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REGENERATIVE PROCESS FOR DESULFURIZATION OF HIGH TEMPERATURE COMBUSTION AND FUEL GASES

MASTER

QUARTERLY PROGRESS REPORT NO. 5
APRIL 1 - JUNE 30, 1977

PROCESS SCIENCES DIVISION
DEPARTMENT OF ENERGY AND ENVIRONMENT

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NOTICE

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Summary

The sulfation rate of reagent-grade monocalcium silicate is in the same order of magnitude as that of limestone and higher than that of reagent-grade calcium oxide. It has been confirmed that the sulfated monocalcium silicate is more regenerable than the sulfated lime, i.e., the regeneration rate is higher with the silicate. X-ray diffraction and IR absorption results indicate that silica is chemically bonded to the calcium sulfate in the sulfated calcium silicate. Results on dicalcium silicates are not definitive at this stage and will be reported later.

Construction of a micro-pilot rotary kiln for regeneration of lime from the sulfated lime has been completed. The Brookhaven processes for regeneration using fly ash from FBC will be tested with this device. Design and construction of a micro-combustor are underway which will be used to test the regenerated lime.

Studies on sulfation of lime continue. Sodium chloride, although catalyzing the sulfation rate, yields too much chloride in the gas phase (60% NaCl at 900°C) which can chlorinate the metals and metal oxides in the combustor. The catalysis by Fe_2O_3 and/or coal ash has been established and its mechanisms have been studied. Effects of the calcination conditions on sulfation are being studied.

A process flow diagram for producing commercial strength sulfuric acid from regenerator off-gas has been prepared. The process would be used in conjunction with BNL's process for regenerating CaO from $CaSO_4$ using carbon as a reductant. A preliminary comparison between a once

through sorbent system and the combined regenerative/H_2SO_4 system indicates that the net energy outputs (useful) of the two systems are approximately the same. The quantity of solid wastes generated by the once through system is about 2.5 times the quantity generated by the combined system.

Regenerative Process for Desulfurization of High Temperature Combustion and Fuel Gases

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April 1 - June 30, 1977

1. Sulfation and Regeneration of Calcium Silicates

1.1. Sulfation of Monocalcium Silicate

Rates of sulfation of CaO, Greer lime and $CaSiO_3$ (supplied by Research Organic/Inorganic Company, N.J.) are compared in Figure 1. This figure includes the sulfation of a reagent-grade CaO, the aforementioned $CaSiO_3$ and a calcined Greer limestone under identical conditions. The CaO and $CaSiO_3$ samples were of powder form and the Greer lime was 16/20 Tyler mesh size. Pore structures and surface areas have not been measured. Two observations were made from these results. First, sulfation rate of $CaSiO_3$ is comparable to that of CaO. Second, the sulfation rate of $CaSiO_3$ plateaus at about 30% completion, whereas the sulfation rate of calcined limestones can in general hold to a much higher level of completion. This fact appears to be attributable to the changes (reduction) in the pore sizes during sulfation.

Sulfation rate of 16/20 Tyler mesh $CaSiO_3$ was also compared with results with 4% Fe_2O_3 and with 4% Fe_2O_3/5% H_2O under identical conditions (Figure 2). It is interesting that with such catalytic environments, the rate does not seem to plateau at a low percentage completion as in the case with $CaSiO_3$ alone. Further discussion on the catalytic effects is not pursued here because we are starting to understand such catalytic effects on a simpler system, i.e., with CaO, as will be seen presently in this report.

1.2. Regeneration of $CaSiO_3$

It is desired to compare the regenerabilities of $CaSiO_3$ and CaO from their sulfated compounds. Preliminary comparisons were made with two regeneration reactions; straight thermal decomposition and decomposition with C as a solid reductant (Ca/C ratio was controlled at 2). Experiments of the latter case have not been completed in this quarter and will be reported later.

The notion of using calcium silicates to desulfurize hot combustion gases was partly based on their probable higher regenerabilities than the plain calcium oxide. The thesis of the higher regenerability was in turn based on the law of nature that the bond to an atom weakens when other bonds are formed to the same atom. The atom in question here is calcium.

The first real test of the above thesis has been performed by a direct comparison of the rates of thermal decomposition of the sulfated monocalcium silicate and of the sulfated calcium oxide, or $CaSO_4$. The rates were measured with the Mettler balance with very small amounts ($\stackrel{\sim}{\sim}$ 20 mg) of powdered materials. The materials were decomposed in a flow of dry N_2 at a velocity of about 8 cm/sec; a velocity high enough to ensure that the partial pressure of SO_2 was zero and there were no mass transfer effects on the rate. The $CaSiO_3$ was 42% sulfated and the $CaSO_4$ was of reagent grade. Size of the $CaSiO_3$ was 325/400 Tyler mesh and the $CaSO_4$ was fine powder -- its size was probably similar to that of the silicate. The rates are shown in Figure 3. Decomposition actually started at temperatures below 1100°C. The rate for the sulfated $CaSiO_3$

was clearly much higher than that of the $CaSO_4$; roughly an order of magnitude higher. This is a highly encouraging result because it shows that the bond between Ca and SO_3 is weaker and more liable to be broken when SiO_2 is also bonded to Ca, and thus supports our basic thesis. The area of the molecular addition compound is an area where only very little and superficial knowledge exists.[7] For example, it is known that in the addition compounds of BF_3, the B-F bonds are appreciably longer and weaker than in BF_3 alone.[7] In our case, we have an addition compound of $CaSO_4$, with SiO_2 being the additive. More understanding of this compound and of the compound $2CaSO_4 \cdot SiO_2$ (that is, the sulfated dicalcium silicates) is yet to be obtained.

1.3. X-ray Diffraction Analyses of $CaSiO_3$ - Sulfated and Regenerated

The x-ray diffraction powder patterns were obtained of 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 wt.) of H_2O and its diffraction pattern did not match any known hydrated silicate. The pattern for the sulfated $CaSiO_3$ did not contain lines of SiO_2 or $CaSO_4$, which indicated that the two were still bonded after sulfation. This pattern is a new pattern which does not exist in any index file. Other discussions can be found in the table.

1.4. Sulfation and Regeneration of Dicalcium Silicates

Work in this area is underway and the results will be presented shortly.

1.5. Infrared Spectroscopic Analyses of the Silicate Systems

Infrared spectroscopy can provide certain information that would compliment the x-ray analyses in understanding the reactions and structural changes. For example, the hydrates and the internal hydroxyl groups can be readily identified by IR whereas it is very difficult with x-ray. The sulfate absorbs IR very strongly at distinct frequencies and changes in the environment or to which the sulfate is bonded can create shifts in the frequencies. And lastly, IR is a rather quick way to identify the chemical groups (but not structure).

IR spectra of rather pure $CaSiO_3$ and $-Ca_2SiO_4$ were taken with the standard KBr pellet technique. The $-Ca_2SiO_4$ was formed from $2CaCO_3 + SiO_2$ at 1400-1500°C with 3% water vapor in the gas phase. The spectra and band assignments are summarized in Table 2. The band frequencies for SiO_3^{-2}, SiO_4^{-4} are established and will be used for future analyses. Two important findings from these analyses are noteworthy. First, in the sulfated $CaSiO_3$, the SiO_3^{-2} bands remained, that means SiO_2 was still chemically bonded to the calcium cation. This supports the foregoing x-ray analyses (or vice versa). Also in this sample, it appears that both SO_4^{-2} and SiO_3^{-2} are bonded to calcium and if this is true, the stretching frequencies should be lowered while the bending modes should be increased based on first principles. Such careful analyses have not been made. The second finding is 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.

2. The Brookhaven Regeneration Process

This process has been described in various publications by the authors and will be briefly summarized here again. Partially sulfated limestone and fly ash, both from fluidized-bed combustors, are mixed and roasted in a kiln-type regenerator. The ratio of the amounts of these two materials is based on the stoichiometry of the following reaction, which is also the major reaction:

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

The major advantage of this process over the other regeneration processes being developed is that the SO_2 concentration in the off gas is thermodynamically controlled, whereas it is kinetically controlled in other processes.

Calcium silicates will also be formed in the regenerator, but it is not known how much and what types are actually formed.

A small, batch-wise regenerator has been constructed. Capacity of this device is about 5-10 grams of solid sample. The regenerator can be rotated at various speeds and the contents can be heated up rapidly from room temperature to the desired regeneration temperature, e.g., 1000°C. Samples (sulfated stones and fly ash) from Argonne National Laboratory and Exxon Research and Engineering Company have been obtained and analyzed and will be tested in the device. Gas samples can be intermittently withdrawn from the exit gas of the reactor and will be analyzed mass spectrometrically. The solid samples will be analyzed and the results will be used to determine the kinetics in this device. Special attention will be paid to the analyses of the silicates formed in this reactor.

The regenerated samples will be subject to further sulfation/reactivity tests. At the present time, such tests will be conducted with the same micro-rotary kiln. The sulfation kinetics in the tumbling bed should be closer than the TGA experiments to that in an FBC. The reactivity will also be tested in a small fluidized-bed combustor/sulfator in the future.

3. Sulfation Kinetics

3.1. Fate of NaCl in a Simulated Combustor

Sodium chloride has been used as a catalyst in both sulfation (absorption of sulfur) and regeneration (decomposition of calcium sulfate). However, little information exists on the effect of sodium chloride additive on corrosion/erosion of boilers under combustion conditions. Such problems are causes for serious concern in existing and planned coal conversion systems. Data simulating fluidized-bed combustion environment are needed for the purpose of economic and environmental considerations.

It has been reported that hydrogen chloride content of the off gas did not go up and a negligible change in chlorine content was found in the bed material as a result of salt addition to a pilot-scale fluidized bed combustor.[1] Where the sodium chloride goes in the combustor, is still not clear. Experiments were performed to understand whether the sodium chloride reacts with the walls or reactors and the immersed tubings or exits with the fly ash. The tests described below were designed to elucidate these questions.

A schematic diagram of the experimental device is shown in Figure 4. All the experiments were performed at 900°C with a simulated combustion gas (0.3% SO_2, 17% CO_2, 5% O_2, 3% H_2O and balance N_2) flowing through the packed bed. Greer limestone and 3% analytical reagent sodium chloride (Mallinckrodt) were packed in the bed. The chlorine was collected by bubbling the off-gas through NH_4OH solution for a certain period of time. In the first experiment only quartz tubings were used (a blank test). In the second experiment, 304 stainless steel tubes and Sauereisen No. 75 (mainly calcium aluminate) were packed on top of the Greer limestone and sodium chloride, and the quartz tubings were replaced by the 304 stainless steel tubings. A trap was used to collect the deposited chlorination products. Sauereisen No. 75 was used because it has been used as the lining of combustors. After collecting the chlorine-containing gas in the NH_4OH solution, the chlorides were analyzed colorimetrically with a Technicon Auto Analyzer. Chlorides were determined via formation of the ferric-thiocyanate complex. Chlorine reacts with undissociated mercuric thiocyanate to release an equivalent amount of thiocyanate ion. This immediately reacts with the ferric ion present to form the red-brown complex, which was measured at 480 mμ.

Tests were run for six hours. In the first blank test, 60.1% total chlorine from the added sodium chloride were collected. In the second experiment with 304 stainless steel and Sauereisen, only 2.67% chlorine was collected in the NH_4 OH solution. Figure 5 shows the accumulative chlorine in NH_4OH solution for several periods of operations. However, there was 41.27% chlorine condensed in the 304 stainless steel line (washed with distilled water) from the chlorination deposit. This added up to 43.94% total chlorine recovery. Some chlorine stayed in the 304 stainless steel tubes. The 41.27% chlorine condensed on cooler walls downstream of the reactor and it was a dark green, water-soluble material. This material is being analyzed by our analytical chemistry group. The corroded 304 stainless steel tubing is also being analyzed. The results will be available shortly and a complete mass (or chlorine) balance will be made.

3.2. Catalysis by Fe_2O_3 and Coal Ash

For the sulfation of CaO, regardless of the true mechanisms of the reaction, the valence of sulfur is changed from +4 to +6 or SO_2 is oxidized to SO_3. The following reactions can be written to represent the process:

$$CaO + SO_2 + 1/2\ O_2 \xrightarrow{r_1} CaO \cdot SO_3 \xrightarrow{r_2} CaSO_4 \qquad (1)$$

For the sulfation of CaO being catalyzed by Fe_2O_3 which is physically separated from the CaO, the following reactions may describe the sequences:

$$CaO + Fe_2O_3 + SO_2 + 1/2\ O_2 \xrightarrow{r_3} CaO + Fe_2O_3 \cdot SO_3$$

$$\xrightarrow{r_4} CaSO_4 + Fe_2O_3 \qquad (2)$$

Reactions (1) and (2) are both rate-limited by the oxidation step, or limited by r_1 and r_3, respectively.

From Figures 6 and 7, r_1 can be expressed by:

$$r_1 = k_1\, P_{SO_2}^{0.50}\, e^{-\frac{3,700}{RT}} \qquad (3)$$

The work of Boreskov and Sokolova[2] and of Kawaguchi[3] showed that

$$r_3 = k_3 \, P_{SO_2}^{1.5} \, e^{-\frac{38,000}{RT}} \quad (4)$$

Here, based on our experimental conditions, we assumed that P_{O_2} constant and that P_{SO_3} is small and also constant.

While it is difficult, if not meaningless, to compare directly r_1 and r_3 on a per mass of solid basis from Boreskov's and our data, the fact that Fe_2O_3 does catalyze the sulfation of CaO indicates that r_3 is greater than r_1. Furthermore, from Figures 8 and 9, the overall rate of the catalyzed sulfation, with 4% Fe_2O_3 in CaO, can be expressed by

$$r_c = k_c \, P_{SO_2}^{0.58} \, e^{-\frac{9,300}{RT}} \quad (5)$$

Comparing Equations (3), (4) and (5), it may be qualitatively concluded that the rate of the Fe_2O_3 catalyzed reaction is contributed by both reactions (1) and (2) and that rates of the two reactions are not greatly different.

From the results on the effects of the size (Figure 10) and of the amount (Figure 11) of Fe_2O_3, the overall rate increases only slightly with the total surface area of the Fe_2O_3; not at all proportional. These results agree well with the foregoing discussion. It may also be noted that CaO indeed is also a good high temperature "catalyst" for the oxidation of SO_2 to SO_3. It may be predicted that certain salts involving CaO, and which do not bond SO_3 in this high temperature range, are good high temperature catalysts for the oxidation of SO_2.

Figure 12 also shows results on the sulfation reactions with 5% water vapor in the gas phase. The catalysis of sulfation of CaO with water vapor has been discussed previously.[4,5] The intriguing result here is that while both water vapor and Fe_2O_3 catalyze the sulfation, the synergestic effect is lower than that with Fe_2O_3 alone. However, this fact can also be explained in line with the foregoing discussion. It is known that water vapor combines very rapidly with SO_3 to form sulfuric acid. Thus, water vapor here simply acts as a scavanger and reduces the catalysis effect by Fe_2O_3. Of course, sulfuric acid also reacts with CaO, but perhaps at a slower rate than SO_3.

The effect of coal ash on sulfation rate is shown in Figure 13. In this experiment, 19% coal ash was used so that the amount of Fe_2O_3 is about 4% of CaO. The catalyzed rate was surprisingly similar to that with 4% Fe_2O_3 alone. This result suggests that perhaps Fe_2O_3 is the only active catalyst existing in the Illinois No. 6 coal ash for the sulfation of CaO. However, with 5% water vapor co-existing in the system, the overall rate is higher than that with coal ash alone. This result obviously represents a very complex system wherein synergestic effects involving the other constituents in the coal ash are operative.

It was also intended to assess the effects of other iron-containing compounds in coal and limestone on the sulfation rate under the fluidized-bed combustion conditions. The compounds under consideration were FeO, Fe_3O_4 and pyrite. An experiment was performed to see if these compounds could maintain their chemical forms in the environment of a simulated combustion gas. The results are shown in Figure 14. The percentage oxidation to Fe_2O_3 was measured gravimetrically as a function of temperature at constant heating rates. It is obvious that all of the compounds convert to Fe_2O_3 very rapidly (much more rapidly than the CaO sulfation rate) at 900°C. Detailed kinetic data of oxidation can be readily calculated from the dynamic TG results,[6] although we have not done so. The conclusion from this experiment is that all the iron compounds being considered are oxidized into Fe_2O_3 rapidly and it subsequently catalyzes the sulfation of CaO in the manner already discussed.

Figure 15 shows the results with the calcined Greer limestone. Catalysis by Fe_2O_3, H_2O and Fe_2O_3/H_2O is again seen on the sulfation rate but is somewhat reduced in magnitude. The many impurities in the Greer limestone would make any further discussion on this result meaningless.

3.3. Effects of Calcination Conditions

This subject is catching increasing attention due primarily to the work done at Westinghouse Labs. We have found that CO_2 as well as H_2O have strong positive effects on the reactivity of the calcined lime. More work in this area is in progress. Our attention will be focused on both chemical and physical (pore structure) aspects.

4. Process Design and Evaluation

A process flow diagram for producing commercial grade (99% wt) sulfuric acid from the CaO regenerator off-gases has been completed. The sulfuric acid process would be used in conjunction with BNL's sorbent regeneration process described in Quarterly Progress Report No. 4 (covering first quarter 1977). Two process flow diagrams were prepared during Second

Quarter 1977, one for a once through sorbent, carbon burn-off cell system (designated SystemI); the other, for a regenerative sorbent system based on BNL's carbon reduction of $CaSO_4$ process (designated System II). The feed to both systems was assumed to be Illinois No. 6 coal with a sulfur content of 3% wt, and both systems were assumed to operate at atmospheric pressure. As mentioned earlier, the sulfuric acid process would be used in conjunction with System II. It is based upon existing technology and consists of an air drying tower, a SO_2 (to SO_3) converter, an SO_3 absorbing tower and auxiliary pumps, coolers etc. Cost data on the process will be compiled shortly so that a preliminary economic comparison between the once through sorbent system and the regenerative/H_2SO_4 system can be made. The objective of the comparison will be to determine an approximate "break-even" selling price of the H_2SO_4 produced by the regenerative/H_2SO_4 process.

With regard to H_2SO_4 market potential, it is estimated that the domestic usage of H_2SO_4 in the year 2000 will be between 75 and 100 x 10^6 tons per year. Based on an anticipated energy contribution of 4.6 quads/year from AFBC systems (MOPPS estimate - ERDA) 15 x 10^6 tons/year of H_2SO_4 would be produced. The current domestic usage of H_2SO_4 is about 35 x 10^6 tons/year so that the market for AFBC generated sulfuric looks promising. However, many other factors such as the anticipated locations of AFBC units and the locations of sulfuric acid users must be carefully examined before a meaningful prediction can be made.

Based on overall process heat and mass balances, the net energy output (useful) of a combined regenerative/H_2SO_4 system would be approximately equal to the net output from the once through system, a result that may seem surprising in light of the fact that the $CaSO_4$ decomposition reaction: $CaSO_4 + 1/2C = CaO + 1/2CO_2 + SO_2$ is very endothermic. However, with sorbent regeneration, less energy is consumed in preheating and calcining the $CaCO_3$ feed to the AFBC. The quantity of solid wastes generated by the once through sorbent system is about 2.5 times greater than the quantity generated by the regenerative/H_2SO_4 system.

During the next quarter the subject flow sheets will be upgraded based on recently acquired data, and a preliminary economic comparison of the subject processes will be made. The flow sheets and comparison will be presented in Quarterly Progress Report No. 6. We will also be examining processes for converting regenerator SO_2 to elemental sulfur rather than to H_2SO_4. A preliminary analysis indicates that since the regenerator off-gas will not contain appreciable quantities of H_2S and/or CO, a typical Claus process may not be the best route to take. Further on into the future, and provided that the experimental results on calcium silicate sorbents look promising, we will begin work on the development of processes utilizing silicates as sorbents for recycling purposes or for producing a cement by-product.

Acknowledgement

Discussions, suggestions and guidance provided by Dr. Andrej Macek of ERDA are appreciated. Discussions with personnel at Argonne, Exxon and Pennsylvania State University were also helpful.

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Table 1. X-ray Diffraction Analyses of Monocalcium Silicate, Its Sulfated and Regenerated Forms and γ-Dicalcium Silicate.

Sample	Reactants	Products	d, Å	Intensity	Remarks
β Calcium Metasilica Hydrate (ROC/RIC, 99.75%)	Reagent Grade	β-$CaSiO_3 \cdot \chi H_2O$	2.83	Strong	Unknown Hydrate Diffraction pattern
			2.00	Strong	
			5.21	Medium	
			3.06	Medium	
			1.63	Medium	
			1.26	Weak	
Partially Sulfated	β-$CaSiO_3 \cdot \chi H_2O + SO_2 + 1/2O_2$	β-$CaSO_4 \cdot SiO_2$	2.66	Strong	Unknown pattern *SiO_2 is chemically bonded to $CaSO_4$
			4.77	Medium	
			1.63	Medium	
		β-$CaSiO_3$	2.98	Strong	Anhydrous reactant β-$CaSiO_3$
			3.31	Strong	
			3.51	Strong	
			3.84	Medium	
			3.10	Medium	
			2.48	Medium	
			2.18	Medium	
			1.835	Medium	
			1.760	Medium	
			1.720	Medium	
**Regenerated partially sulfated β calcium Metasilica	β-$CaSO_4 \cdot SiO_2 + 1/2\ C$	$CaSO_4 \cdot SiO_2$	2.65	Strong	Regeneration not complete
			4.7	Medium	
			1.63	Medium	
		$CaS \cdot SiO_2$	2.60	Strong	Unknown pattern
			1.87	Strong	
		β-$CaSiO_3$	3.3	Strong	Regenerated product and unreacted starting material
			3.5	Strong	
			2.97	Strong	
			3.09	Medium	
			2.48	Medium	
			1.75	Medium	
γCalcium Orthosilicate	$CaCO_3$ (Chemstone) + SiO_2) (Silica Gel)	γ-Ca_2SiO_4	2.72	Very strong	Formed at 1500°C
			1.91	Strong	
			2.99	Strong	
			1.80	Strong	
			1.63	Medium	
			1.68	Medium	
			1.75	Medium	

*The distinguished strongest $CaSO_4$ d line 3.49 Å does not exist here.

**SiO_2 is chemically bonded to $CaSO_4$ because the distinct strongest d lines do not exist here for the reaction products CaS (2.846 Å) and $CaSO_4$ (3.49 Å), e.g.

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2$$

$$3CaSO_4 + CaS \rightarrow 4CaO + 4SO_2$$

and the possible products $Ca(OH)_2$ (2.63 Å) and $CaCO_3$ (3.40 Å, 3.04 Å) μ-$CaCO_3$ (2.73 Å).

Table 2. Infrared Absorption Frequencies of Silicates and Sulfated Silicates.

Compound	Chemical Group	Frequency (cm^{-1})	Intensity	Remarks
Sulfated CaO	SO_4^{-2}	1130	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 $CaSiO_3$		1120	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}
γ-Ca_2SiO_4	SiO_4^{-4}	970	s, sh	Stretching
		860	s, b	Stretching
		< 600	s	Not measured

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

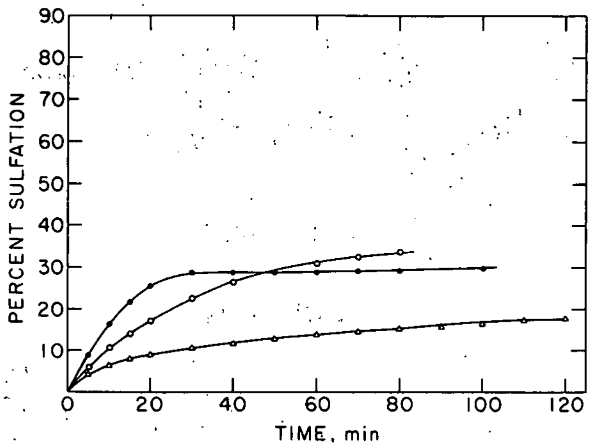

Figure 1. Sulfation rates at 850°C with 0.25% SO_2 and 5% O_2 in N_2. O Greer CaO (Tyler 16/20); ● Powdered $CaSiO_3$ (ROC/RIC, 99.75%); Powdered reagent CaO (Mallinckrodt).

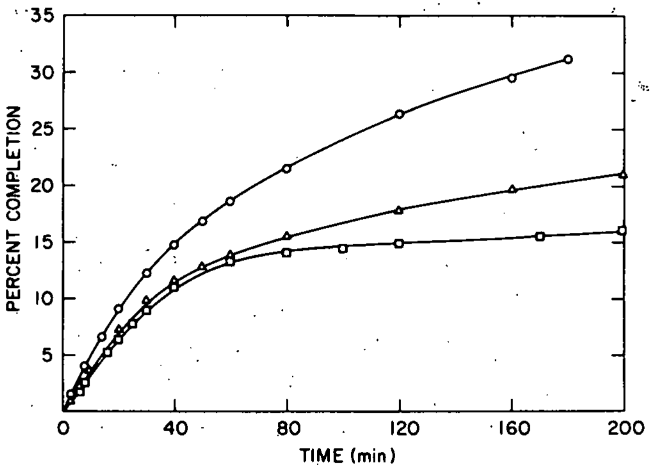

Figure 2. Sulfation rate of $CaSiO_3$ (ROC/RIC, Tyler 16/20) with 0.25% SO_2 and 5% O_2 in N_2 at 850°C. $CaSiO_3$; ■ $CaSiO_3$ and 4% Fe_2O_3 (Baker, Tyler 200/325); ○ $CaSiO_3$, 4% and Fe_2O_3 and 5% steam.

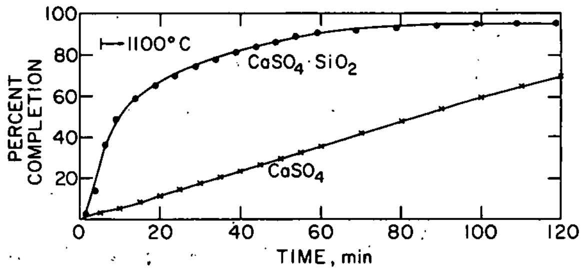

Figure 3. Regeneration (thermal decomposition) rates at 1100°C in N_2. X Powdered reagent $CaSO_4$ (Baker); 42% Sulfated powdered $CaSiO_3$ (ROC/RIC).

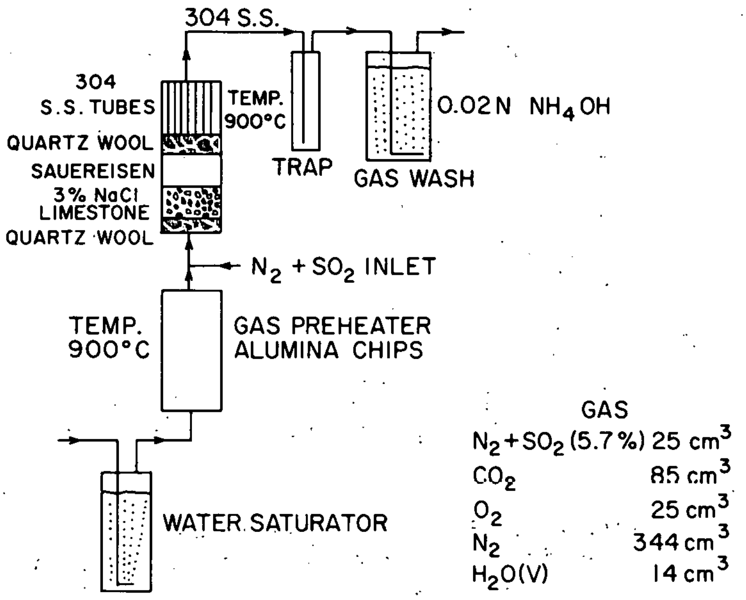

Figure 4. Schematic diagram of chlorine test equipment.

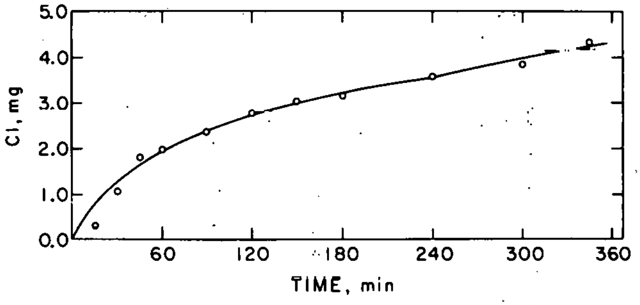

Figure 5. Cumulative chlorine collected in NH_4OH solution vs. time.

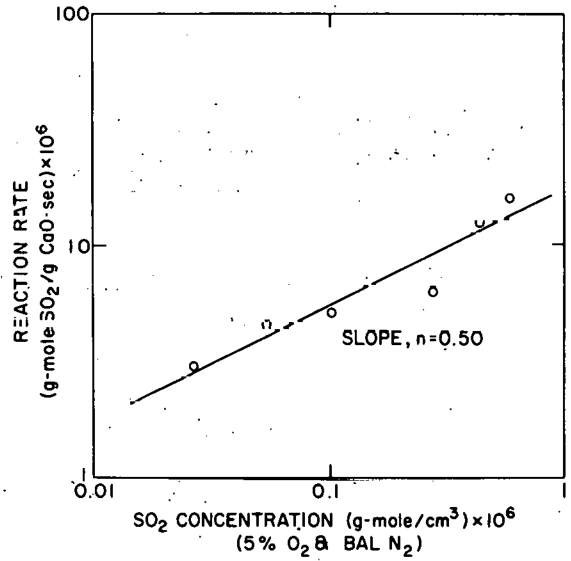

Figure 6. Effect of concentration on sulfation of powdered reagent CaO (Mallinckrodt) at 850°C.

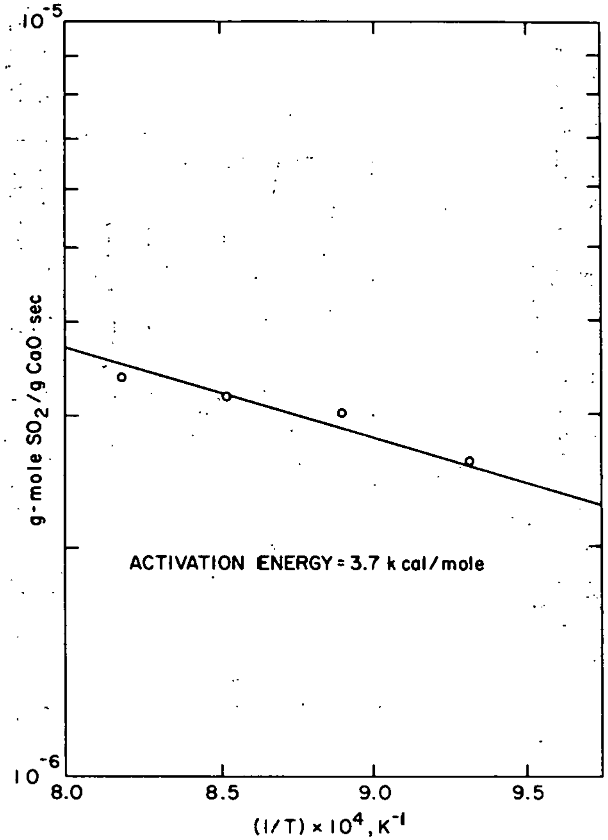

Figure 7. Effect of temperature on sulfation of powdered reagent CaO (Mallinckrodt) with 0.25% SO_2 and 5% O_2 in N_2.

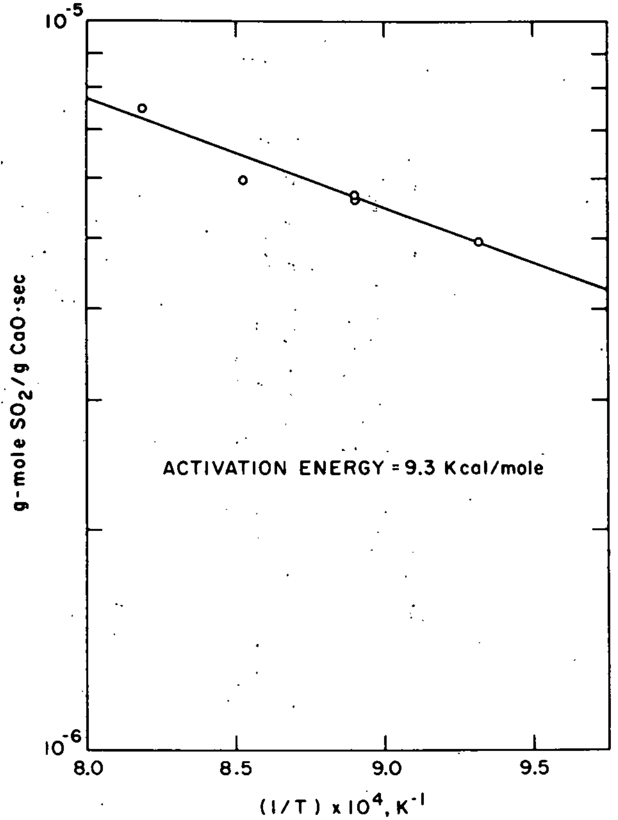

Figure 8. Effect of temperature on sulfation of powdered reagent CaO (Mallinckrodt) and 4% Fe_2O_3 (Baker, Tyler 200/325) with 0.95% SO_2 and 5% O_2 in N_2.

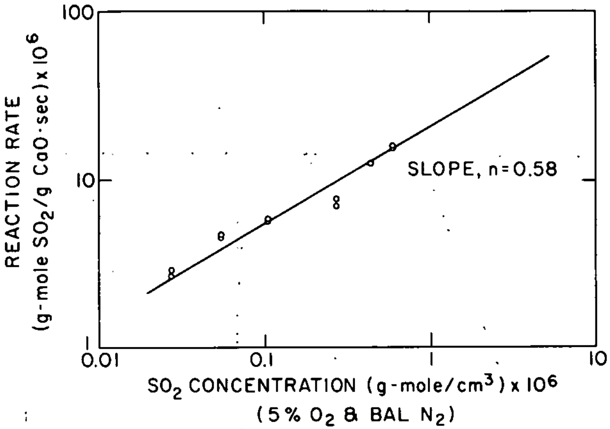

Figure 9. Effect of concentration on sulfation of powdered reagent CaO (Mallinckrodt) and 4% Fe_2O_3 (Baker, Tyler 200/325) at 850°C.

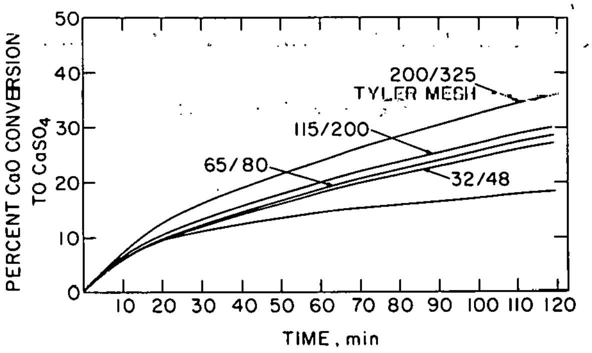

Figure 10. Effect of size of Fe_2O_3 (Baker, 4%) on sulfation rate of powdered reagent CaO (Mallinckrodt) with 0.25% SO_2 and 5% in N_2 at 850°C.

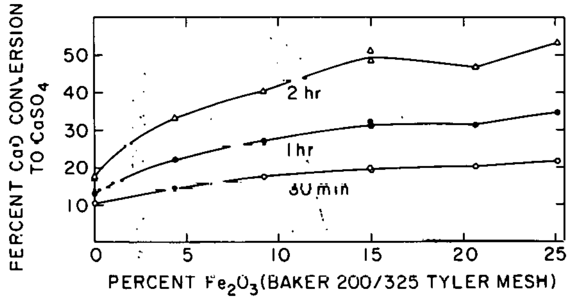

Figure 11. Effect of concentration of Fe_2O_3 (Baker, Tyler 200/325) on sulfation rate of powdered reagent CaO with 0.25% SO_2 and 5% O_2 in N_2 at 850°C.

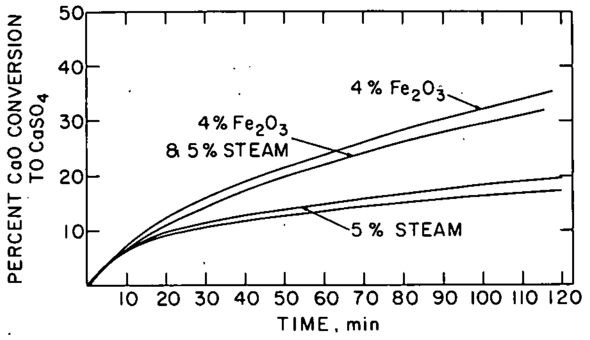

Figure 12. Sulfation rate of powdered reagent CaO (Mallinckrodt) with Fe_2O_3 (Baker, Tyler 200/325) or steam at 850°C (0.25% SO_2 and 5% O_2 in N_2).

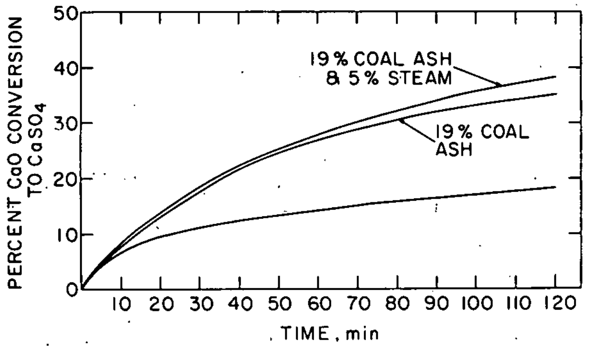

Figure 13. Sulfation rate of powdered reagent CaO (Mallinckrodt) with Ill. No. 6 coal ash (0% C, Tyler 200/325) or steam at 850°C (0.25% SO_2 and 5% O_2 in N_2).

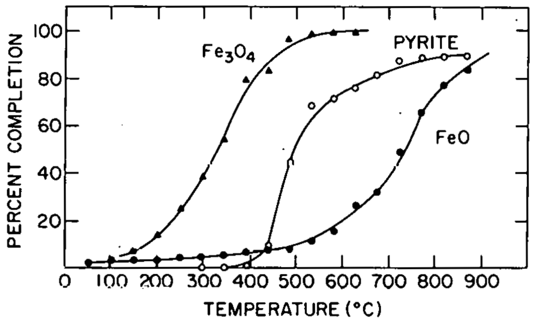

Figure 14. Percent oxidation to Fe_2O_3 vs. temperature. • FeO (Bioclinical Labs, Tyler 200/400); o Pyrite (Rico, Colorado, Tyler 200/400); Fe_3O_4 (D.F. Goldsmith Metal Corp., < 5 μ).

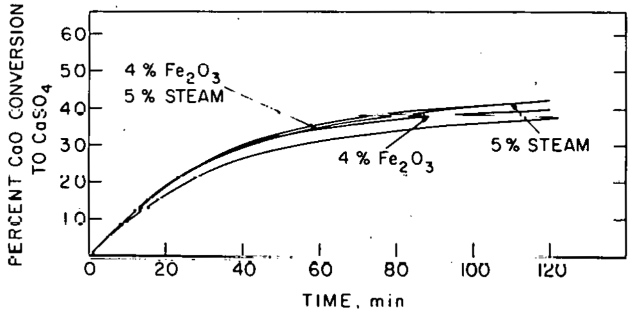

Figure 15. Sulfation rate of calcined Greer lime with Fe_2O_3 (Baker, Tyler 200/325) or steam at 850°C (0.25% SO_2 and 5% O_2 in N_2).

Distribution:

A. Macek, FE/ERDA (25)
W. E. Winsche, BNL
J. M. Hendrie, BNL
B. Manowitz, BNL
M. Steinberg, BNL
R. T. Yang, BNL
N. Abuaf, BNL
A. S. Albanese, BNL
J. M. Chen, BNL
G. Farber, BNL
F. B. Kainz, BNL
C. R. Krishna, BNL
J. Pruzansky, BNL
M-S. Shen, BNL
R. H. Whisker, BNL
D. Schweller, ERDA (BNL)
R. Smol, BNL
D. B. Henschel, EPA
J. W. Jones, EPA
F. Princiotta, EPA
H. B. Levine, Jaycor