism is obviously involved in these sulfation reactions. Further mechanistic studies are in progress. However,

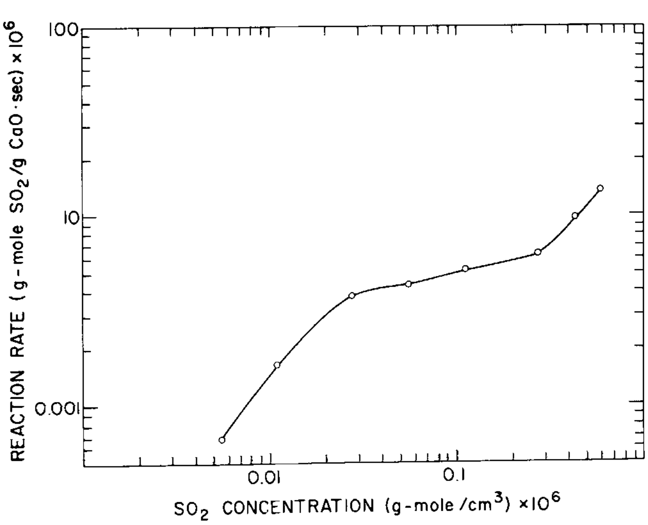

Figure 5. Effect of SO_2 concentration on sulfation of reagent grade $CaSiO_3$ (ROC/RIC, 99.75%, 325/400 mesh) at 850°C.

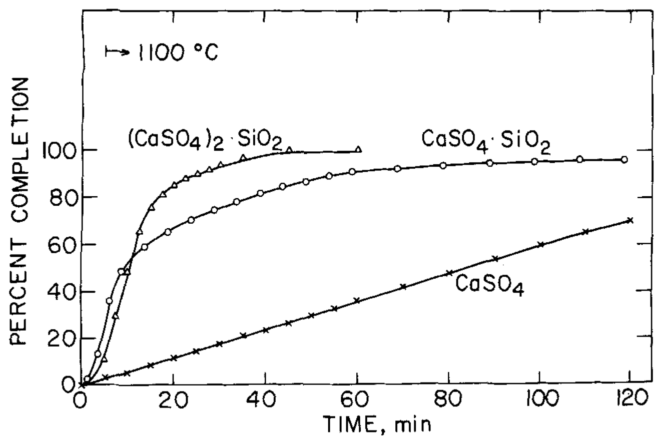

Figure 6. Regeneration (thermal decomposition) rates of powdered reagent $CaSO_4$ (Baker), 42% sulfated powdered $CaSiO_3$ (ROC/RIC) and 40% sulfated powdered Ca_2SiO_4 (EDS) at 1100°C in N_2.

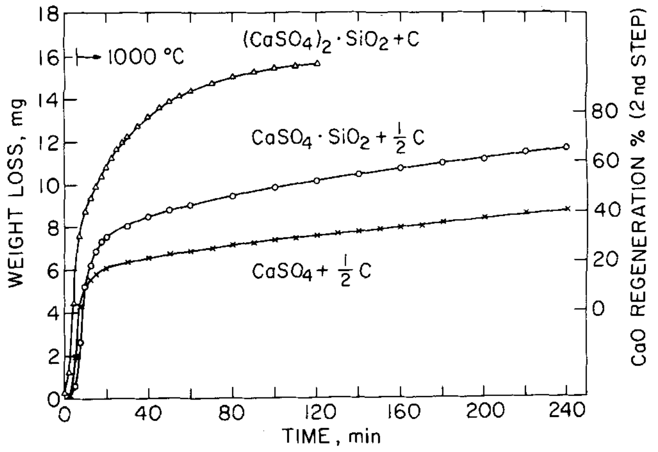

Figure 7. Regeneration rates of powdered reagent $CaSO_4$ (Baker), 42% sulfated powdered $CaSiO_3$ (ROC/RIC) and 53% sulfated powdered Ca_2SiO_4 (EDS) at 1 000°C in N_2 with coconut charcoal (200/250 mesh) as a solid reductant.

with large particles such as those used in fluidized-bed combustion, and in the latter stage of the reaction, the pore diffusion rate, which is approximately first order in P_{SO_2}, becomes important in determining the overall rate. Therefore, the first-order dependency is still a good assumption for modeling and design purposes.

Rates of regeneration of the sorbent were measured by two types of reactions. One was direct thermal decomposition of the sulfated compounds. The other was reductive decomposition with carbon as a solid reductant.

The thermal decomposition rates of the sulfated calcium oxide and $CaSiO_3$ are shown in terms of X-t curves in Figure 6. Nature of the sulfated $CaSiO_3$ will be discussed later in this paper. The rate of regeneration of $CaSiO_3$ was more than an order of magnitude higher than that of calcium oxide. This result is a direct evidence that the bond between sulfur trioxide and $CaSiO_3$ is weaker than the bond between sulfur trioxide and calcium oxide.

Rates of reductive decomposition are shown in Figure 7 also in terms of X-t curves. It is known that this reaction proceeds in two steps. The first step is the calcium sulfide formation and in the second step, the calcium sulfide further reacts with the remaining calcium sulfate to form calcium oxide and sulfur dioxide (Yang et al., 1978*a*). Mechanism of the apparently solid-solid reaction between calcium sulfide and calcium sulfate has been studied, and a two-step mechanism has been established (Yang and Shen, 1979; Chen and Yang, 1979). The mechanism of the $CaSiO_3$ regeneration reaction will not be discussed here because we do not have enough experimental results. Nevertheless, it is clear that the $CaSiO_3$ regeneration reaction is faster than the calcium oxide regeneration reaction, although the comparison is not as contrasty as that in thermal decomposition.

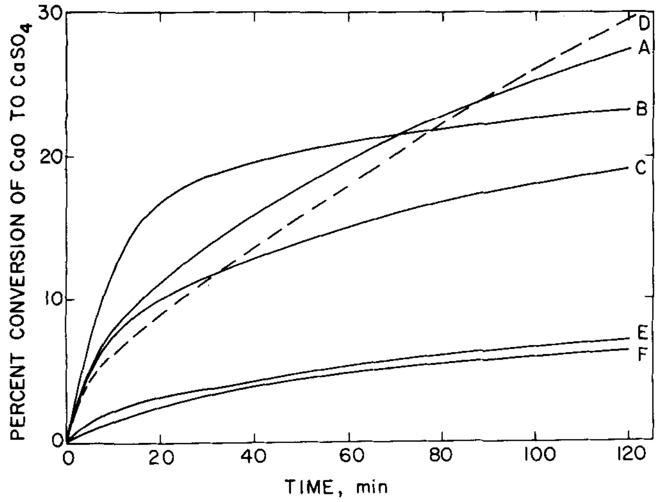

Figure 8. Sulfation rates of dicalcium silicate and lime with gas containing 0.25% SO_2, 5% O_2 in N_2 at 850°C.

A = β-Ca_2SiO_4 (PCA, 98%, 325/400 mesh)
B = β-Ca_2SiO_4 (Atomergic, 325/400 mesh)
C = reagent grade CaO (Mallinckrodt, 325/400 mesh)
D = reagent grade β-Ca_2SiO_4 powder (EDS)
E = triclinic Ca_3SiO_5 powder (PCA, 98% 1620°C burn)
F = γ-Ca_2SiO_4 powder (PCA, 98%, 1454°C burn).

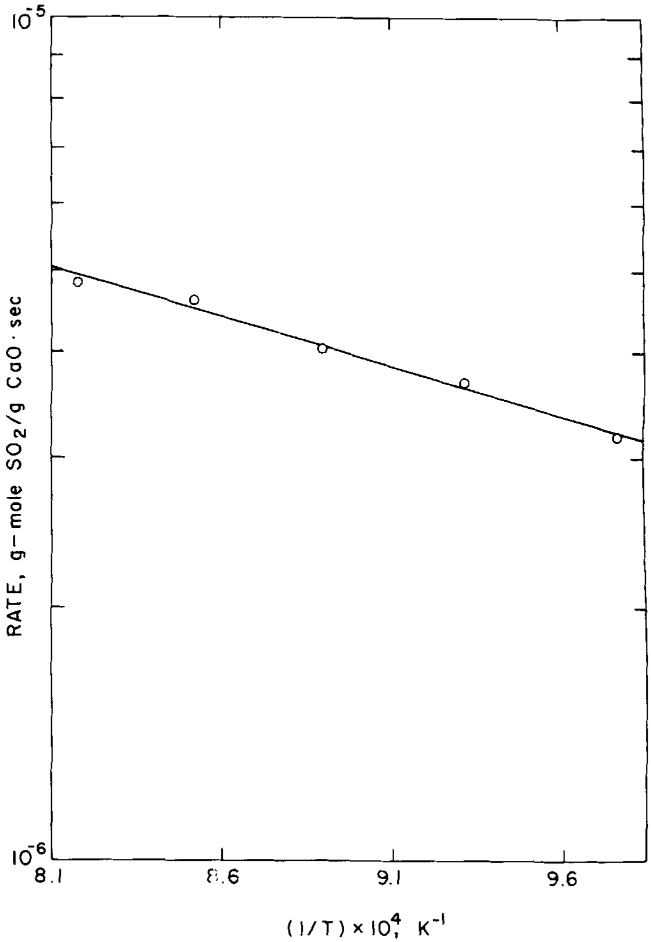

Figure 9. Effect of temperature on sulfation of reagent grade β-Ca_2SiO_4 powder (EDS) with 0.25% SO_2 and 5% O_2 in N_2.

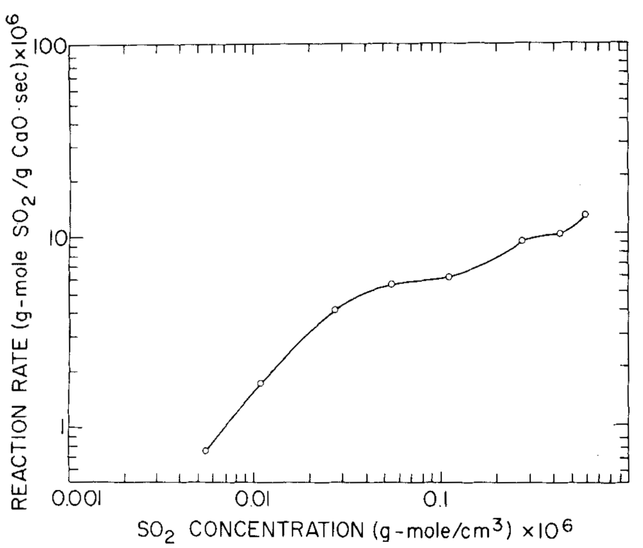

Figure 10. Effect of SO_2 concentration on sulfation of reagent grade β-Ca_2SiO_4 powder (EDS) at 850°C.

Rates of Sulfation and Regeneration of Ca_2SiO_4 and Ca_3SiO_5

Rates of sulfation of dicalcium and tricalcium silicates were compared with that of calcium oxide, in terms of X-t curves, as shown in Figure 8. The β-Ca_2SiO_4 was more porous than both calcium oxide and $CaSiO_3$ (Figure 3). Rate of sulfation of this sample was also higher than that of calcium oxide. The γ-Ca_2SiO_4 sample was formed at a temperature of 1 454°C, and the Ca_3SiO_5 was formed at 1 620°C. These high temperature samples showed substantially lower rates of sulfation. From the results of many experiments that we have performed with dicalcium silicates, it is clear that the temperature of preparation of the sample is a crucial factor in determining its sulfation reactivity. It may be proper to discuss, at this point, the sample preparation procedures. It is somewhat difficult to prepare β-Ca_2SiO_4 in the pure form as the composition inverts readily to the γ form on cooling. The presence of small amounts of metal oxides in the material is very effective in preventing the $\beta \rightarrow \gamma$ inversion. The samples prepared by Portland Cement Association were obtained with a potassium oxide stabilizer. The sample prepared by the EDS technique at the Pennsylvania State University, however, was in the pure form without stabilizers. Several different processes have been tested in our laboratory. The most effective method for preparing pure β-Ca_2SiO_4 is as follows: a mixture of 2 calcium carbonate + 1 silica is molded with water, pressed into a compact mass (137 857 KPa or 20 000 lb/in.^{2}), and burnt at 1 050°C for 2 hr. The product is ground, remolded with water, and pressed and burnt at 1 050°C for 2 hr again. After the process is repeated for three times, a pure β-Ca_2SiO_4 is obtained. Rates of sulfation of the samples prepared by this procedure showed similar rates as that with the β-Ca_2SiO_4 sample prepared by PCA (Figure 8) and are not shown here.

The EDS β-Ca_2SiO_4 sample showed a relatively high capacity for sulfation (Figure 8). This was attributed to the small particle size ($\sim 1 \times 10^{-6}$ m) of the sample.

TABLE 1. X-RAY DIFFRACTION ANALYSES OF MONOCALCIUM SILICATE AND ITS SULFATED AND

Sample	Reactants	Products	$d \cdot 10^{-10}$ m
β calcium metasilicate	Reagent grade	β-$CaSiO_3 \cdot xH_2O$	2.83 2.00 5.21 3.06 1.63 1.26
Partially sulfated β calcium metasilicate	β-$CaSiO_3 \cdot xH_2O + SO_2 + \frac{1}{2} O_2$	β-$CaSO_4 \cdot SiO_2$	2.66 4.02 1.63
		β-$CaSiO_3$	2.96 3.31 3.51 3.84 3.10 2.48 2.18 1.83 1.75 1.72 1.60
Regenerated partially sulfated β calcium metasilicate	β-$CaSO_4 \cdot SiO_2 + \frac{1}{2}$ C	$CaSO_4 \cdot SiO_2$	2.65 4.02 1.62
		$CaS \cdot SiO_2$	2.60 1.87
		β-$CaSiO_3$	3.31 3.51 2.96 3.10 2.48 1.75

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[*] S = strong, M = medium, and W = weak.

[†] The distinguished strongest $CaSO_4$ d line 3.49 × 10^{-10} m does not exist.

Kinetic parameters were also obtained with the EDS β-Ca_2SiO_4. The activation energy was 2.26×10^4 J (Figure 9). The rate of dependence on P_{SO_2} was again similar to that of calcium oxide, and was first order for P_{SO_2} less than about 3 000 ppm of 1 atm (Figure 10).

Regeneration rates of the β-Ca_2SiO_4 (EDS), via thermal and reductive decompositions, are shown in Figures 6 and 7. The rates were much higher than those with $CaSiO_3$ and calcium oxide. However, these high rates may be partly due to the fine size of the sample.

Chemical Nature of the Reaction Products

The X-ray diffraction powder patterns were obtained with the $CaSiO_3$, the sulfated $CaSiO_3$, and the regenerated $CaSiO_3$. The d spacings of the three compounds are presented in Table 1. The starting material, $CaSiO_3 \cdot xH_2O$, contained about 20% (by weight) of water and its diffraction pattern did not match any known hydrated silicates. The pattern for the sulfated $CaSiO_3$ did not contain lines of silica or calcium sulfate, which indicated that the two were still bonded after sulfation. This pattern is a new one which does not exist in any index file. It is also noted that in the patterns of the regenerated $CaSiO_3$, no diffraction lines could be detected of calcium oxide, $Ca(OH)_2$ (2.63×10^{-10} m), or $CaCO_3$ (2.4×10^{-10}, 3.04×10^{-4} m). The silicate was indeed regenerated without being separated into calcium oxide and silica.

Infrared absorption spectra of $CaSiO_3$ and the sulfated $CaSiO_3$ were taken with the standard potassium bromide pellet technique. The spectral band assignments are summarized in Table 2. Two important findings from these analyses are noteworthy. First, in the sulfated $CaSiO_3$, the SiO_3^{-2} bands remained; that means silica was still chemically bonded to the calcium cation. This result supports the foregoing X-ray analyses (or vice versa). Also in this sample, it appeared that both SO_4^{-2} and SiO_3^{-2} were bonded to calcium, and if this was true, the stretching frequencies should be increased based on first principles. Such careful analyses have not been made. The second finding was that, in the sulfated $CaSiO_3$, there was a sharp and strong band formed at 790 cm^{-1}. The origin of this band is not understood at this point.

Regenerated Forms	
Intensity*	Remarks
S	Unknown hydrate diffraction pattern
S	
M	
M	
M	
W	
S	Unknown pattern† SiO_2 is chemicall bonded to $CaSO_4$
S	
M	
S	Anhydrous reactant β-$CaSiO_3$
S	
S	
M	
M	
M	
M	
M	
M	
M	
M	
S	Regeneration not completed
S	
M	
S	Unknown pattern
S	
S	Regenerated product and unreacted starting material
S	
S	
M	
M	
M	

Table 2. Infrared Absorption Frequencies of Silicates and Sulfated Silicates

Compound	Chemical group	Frequency (cm^{-1})	Intensity	Remarks
Sulfated CaO	SO_4^{-2}	1 130	vs, b	ν_3
		680	s	ν_1
		620	m	ν_2
$CaSiO_3$	SiO_3^{-2}	975	m, b	
		925	m, sh, b	
		495	m	
		460	m	
Sulfated $CaSiO_3$		1 120	s, b	SO_4^{-2}
		975	m, b	SiO_3^{-2}
		925	w, sh, b	SiO_3^{-2}
		790	s	??
		680	vw	SO_4^{-2}
		610	s	SO_4^{-2}
		490		SiO_3^{-2}
		460		SiO_3^{-2}

---

vs = very strong, m = medium, w = weak, vw = very weak, b = broad, sh = shoulder, ν_3 = asymmetric stretching, ν_1 = symmetric stretching, ν_2 = deformation.

X-ray diffraction analyses were also made on the β-Ca_2SiO_4 system. Diffraction patterns were obtained of β-Ca_2SiO_4, its partially sulfated sample, and the subsequently regenerated sample. The *d* spacings will not be presented here, but the results will be summarized as follows. Strong calcium sulfate and silica lines were both found in the pattern of the sulfated sample, along with some weak unassigned lines. After the sample was completely regenerated, only β-Ca_2SiO_4 diffraction lines were found; the lines of calcium oxide and silica were completely absent. The results indicated that in the sulfated β-Ca_2SiO_4, the chemical bond between calcium and silica was broken and was replaced by the calcium sulfate bond. More important, the calcium sulfate and silica in the sulfated sample remained intimately mixed, and the bond between calcium and silica was formed upon regeneration.

Chemical Reactivities of the Sorbents

To the kinetics of absorption of sulfur dioxide by limestone, it has been well established that the openness of the pores is of vital importance. Small pores are liable to be closed at the entrance owing to the increase of the crystal volume upon changing from calcium oxide to calcium sulfate. Borgwardt (1972) found that for eleven limestones and dolomites, pores larger than 0.1×10^{-6} m can react throughout the internal structure to a high (~ 50%) conversion. Recent work at Argonne has demonstrated further that it is the larger pores, that is, sizes greater than 0.1-0.2 $\times 10^{-6}$ m, rather than the total surface area that determines the reactivity and the capacity of a lime sorbent. On the other hand, much understanding has been advanced on the interplay of the chemical rate with the diffusion rates in the pores and in the

Table 3. Comparison of the Chemical Rate Constants of the Sorbents

	Surface area, m^2/g	$k_s \times 10^9$, k gmole $s^{-1}\,m^{-2}\,atm^{-1}$
CaO	5.2	2.3*
$CaSiO_3$ (Fibreboard)	~10	~2*
$CaSiO_3$ (RIC/ROC)	1.0	18*
β-Ca_2SiO_4 (PCA)	1.7	3.5†
β-Ca_2SiO_4 (EDS)	~2	~2†
γ-Ca_2SiO_4	1.1	0.6†
Ca_3SiO_5	1.2	0.7†

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* At 900°C.
† At 850°C.

product layer of the lime sorbents (Wen and Ishida, 1973; Hartman and Coughlin, 1976; Ramachandran and Smith, 1977). In this work, the pore structure of the silicate, unlike the lime sorbents, is highly dependent on the procedure of sample preparation. It was, therefore, not intended to correlate the overall rate with the pore structure. Instead it was desirable to only establish the chemical reactivities of the calcium silicates toward sulfur dioxide. The chemical reactivity was approximated by the initial rate divided by the initial surface area.

In these gas-solid reactions, the rate may be expressed as

$$r = k\, P_{SO_2}(1 - X)\eta \tag{9}$$

The first-order rate dependence on P_{SO_2} is assumed for conditions normally encountered in the combustion gases, for example, P_{SO_2} is smaller than 3 000 ppm of 101.3 KPa (or 1 atm). The effectiveness factor η may be approximated as 1 owing to the fine sizes of the samples, for example, 3.7 to 4.4 × 10^{-5} m (325 to 400 Tyler mesh) (Borgwardt and Harvey, 1972). We obtain for the initial rate

$$r_0 = k\, P_{SO_2} \tag{10}$$

or

$$r_0 = k_s\, P_{SO_2}\, S_0 \tag{11}$$

Values of the rate constants k_s and the initial surface areas are shown in Table 3. The activation energies of the sulfation of calcium oxide, $CaSiO_3$, and β-Ca_2SiO_4 are, respectively, 1.55 × 10^4 J (Yang et al., 1978*b*), 2.26 × 10^4, and 2.89 × 10^4 J. Using the values of k_s along with the above values of activation energies, one can calculate the values of k_s at various temperatures. The k_s values as shown in Table 3 indicate that, except for the $CaSiO_3$ from ROC/RIC, all the low temperature calcium silicates possess the same chemical reactivity toward sulfur dioxide as does calcium oxide. The term low temperature here means temperatures below 1 100°C. The high temperature species, γ-Ca_2SiO_4 and Ca_3SiO_5, have lower reactivities. The reason for the exceptionally high chemical reactivity of the $CaSiO_3$ sample from ROC/RIC is not known.

The above data on the chemical reactivities of the calcium silicates, along with proper models, may be used to predict the rates of absorption of sulfur dioxide with the silicates.

Silica Supported Lime: A Synthetic Sorbent

Since strong, high surface area silica granules are commercially available (at a low cost), we set forth to study the silica supported lime as a synthetic sorbent.

The silica granules used in this work were grade 05, type RD, Davison granular silica gels supplied by Grace Davison Chemical Company. The properties of the granules were as follows: particle size = 1-3.36 × 10^{-3} m (6 to 16 Tyler mesh); surface area = 720-760 m^2/kg; pore volume = 4.3 × 10^{-4} m^3/kg maximum total volatiles =

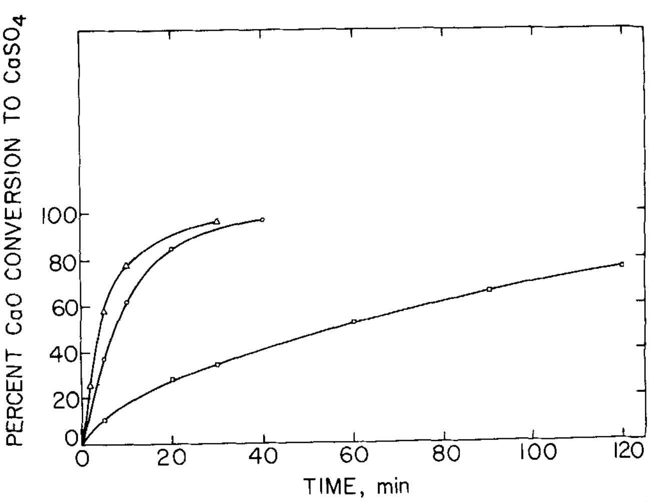

Figure 11. Sulfation rates of silica supported synthetic sorbents with 0.25% SO_2, 5% O_2, 5% steam in 900°C.

△ = **3.15% CaO (from calcium acetate) in granular silica gels, heat treated at 1 000°C.**

○ = **7.7% CaO (from calcium acetate) in granular silica gels, heat treated at 1 000°C.**

□ = **1.2% β-$CaSiO_3$ (from calcium nitrate) in granular silica gels, heat treated at 1 075°C.**

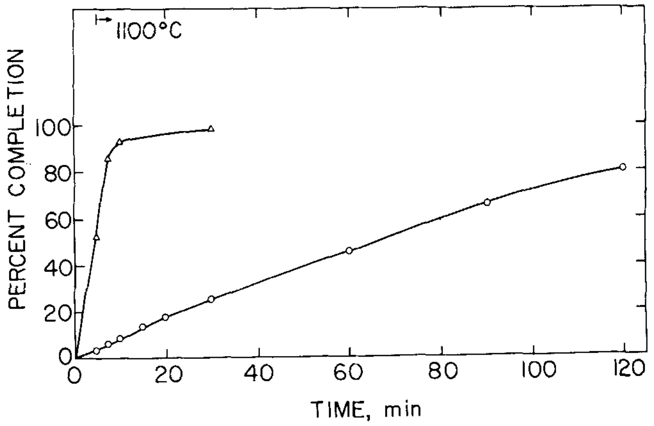

Figure 12. Regeneration of sulfated silica-supported synthetic sorbents, using N_2 at 1 100°C.

△ = **1.2% β-$CaSiO_3$ in granular silica gels**

○ = **7.7% CaO in granular silica gels.**

Table 4. Cyclic Sulfation and Regeneration of β-Ca_2SiO_4

Cycle No.	Conversion in sulfation,* %	Regeneration time,† min
1	44.3	18**
2	54.6	25††
3	47.4	21
4	50.8	25
5	49.3	27
6	36.3	26
7	42.0	20
8	45.1	21

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* Sulfation condition: 900°C, 0.25% SO_2, 5% O_2, bal. N_2, 2 hr.
† Regeneration condition: 1 000°C, 5% CO, 95% N_2; 100% conversion except ** and ††.
** 93.5% completion.
†† 87.3% completion.

5.5 wt % at 955°C. The particles were spherical in shape and appeared to be much stronger than limestone.

The silica granules were impregnated with an aqueous calcium nitrate or calcium acetate solution, followed by a heat treatment at 1 000° or 1 075°C for 4 hr. X-ray diffraction analyses showed that the sample heat treated at 1 000°C was predominantly calcium oxide, and the sample heat treated at 1 075°C was in the form of β-$CaSiO_3$. The 1 000°C heat treated sample had a slight tendency of dusting, whereas the 1 075°C sample did not present this problem.

Sulfation and regeneration experiments were performed with samples of various calcium oxide loading. The conditions for sulfation were, again, similar to those in fluidized-bed combustion. Rates of sulfation are shown in Figure 11. All the rates were substantially higher than those with lime or calcined dolomite (which are not shown in this figure but may be found elsewhere). The rate was higher for the lower calcium oxide loading (3.15%). The sample with a heat treatment of 1 075°C showed a lower reactivity than the 1 000°C samples.

The rates of regeneration of the sulfated samples, via thermal decomposition, are shown in Figure 12. Regeneration of the supported β-$CaSiO_3$ was much faster than that of the supported calcium oxide. The most interesting result was that the ratio of the two decomposition rates, calculated by taking the slopes in the figure which gave rate = $(1/W)(-dW/dt)$, was 15. The ratio was identical with that calculated from Figure 6 for the bulk calcium silicates and calcium oxide. This ratio is indicative of the relative bond strengths between sodium trioxide and the sorbents.

An interesting comparison may be made between the silica-supported and the aluminum oxide-supported lime sorbents. It was reported that the aluminum oxide-supported lime was mostly calcium aluminates after heat treatment (Snyder et al., 1976). Rates of sulfation were about the same for the two types of sorbents. However, the rate of regeneration of the β-$CaSiO_3$ supported on silica (Figure 12) was substantially higher than with the calcium aluminates supported on aluminum oxide (Figure 9 in Snyder et al., 1976). The above comparison was made with their rates of regeneration in a gas containing 0.1% hydrogen, since rates of straight thermal decomposition were not available from their work. The comparison should be more favorable for the silica-supported sorbent on the same basis because the decomposition rate is higher when hydrogen is present in the gas phase.

Cyclic Sorption and Regeneration of β-Ca_2SiO_4

The β-Ca_2SiO_4 sample prepared by the EDS technique was further subjected to cyclic sulfation and regeneration experiments. The results, along with the experimental conditions, are summarized in Table 4. As seen from these results, there was no tendency of decaying of the reactivities of β-Ca_2SiO_4 in both sulfation and regeneration. It should be noted that the lower extent of sulfation in the sixth cycle was due to a prolonged period of cooling after regeneration. The reactivity was, however, restored upon further cycling.

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NOTATION

k = rate constant based on weight of sorbent, kg mole/atm s-kg
k_s = rate constant based on reacting surface, kg mole/s atm m^2
P_{SO_2} = partial pressure of sulfur dioxide, atm
r = reaction rate, kg mole/kg s
r_0 = initial reaction rate, kg mole/ kg s
S_0 = initial BET surface area, m^2/kg
t = time, s
W = weight, kg
X = fractional conversion
η = effectiveness factor

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