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REGENERATIVE PROCESS FOR DESULFURIZATION OF HIGH TEMPERATURE COMBUSTION AND FUEL GASES

QUARTERLY PROGRESS REPORT NO. 6
JULY 1-SEPTEMBER 30, 1977

PROCESS SCIENCES DIVISION
DEPARTMENT OF ENERGY AND ENVIRONMENT

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Contributors:

R.T. Yang	F.B. Kainz
A.S. Albanese	J. Pruzansky
J.M. Chen	M-S. Shen
G. Farber	R. Smol

M. Steinberg

M. STEINBERG, Head
R.T. YANG, Project Leader

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BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

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Summary

The Brookhaven Regeneration Process, which comprises reacting the sulfated limestone with the fly ash from a FBC in a solid-solid contacting kiln-type reactor, has been further shown more promising than the other processes currently under development. A quartz rotary kiln, with about 10-g limestone capacity, has been in operation for gathering kinetic and process development data on this process. Typical (not the best) results are: With a partially sulfated limestone and a fly ash (12% unburnt carbon), both from Argonne's pilot FBC, 5% SO_2 was obtained in the kiln off gas for up to about 50% lime regeneration (in 80 min.) at 1000°C and 1 atm. Much improvement can be made by optimizing the operating conditions which are primarily: gas flow rate, degree of agitation (rpm), additives (both solids and gases, e.g. steam), types of carbon, etc. TGA kinetic studies also showed promising results. Cyclic studies, involving the kiln regenerator and a quartz fluidized-bed sulfator, are being conducted for both cyclic reactivity and attrition information.

Various dicalcium silicates have been studied for their reactivities for sulfation. Most of the dicalcium silicates (formed in our laboratory and obtained from various sources) showed equal or higher sorption reactivities than lime, on a weight SO_2 per weight sorbent basis. More reactive calcium silicates are being sought, as well as the means of forming them. The highly encouraging results are on the regenerabilities of the calcium silicates from their sulfated states. For all the mono- and dicalcium silicates studied, the regeneration

rates are about an order of magnitude higher than that of lime or limestone, in both straight thermal decomposition and regeneration with carbon.

Studies on catalytic sulfation continued. A chlorine balance has been made over a simulated FBC with 3% NaCl added to the limestone at 900°C. Sixty percent of the Cl in NaCl was collected in the off gas without iron, steel and refractory lining materials in the sulfation zone. With these materials, which is the case in a FBC, the Cl collected in the off gas was 44%. The 16% Cl balance was presumably reacted with the materials in the simulated FBC. The 44% Cl collected in the latter case contained primarily Fe chlorides.

Calcination of limestones in atmospheres containing steam or CO_2 increases the reactivities of the calcined stones significantly.

Work on kinetics in pressurized FBC has been started with a pressurized TGA. Both sulfation and regeneration kinetics are being studied. Increasing the total pressure would increase the sulfation rate for most limestones, as has been observed elsewhere (Westinghouse). However, our preliminary results indicated that this may not be true for some industrially important stones, and it may be just the opposite for the calcium silicates sorbents.

Silicate-based synthetic sorbents are being developed. This new class of synthetic sorbents appears to be more promising than the ones developed previously by other laboratories.

Regenerative Process for Desulfurization of High Temperature Combustion and Fuel Gases

Quarterly Progress Report No. 6
July 1 - September 30, 1977

1. The Brookhaven Regeneration Process

1.1 Introduction

The Brookhaven Process comprises reacting the $CaSO_4$ from a FBC to form CaO and SO_2. This process differs with the one-step reductive decomposition mainly in two ways: (a) the mode of operation is basically a solid-solid contact reaction system as opposed to fluidized-bed and (b) fly ash is utilized for its residual carbon. The detailed chemistry has been described in our previous reports.

1.2 TGA Studies

Figure 1 shows the regeneration rate of CaO of a 27.4% sulfated 2203 limestone (from Argonne's FBC) and a coal ash containing 8.55% carbon at $1000^{\circ}C$. The coal ash was recovered from Argonne's FBC using Sewickley coal (Penna., bituminous) and 1337 dolomite at 3 atm. Pressure and $900^{\circ}C$ bed temperature. This ash also contains 2.89% S 8.91% Ca and 1.08% $CO_3^{=}$. It can be seen from Figure 1 that more than 90% of the sulfated stone was regenerated within 10 minutes.

In relation to this regeneration process, experiments are being performed to see if the rate of the regeneration reaction is independent of the types of reductant materials used, e.g., C, CO, H_2, CH_4, etc., to see if the two-step regeneration reaction mechanism is common to $CaSO_4$ regeneration. That is, one-fourth of $CaSO_4$ is first rapidly converted to CaS and subsequently three moles of $CaSO_4$ react with one mole of CaS to form CaO and SO_2. As we mentioned in the previous report (No. 5) the calcium silicate system (e.g. $CaSO_4 \cdot SiO_2$, $(CaSO_4)_2 \cdot SiO_2$ etc.) also shows the two-step regeneration reaction mechanism.

1.3. Kiln Studies

A small, batch-wise kiln has been used to regenerate the sulfated limestone. The reaction being considered is

$$CaSO_4 + 1/2C \rightarrow CaO + 1/2\ CO_2 + SO_2$$

Sources of the reactants are partially sulfated Greer limestone and fly ash, both from fluidized bed combustors. Variables affecting the performance of this process have been studied and are described in the following.

1.3.1 Experimental

Materials:

Both the sulfated Greer limestone and the fly ash were supplied by Argonne National Laboratory. The compositions were:

fly ash (primary cyclone)	carbon = 12.5%, S = 5.24%, SO_4 = 14.6% Mg = 10.3%, CO_3 = 7.24%, others (balanced)
Sulfated Greer	Ca = 34.5%, S = 8.7%, CO_3 = 1.24%, SiO_2 = 7% others (balanced)

The sizes were 200/270 Tyler mesh for the fly ash and 20/24 mesh for the sulfated stone.

Apparatus and Procedure:

The apparatus is shown schematically in Figure 2. The weighed sample of the solid reactants, with the molar ratio of C/S=1/2, was fed to the reaction zone of a 27 mm OD rotating quartz kiln reactor, which contains four evenly spaced quartz vances to increase solid mixing (Figure 3). This reactor was heated by a clam shell furnace, which heated the reactor to the desired temperature within 2 minutes. A thermocouple, located at the center of the reactor tube, was used to measure the reaction temperature, while the wall temperature is measured by an optical pyrometer, In all the experiments, the speed of rotation was kept at 5 rpm.

In these experiments, Ar was used as the carrier gas. It passed through a tube packed with copper turnings held at 550°C for residual oxygen removal. The gas, before entering the reaction zone, was preheated by passing through approximately 100 mm length of heated silicon carbide chips. Samples of the off gas were withdrawn intermittently and were analyzed mass spectrometrically. From the ratio of SO_2 to Ar the amount of SO_2 evolved as a function of time was calculated. After finishing each experiment the weight loss also gave the extent of regeneration.

1.3.2 Results and Discussion

Four regeneration experiments (designated run numbers 1-4 in Table 1) at temperatures ranging from 950°C to 1050°C, and with flow rates (Ar), 0.37 m, moles/min to 1.46 m moles/min have been made. These results are summarized in Table 1. The off gases were found to be predominantly SO_2, CO_2 and Ar. The SO_2 concentrations in the off gas $[SO_2/(SO_2+Ar+ CO_2)]$ at various times are given in Figure 4, while CO_2 fraction $[(CO_2/(SO_2+Ar+CO_2)]$ is shown in Figure 5. These figures clearly indicates that reaction (1) is a two-step reaction:

$$1/4\ CaSO_4 + 1/2\ C \rightarrow 1/4\ CaS + 1/2\ CO_2 \qquad (3)$$

$$1/4\ CaS + 3/4\ CaSO_4 \rightarrow CaO + SO_2 \qquad (4)$$

and reaction (4) is the rate controlling step.

Thermodynamic equilibrium partical pressures of SO_2 for reaction (4) are given in Figure 6. From Figures 4 and 6, it is apparent that, except for run (4), the SO_2 gas concentration has not reached thermodynamic limit. This may be because that reaction 2 is an endothermic rate process with heat of reaction approximately 58 kcal/mole. The temperature of the reacting interface is lower than the measured temperature. It may also be due to the concentration gradient existing inside the solid particle resulting in a lower SO_2 concentration in the gas phase.

Runs (2) and (3) gave essentially the same SO_2 percentage at various flow rates indicating that the reaction was suppressed by the SO_2 in the gas phase. Decrease of the SO_2 concentration with time indicated that a diffusion resistance in the product layer may also restrict the reaction rate. This point is clear when one compares the shapes of the four curves; zhe higher the initial rate, the faster the rate declines.

The extent of regeneration as a function of time was plotted in Figure 7. Eighty percent of the sulfated limestone could be regenerated is one hour at 1050°C under our operating conditions. At 1000°C since both flow rates (runs (2) and (3)) gave the same SO_2 concentration, the rate of regeneration under the operating conditions is controlled by the "sweeping rate" of the carrier gas. In the regeneration processes, two factors must be considered: 1) rates of the lime regeneration, 2) SO_2 concentration in the gas phase. To convert SO_2 into sulfuric acid, a desirable SO_2 concentration would be 4 ∿ 5%. Since the reactivity of the regenerated lime decreases with the increasing temperature, the temperature range of 1000-1050°C seems to be an optimum temperature under our present experimental conditions.

Further work will be conducted to investigate the effects of the gas flow rate, particle sizes, degree of agitaion, etc. on the regeneration rate and the SO_2 concentration. The reactivity of the regenerated lime will be tested in TGA, and in a small (30 mm ID, quartz) fluidized bed sulfator. The small fluidized bed sulfator is under construction and will be finished in the next quarter.

2. Sulfation and Regeneration of Calcium Silicates

2.1 Sulfation of Dicalcium Silicates

As we mentioned in the previous quarterly progress report, in the regeneration process with coal ash containing unburnt carbon, CaO is the predominant product with small amounts of calcium silicates. However, at the steady state in a continuous recycling process, the amounts of the silicates would be much higher because for each particle, as it is being recycled, contents of silicates would increase with the number of cycles due to the fact that the silicates stay in the structure once formed. Therefore, there would be always a mixture of CaO and silicates. Sulfation rates of the reagent-grade CaO (mallinckrodt, 325/400 mesh) were compared with the mixture of CaO and β-dicalcium silicate (Atomergic research grade, 325/400 mesh, x-ray diffraction intensity estimated about 50% CaO and 50% β-dicalcium silicate). As shown in Figure 8, the rate of the mixture of CaO and β-dicalcium silicate is higher than that of the CaO alone with the same size. It implies that the sulfation reactivity of β-dicalcium silicate is higher than that of CaO. This can be seen in Figure 9. The sulfation rate of dicalcium silicate (Portland Cement Association, 90% β form and 8% α' form estimated by x-ray diffraction, 325/400 mesh) is higher than that of the reagent CaO (325/400 mesh). The temperature at which the dicalcium silicates were prepared by Portland Cement Association may be too high (> 1080°C) to have high sulfation reactivity. These β-dicalcium silicates are stabilized by the addition of small amounts of metal oxides which are actually presented in FBC. The rates are not high but are in the same order of magnitude as that with limestones. However, limestones contain Fe_2O_3, SiO_2, MgO and Al_2O_3 some of which are thought to be catalysts for sulfation reaction. Also, the reaction system was free of water vapor which has been shown to catalyze the sulfation of limestones drastically.

2.2 Regeneration of Calcium Silicates

As we mentioned before, the advantage of using calcium silicates to desulfurize hot combustion gases was partly based on their higher regenerabilities than the plain calcium oxide. It has been reported in the previous quarterly progress report (No. 5) that the thermal decomposition rate of the sulfated monocalcium silicate is higher than that of the $CaSO_4$ as shown in Figure 10, i.e., the sulfated monocalcium silicate is more regenerable than the sulfated lime. In Figure 10, it is shown that the thermal decomposition rate is higher with sulfated dicalcium silicate. It is seen that more than 90% of the sulfated dicalcium silicate was regenerated within 20 minutes.

Figure 11 shows the regeneration with carbon as a solid reductant (Ca/C ratio was controlled at 2) at 1000°C. The regeneration rate of the sulfated $CaSiO_3$ was moderately higher than that of $CaSO_4$. However, the regeneration rate of the sulfated Ca_2SiO_4 was very high, about 70% was regenerated in 30 minutes. These evidences of higher regenerabilities with calcium silicates supported the law of nature that the bond to an atom weakens when other bonds are formed to the same atom.

The x-ray diffraction pattern of the regenerated β-dicalcium silicate did not contain lines of CaO and CaS, which indicated that silica was chemically bonded to the calcium sulfate in the sulfated dicalcium silicate.

In a reaction between partially sulfated Greer limestones (65% $CaSO_4$, 16/20 mesh) and complete burnt Illinois No. 6 coal ash (0% C, 200/270 mesh) at 1100°C, the x-ray diffraction analysis shows that β-dicalcium silicate (Larnite) is the major reaction product.

3. Kinetics of Sulfation of Limestones

3.1 Catalytic Sulfation of Lime

We have reported catalytic sulfation of lime with iron compounds and coal ash. Another good high temperature catalyst for SO_2 oxidation,

V_2O_5, was also tested for the sulfation reaction with the purpose of further unraveling the sulfation mechanism. As shown in Figure 12, a moderate catalytic effect was observed. However, the V_2O_5 was of reagent grade and was not a commercial catalyst which contains various alkali-metal promoters.

A note should be made here on the rate dependence on the partial pressure of So_2. Sulfation of lime was thought to be a first-order reaction with respect to SO_2 by various workers, e.g., Borgwardt.[1] However, their experiments were performed in the lower range of the partial pressure of SO_2. For example, Borgwardt's data were for SO_2 concentrations below $6.4x\ 10^{-8}$ g-mole/cm^3 (total pressure=1 atm), which were in agreement with our data as shown a dashed line in Figure 13. The reaction order for sulfation of CaO with 4% Fe_2O_3 is slightly higher, e.g., 1.05 as shown a dashed line in Figure 14. In Figures 13 and 14, a straight line does not seem to fit the data at higher partial pressure (the slopes of the solid lines in the figures were outlined by using the least-square linear regression method). The data tend to follow a quadratic form. A complicated rate expression is likely to exist for the sulfation reaction of lime. Thence we measured the activation energy at simulated combustion SO_2 concentration, e.g., $2.7x10^{-8}$ g-mole/cm^3 (total pressure=1 atm) which are shown in Figure 15 (CaO) and Figure 16 (CaO with 4% Fe_2O_3). The activation energy of sulfation of CaO is somewhat greater than that of CaO mixed with 4% Fe_2O_3.

Figure 17 shows tha sulfation rate of a calcined Tymochee dolomite with and without 5% steam. Again steam catalyzes the sulfation reaction. The sulfation rate of the calcined Tymochtee dolomite is about twice higher than that of Greer limestone.

3.2 Fate of NaCl in a Simulated FBC

In the experiment with Greer limestone and 3% NaCl packed with 304 stainless steel tubes and Sauereisen No. 75 (lining material of furnaces) in a simulated combustion gas (See the schematic diagram of chlorine test equipment in the previous quarterly progress report.), at 900°C, about 41% chlorine was condensed on the 304 stainless steel walls downstream of the reactor, and about 3% chlorine in the off-gas was collected in the bubbler containing NH_4OH solution. The total chlorine recovery was about 44%. In the blank experiment, where only quartz tubes were used, 60% total chlorine was found. The deposition of chlorine in the bed material must be the reason for a 16% chlorine discrepancy in the mass balance. The mass balance. The mass balance was therefore attempted and the results were as follows. In the blank test, 60.1% Cl was found in the NH_4OH bubbler solution and 0.5% Cl remained in the Greer lime. In the experiment where Greer lime, Sauereisen No. 75, 304 stainless steel tubes and 304 stainless steel line going to the trap were used, the chlorine balance was 2.7% in the NH_4OH bubbler, 41.3% condensed in the 304 stainless steeel line, 8.6% remained in the Greer lime, 1.0% in Sauereiswn No. 75, 0.2% in 304stainless steel tubes. In comparison to the blank test, there were about 6.8% insoluble chlorine compounds formed.

The 41% chlorine condensed in the cooler 304 stainless steel line was a dark green, water-soluble material and was analyzed as: Fe, major constituent; Cr, ∿ 0.6 mg/ml; Ni, 0.05-0.6 mg/ml. The corroded 304 stainless steel tubing was analyzed as: Fe, major constituent; Cr, ∿ 3%; Ni, 0.5-0.6.

3.3 Effects of Calcination in Steam

It has generally been observed[2,3] that calcination history can greatly affect the sulfation performance of the limestones. The performance, especially the SO_2 sorption capacity, can critically determine the ratio of Ca/S required for fluidized bed combustion process. For economic concern, it is important in searching for the best calcination condition to yield the highly reactive limes. This will be particularly useful for the once-through FBC systems.

A great increase in SO_2 sorption capacity of CO_2 calcined limes, compared with pure N_2-calcined limes, has been found by the Westinghouse Research Laboratory.[2] To continue research on this objective, this work was conducted to investigate the sulfation rates of the steam-calcined limes.

Experimental:

The rates of sulfation were measured gravimetrically. A Cahn-TGA system was used. Details of the experimental procedure and the apparatus for the measurements have been described elsewhere.

The weighed samples (about 80 mg) of Greer limestone (16/20 mesh) were calcined in-situ at a heating rate of 20°C/min and were sulfated subsequently. The calcination temperatures were kept the same as the sulfation temperatures. Total gas flows through the system were kept at 1000 SCCM which corresponded to a linear flow velocity of 10 cm/sec.

Results and Discussion:

The sulfation rates of N_2-calcined, H_2O/N_2-calcined, and CO_2/N_2-calcined limes at 1 atm in the temperature range of 900°C to 1000°C have been measured and the results are shown in Figures 18, 19 and 20. In each experiment, the sulfation rates have been measured for more than two hours.

From these results, it is clear to show that both CO_2 and steam treated limes have higher SO_2 absorption capacity than pure N_2 treated ones. The higher the steam concentration, the larger the capacity for SO_2. Also, the increase in capacity for CO_2 and steam calcined limes seems to decrease with increasing temperature.

The effect of CO_2 on the sorption capacity is believed to be due to its effect on the port development during calcination. O'Neill et al.[2] suggested that CO_2 calcined limes gave larger pores than N_2 calcined limes. Since the capacity of a lime is determined by closing of the pore mouths as the calcium sulfate (which has a larger specific volume than calcia) is formed within the pores. Thus, particles with larger pores showed higher capacities.

Senum et al[3] have shown that the reactivity of the steam calcined lime is larger than the non-steam calcined lime, but the surface area is essentially the same for both calcined limes. However, the port size distribution is more favorable toward larger pores for steam calcined limes than for non-steam calcined ones. This differnece in the pore sizes, again, may result in the increase of sorption capacity.

Further work may continue to study the sulfation capacities of the limes at various steam concentrations, and the combined effect of CO_2 and H_2O in the combustion flue gas on sulfation will also be investigated.

4. Pressurized TGA

High Pressure TGA:

This study is in support of the development of the Pressurized Fluidized Bed Combustion (PFBC). Kinetic studies are being performed on both sulfation and regeneration reactions.

The construction of a high pressure, high temperature, vertical TGA system has been completed. This system is capable of operating at temperature up to 1800°C and pressures up to 10 atmospheres. It is currently used for sulfation rate measurements at 10 and 1 atmospheres and in the temperature range of 800°C to 1000°C.

4.1 Apparatus

The scheme of the apparatus is essentially the same as 1 atm TGA. A Cahn balance (model R-100) is housed in a 1/4" thick stainless steel bell dome. Connected to the balance is a 1" I.D., 1/4" thick alumina (high purity) tube. A platinum wire is used to hang a 3/16" diameter alumina sample pan. The reaction zone is heated by a 1 ft deep temperature programmable furnace, and the temperature is measured by a Pt-Pt/10% Rh thermocouple, whose tip is about 1/4" below the sample pan. During the experiments, a constant flow of N_2 is pured through the balance to prevent corrosion. This N_2 merges with the reactant gases from the side wall and exits from the bottom of the tube.

In general, 1/4" stainless steel tubing is used for gas transport. The flow rates of gases are measured by calibrated Tylan mass flow meters. The experimental procedure for the sulfation rate measurement is the same as in the atmospheric pressure experiments.

4.2 Results and Discussions

Sulfation rates at various pressures were measured at 900°C using Greer limestone. The stone was 16/20 Tyler mesh in size and was calcined in TGA at 900°C with 25°C/min temperature rise. In all these experiments, high overall gas flow rates (1100 SCCM) and small amount of sample weight (about 30 mg limestone) were used to eliminate the possible mass transfer effects. Figure 21 gives the conversion x versus time data under the conditions of SO_2: 0.5%, O_2: 5%, N_2: 94.5%, P = 1 atm (curve 1); SO_2: 0.5%, O_2: 5%, N_2: 94.5%, P = 10 atm (curve 2), and SO_2: 5%, O_2: 5%, N_2: 90%, P = 1 atm (curve 3) respectively. Also, from the DTG curves, the reaction rates $\frac{dx}{dt}$ were obtained and these results are plotted versus conversion in Figure 22.

Figure 21 shows that increasing the system pressure increases the sulfation rates under the same gas compositions (cf. curves 1 and 2). This is because that increasing the system pressure increases the partial pressure of SO_2 resulting in higher chemical rates.

Similar results for dolomite sulfation were observed by O'Neill et al.[2,4] However, the initial sulfation rates at 10 atm were lower than 1 atm under the same SO_2. Partial pressures (cf. curves 2 and 3). Some of the differences in rates during the initial stages can be qualitatively explained by the grain model[5,6] and are described in the following:

Since most of the accessible surface area in the calcined lime exists inside the pores,[1] pore diffusion plays an important role even in the initial conversion stage. Using grain model Ishida and Wen[6] have shown that

$$\text{Reaction rate} \propto \sqrt{k_s De} \cdot P_{SO_2}$$

(product layer diffusion through each grain is assumed negligible in the initial stage), where k_s is surface reaction rate constant, De is pore diffusion coefficient and P_{SO_2} is the partial pressure of SO_2. Since diffusivity De is inversely proportional to total pressure,[7] the reaction, at 10 atm, based on the grain model, would be 10 times lower than that at 1 atm under the same compositions. The fact that it is higher is because of the higher chemical rate. According to the Wen-Ishida model, the overall rate should be higher by a factor of 10/ 10 or 10. The rates at 5% SO_2, 1 atm would be 10 times higher than the 0.5% SO_2, 1 atm rates. The experimental results given in Figure 21 at conversions less than 3% seem to conform with the above analysis. However, this model can not be used to explain the difference between curves 2 and 3. Rates in curve 3 could be limited by P_{O_2} (not P_{SO_2}). Higher P_{O_2} will be used in the future.

The extent of sulfation for 6 hours for the above results is given in Table 2. It was surprising to find that lime sulfation at 10 atm had higher capacity than that at 1 atm under the condition of same SO_2 partial pressure. Figure 21 shows that both 1 atm runs reached plateau conversion value lower than 52%, the maximum conversion for pore enclosure for lime sulfation.[8] For 10 atm sulfation, while the reaction profile did not flatten below 52%. Factors for this increase in capacity is still unknown. It was suspected that the buoyancy effect due to pressure might result in the error in measurements. However, experimental results showed that pressurizing the system from 1 to 10 atm using N_2 and O_2 flows caused only 2 mg weight increase, and introducing SO_2-N_2 mixture flow 100 SCCM) to start sulfation only increased 100 mm 4g in system pressure. Thus, the weight increase due to the introduction of SO_2 would be less than 0.03 mg. This value compared with the total weight gain in 6 hours (12 mg) can be neglected. Thus, it was concluded that the weight increase during sulfation was not resultant from buoyancy effect.

Using pore enclosure to explain the SO_2 absorption capacity, one would expect that the capacity at 10 atm (curve 2) would be lower than that at 1 atm (curve 3), since the diffusion barrier is increased by pressure. The penetration depth for SO_2 would be lower at higher pressures, and the available portion of lime in the particles is thus reduced. This seems to be contrary to the experimental findings. Further work on the cause of the increased sulfation capacity due to pressure will continue.

The effect of calcination pressure on sulfation has also been investigated. Sulfation rates of nitrogen calcined lime at 1 atm and 10 atm are given in Figure 23. No difference in rates was observed.

5. Silicates - Based Synthetic Sorbents

In recent years, regenerable synthetic sorbents have been sought for application to FBC at several laboratories. They have found very good regenerable sorbents but unfortunately, the sorbents all turned out to be too expensive to be practical. Examples are: barium titinate (Exxon), alkalized alumina (Bu. Mines) and CaO deposited on α Al_2O_3 (Argonne and Dow Chemical).

Concerning the last-mentioned sorbent, the sample was prepared in the following manner: the α-Al_2O_3 (a high temperature and high surface area form) pellets were immersed in a concentrated aqueous solution of $Ca(NO_3)_2$, removed and dried (at an unspecified temperature) subsequently. The pellets were then heat treated at 800°C or 1100°C. The calcium loading ranged from 3.3 to 14.8% by weight of CaO in Al_2O_3. X-ray diffraction showed that most of the CaO was in the forms of calcium aluminates, not free CaO islands or crystallites. Rates of sulfation and regeneration were shown to be much superior than the natural lime. But, as mentioned, the cost would be too high for production of such sorbents, mostly due to the high cost of the α-Al_2O_3.

With the above background, and being aware of the fact that only about 30% of the lime, mostly on the outer surface layer, is sulfated in the fluidized bed combustion pilot plants, let us discuss the synthetic sorbents based on silica rather than alumina.

We impregnate CaO on the internal surface of a porous siliceous material. The impregnated material is then heat-treated at 700-1000°C. A highly reactive mixture of calcium silicates is formed on the pore surface. This material is also highly regenerable. Such sorbents can be made at low costs: (a) The siliceous pellets may be a porous silica or silicate, or it could be a sintered, pelletized coal ash pellets; (b) the CaO can be impregnated on the siliceous surface in a process similar to the Battelle Lime-Treated Coal process. The lime loading in this sorbent would be around 5-20%. Experiments on this new sorbent are in progress in our laboratory, and results will be reported shortly.

6. Process Design and Evaluation

Extensive changes in the subject process flow diagrams (PFD's) prompted by newly acquired process data, have caused a delay in completing the PFD's pertinent to sorbent regeneration and SO_2 conversion to H_2SO_4. As soon as the PFD's are completed, we will prepare an economic comparison between the once through sorbent system (base case) and the regenerative/H_2SO_4 system.

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Discussions and guidance provided by Dr. Andrej Macek of the U. S. Department of Energy have been very helpful.

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Table 1: Results of Lime Regeneration in the Kiln Reactor
$2CaSO_4 + C \rightarrow 2CaO + CO_2 + 2SO_2$

Run No.	Temp. (°C)	Flow (Ar) (m moles/min)	% SO_2 (max)	Time period (min)	Final Extent of regeneration (%) Based on gas phase	Based on solid phase[c]
1	960[a]	1.462	2.5	210	37	37
2	1000[a]	0.365	4	180	25	22
3	1000[b]	1.462	5	200	67	80
4	1050[b]	1.462	20	240	100	100

a: from optical pyrometer, b: from thermocouple. Wt: coal ash: 0.4998 g, sulfated Greer lime: 3.8508 g, c: assuming complete first step reaction.

Table 2: Extent of Sulfation at 6 Hours

Operating Conditions	Extent
1 atm, SO_2: 0.5%	40%
10 atm, SO_2: 0.5%	73%
1 atm, SO_2: 5%	48%

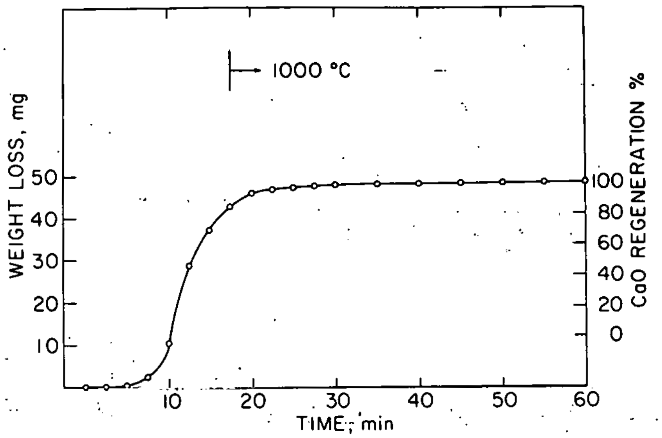

Figure 1. Regeneration rate of 100 mg 27.4% sulfated limestone 2203 from Argonne FBC (Sample E11032) with 18.8 mg Sewickley coal ash from Argonne FBC (8.55% carbon, 2.89% S).

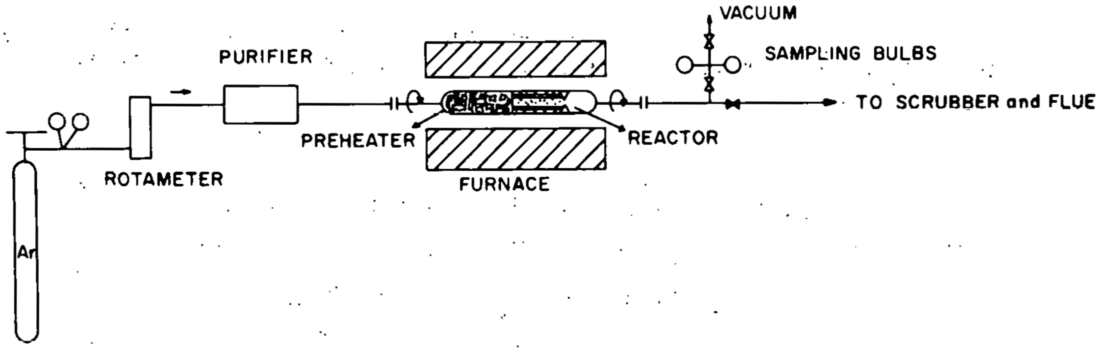

Figure 2. Schematic diagram of the rotary kiln regenerator.

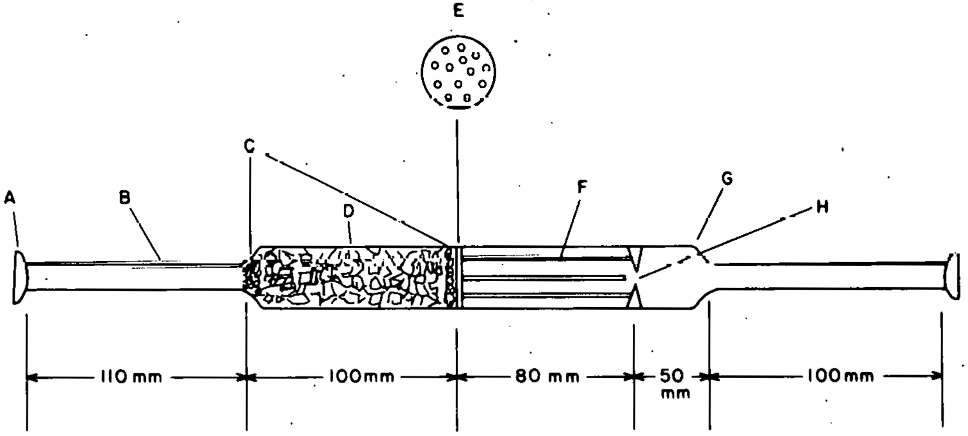

Figure 3. Design of the kiln regenerator.

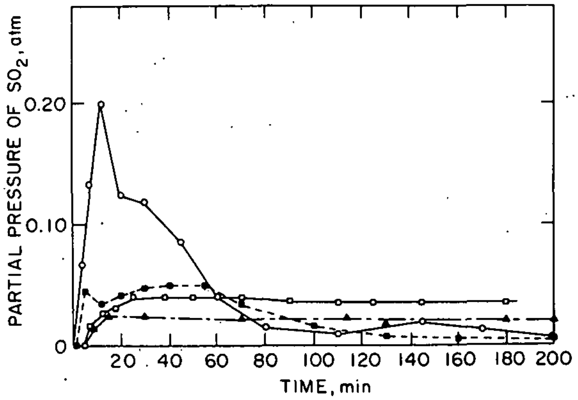

Figure 4. SO_2 concentration in the off gas from the kiln regenerator. Total press. = 1 atm. At the following temperatures and gas (Ar) flow rates: 1050°C and 1.46 m moles/min (o); 1000°C and 1.46 m moles/min (■); 1000°C and 0.37 m moles/min (□); 960°C and 1.46 m moles/min (Δ).

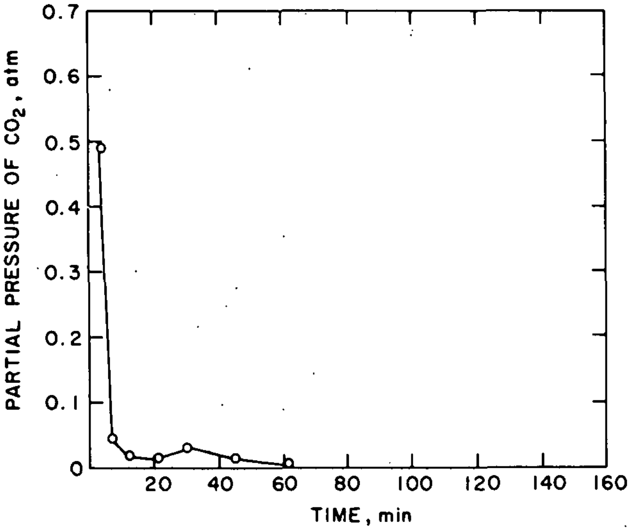

Figure 5. CO_2 concentration in the kiln off gas. Conditions same as the circles in Figure 4.

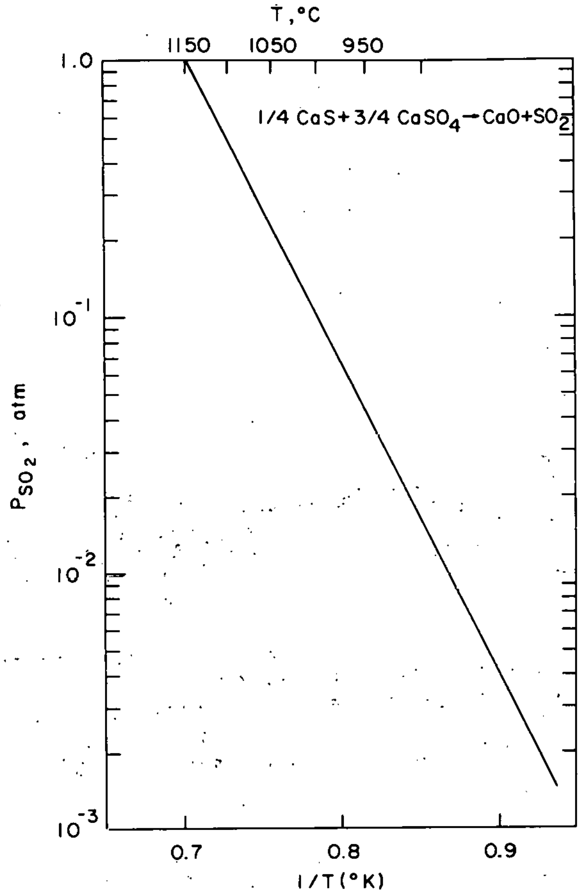

Figure 6. Thermodynamic equilibrium partial pressure of SO_2 for the reaction: $CaS+3CaSO_4 \rightarrow 4CaO+4SO_2$.

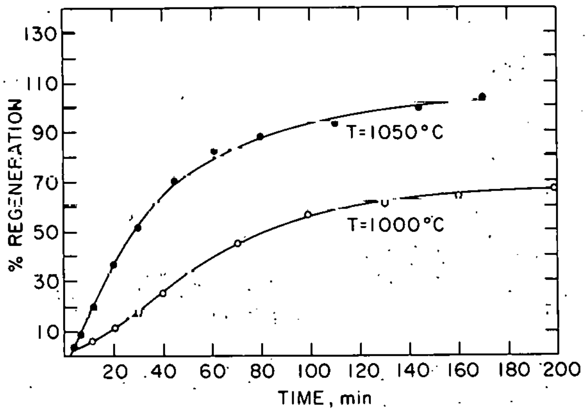

Figure 7. Rate of regeneration of lime in the rotary kiln. Flow rate of Ar = 1.46 m moles/min.

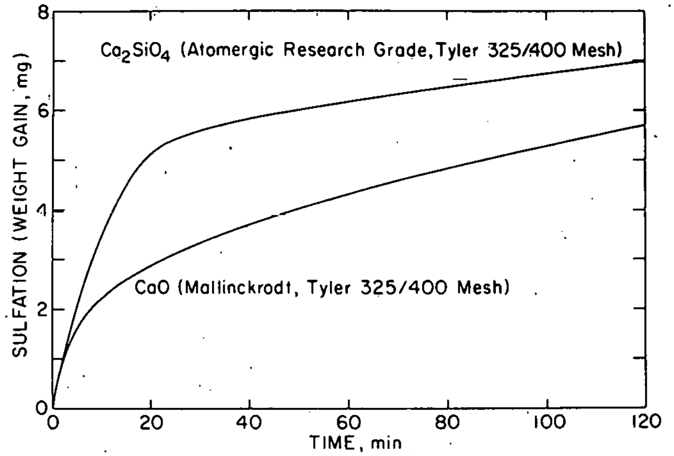

Figure 8. Comparison of rate of sulfation at 850°C between 325/400 mesh Ca_2SiO_4 (Atomergic) and 325/400 mesh CaO (Mallinckrodt) in 0.25% SO_2, 5% and a balance of N_2.

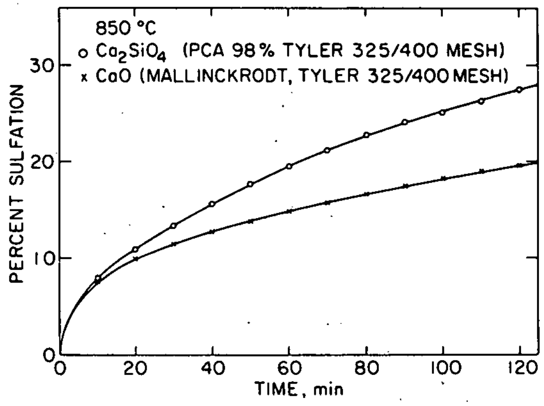

Figure 9. Comparison of rate of sulfation at 850°C between 325/400 mesh Ca_2SiO_4 (PCA) and 325/400 mesh CaO (Mallinckrodt) in 0.25% SO_2, 5% O_2 and a balance of N_2.

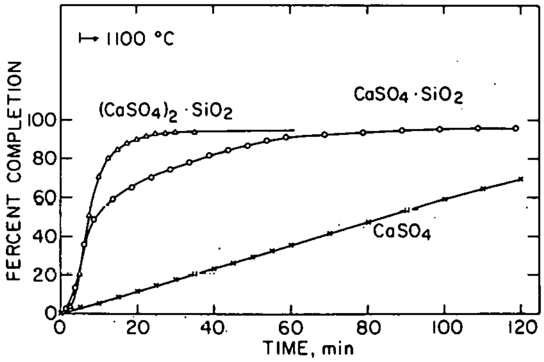

Figure 10. Regeneration (thermal decomposition) rates of powdered reagent $CaSO_4$ (Baker), 42% sulfated powdered $CaSiO_3$ (ROC/RIC) and 46% sulfated powdered Ca_2SiO_4 (PCA) at 1100°C in N_2.

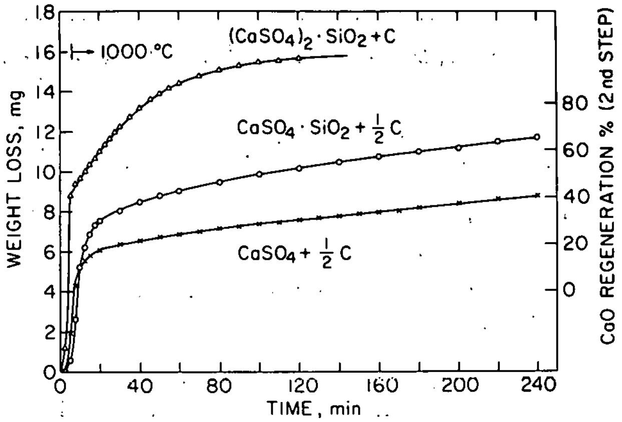

Figure 11. Regeneration rates of powdered reagent $CaSO_4$ (Baker), 42% sulfated powdered $CaSiO_3$ (ROC/RIC) and 46% sulfated powdered Ca_2SiO_4 (PCA) at 1000°C in N_2 with coconut charcoal (Tyler 200/250) as a solid reductant.

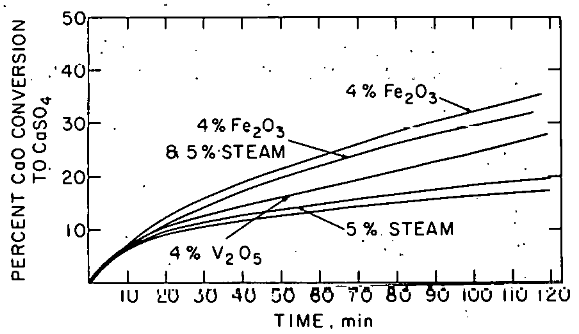

Figure 12. Sulfation rate of powdered reagent CaO (Mallinckrodt) with Fe_2O_3 (Baker, Tyler 200/325), V_2O_5 (Fisher, Tyler 200/325) or steam at 850°C in 0.25% SO_2, 5% O_2 and a balance of N_2.

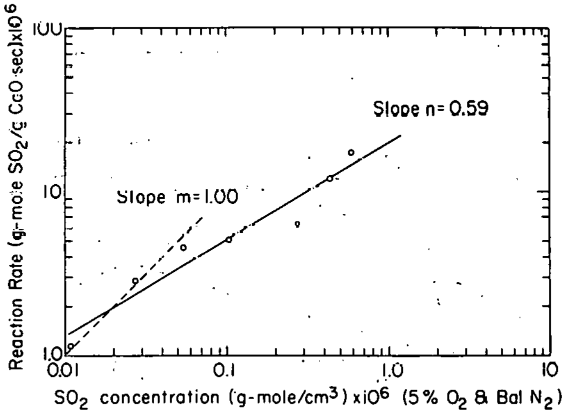

Figure 13. Effect of SO_2 concentration on sulfation of powdered reagent CaO (Mallinckrodt) at 850°C.

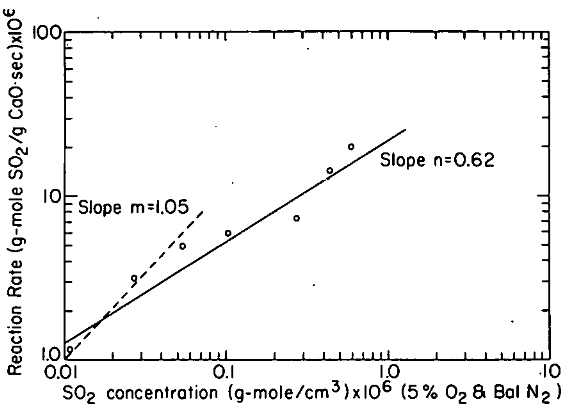

Figure 14. Effect of SO_2 concentration on sulfation of powdered reagent CaO (Mallinckrodt) and 4% Fe_2O_3 (Baker, Tyler 200/325) at 850°C.

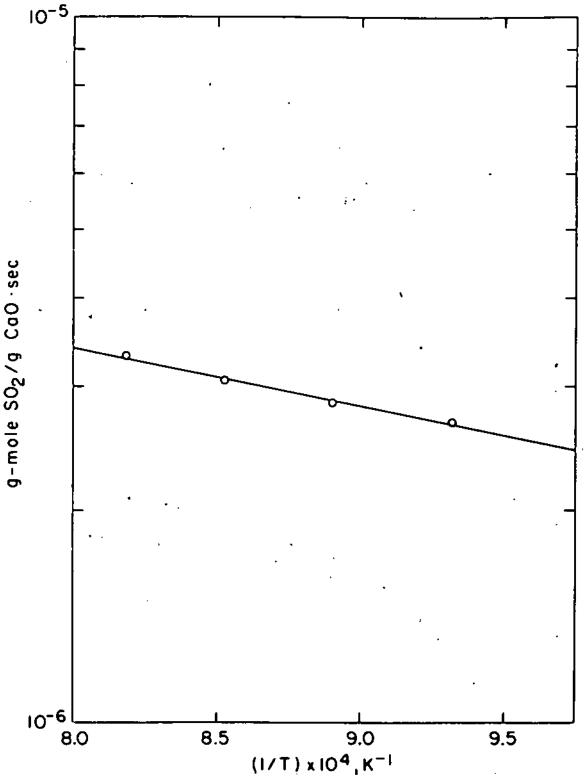

Figure 15. Effect of temperature on sulfation of powdered reagent CaO (Mallinckrodt) with 0.25% SO_2 and 5% O_2 in N_2.

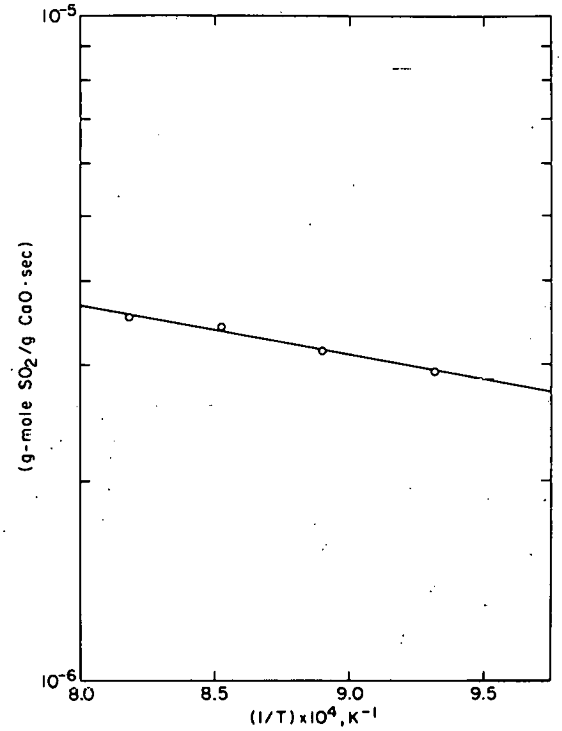

Figure 16. Effect of temperature on sulfation of powdered reagent CaO (Mallinckrodt) and 4% Fe_2O_3 (Baker, Tyler 200/325) with 0.25% SO_2 and 5% O_2 in N_2.

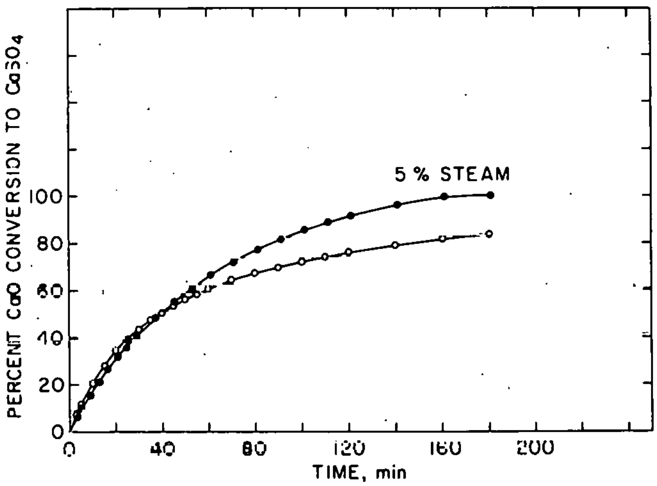

Figure 17. Sulfation rate of Tymochtee Dolomite (Tyler 16/20, calcined at 850°C) with 5% steam and without steam at 850°C in 0.25% SO_2, 5% O_2 and a balance of N_2.

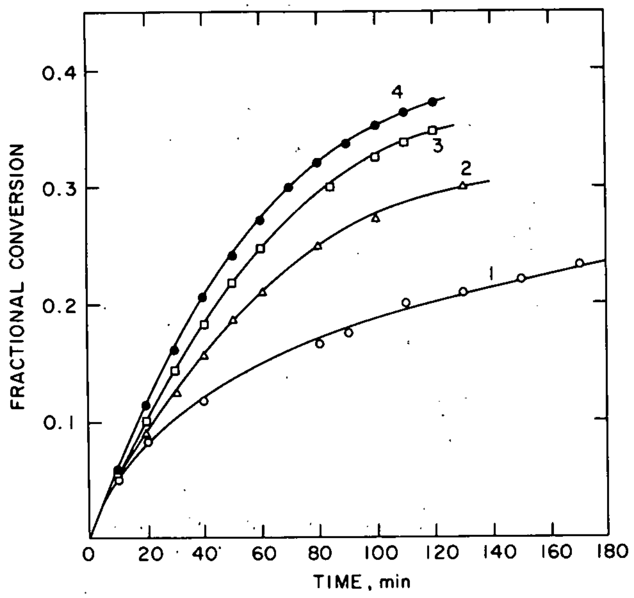

Figure 18. Effects of the calcination environment on the sulfation rate. Greer stone calcined at various conditions and sulfated at 900°C, with 0.25% SO_2, 5% O_2 and N_2 (bal.). Calcination conditions were: 1: N_2, 2: 10% steam in N_2, 3: 30% steam in N_2 and 4: 60% CO_2 in N_2.

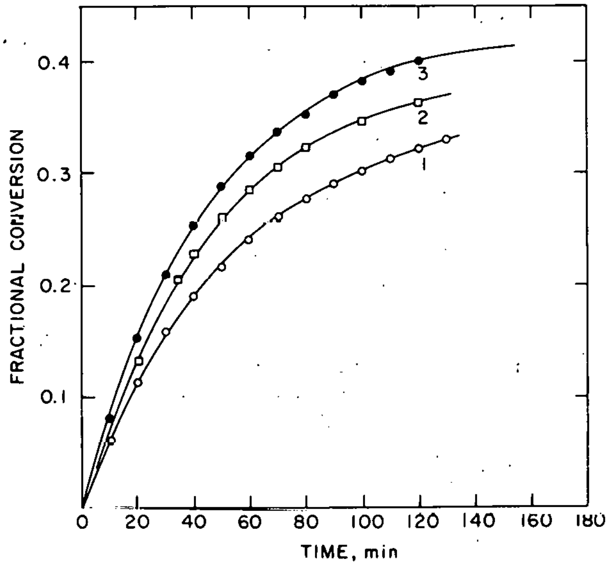

Figure 19. Same as Figure 18, except both calcination and sulfation were at 950°C. Calcination conditions were: 1: N_2, 2: 10% steam in N_2 and 3: 60% CO_2 in N_2.

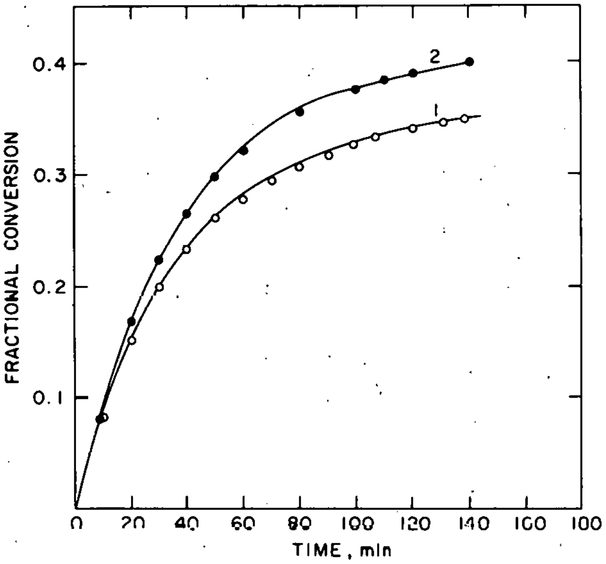

Figure 20. Same as Figure 18, at 1000°C. Calcination conditions were: 1: N_2 and 2: 60% CO_2 in N_2.

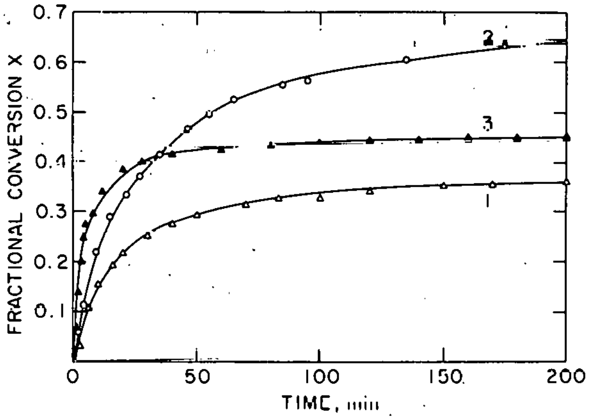

Figure 21. Sulfation rates of Greer lime (16/20 mesh) at 900°C and various pressures: Curve 1: p = 10 atm, SO_2 = 0.5%, O_2 = 5%, N_2 = bal.; Curve 2: p = 10 atm, SO_2 = 0.5%, O_2 = 5%, N_2 = bal.; Curve 3: p = 1 atm, SO_2 = 5%, O_2 = 5% and N_2 = bal.

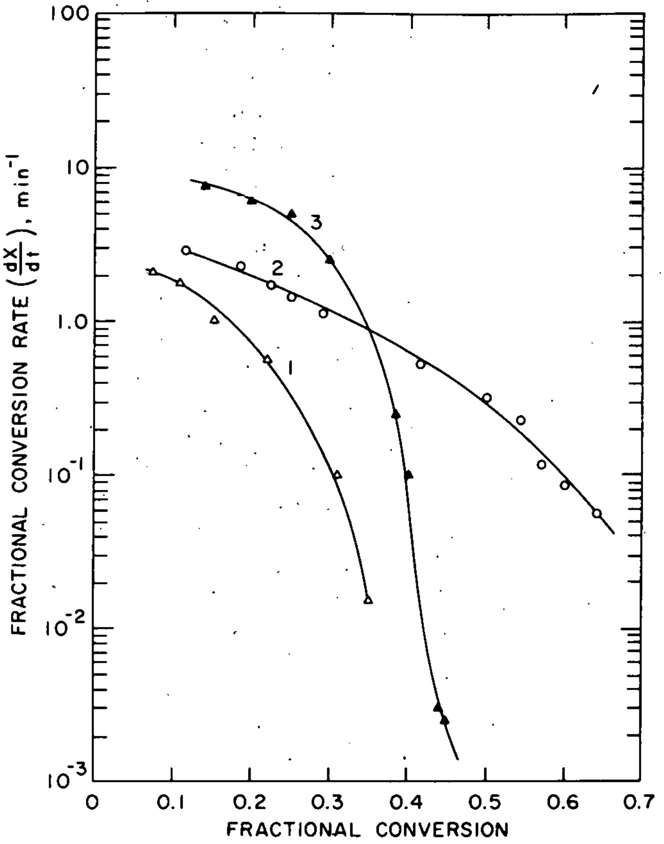

Figure 22. Sulfation rates versus % conversion. Legends same as in Figure 21.

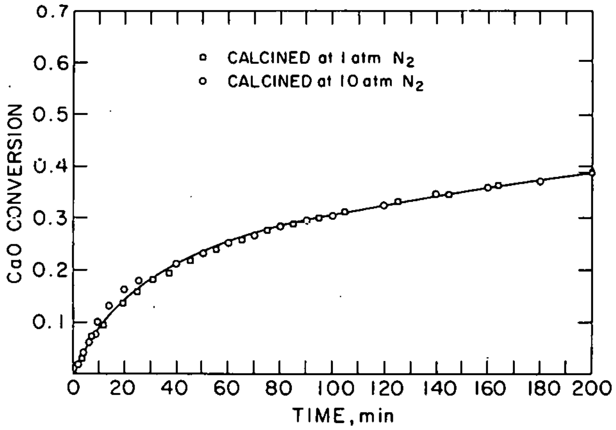

Figure 23. Sulfation rates of Greer lime calcined at 1 atm (□) and 10 atm (o) of N_2. Sulfated with 0.2% SO_2, 5% O_2 and N_2 at 900°C.

Distribution:

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