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REGENERATIVE PROCESS FOR DESULFURIZATION OF HIGH TEMPERATURE COMBUSTION AND FUEL GASES

QUARTERLY PROGRESS REPORT NO. 3
OCTOBER 1 - DECEMBER 31, 1976

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PROCESS TECHNOLOGY DIVISION
DEPARTMENT OF APPLIED SCIENCE

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REGENERATIVE PROCESS FOR DESULFURIZATION OF HIGH TEMPERATURE COMBUSTION AND FUEL GASES

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PROCESS TECHNOLOGY DIVISION

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Abstract

A regenerative process based on using carbon for lime regeneration has been studied. Ten sulfation/regeneration cycles using Greer limestone have been conducted in a TG system and there was no sign of weakening of the SO_2 sorption activity. Work on the regenerative process based on silicates is being continued. For pure silicates, the sulfation rate of the mono-calcium silicate appeared to be higher than that of the calcined Greer limestone and dicalcium silicate; the latter two being similar.

Procedures for particle strength test and for generating coal ash with controlled carbon content are being established. A micro-, semi-pilot plant for studying the regenerative processes is being constructed.

Regenerative Process for Desulfurization of High
Temperature Combustion and Fuel Gases

Quarterly Progress Report No. 3

October 1 - December 31, 1976

Introduction

A major advantage of fluidized-bed combustion is its ability to burn coal cleanly and to produce economically a desulphurized hot gas. However, economic and environmental considerations require the regeneration of the lime additives from the sulfates.

One of the processes being developed in this program utilizes coal ash for the regeneration step. The fly ash from the primary cyclone of the combustor contains significant amounts of carbon. The basic reactions in the regenerator are between the sulfate and the carbon and the silica, forming calcium oxide and calcium silicates, respectively. The products are recycled as a sorbent.

Within the framework of this scope, two basic processes are being developed. One is based on regeneration and recycling of the silicates as sorbents (starting materials are limestone and siliceous matters) which has been described in the preceding reports.¹ Another process is based on regeneration of CaO from CaSO_4 by roasting it with carbon. The two processes can also be combined and such may be the case wherein fly ash from the fluidized-bed combustors (FBC) is used.

The mode of operation of the regenerator, e.g., kiln-type fixed bed or fluid bed, will be determined when all the basic chemistry and kinetic information and a complete process and cost analysis are available.

In the past quarter, the scheme using carbon for regeneration of CaO has been tested, in cyclic operation, in a static bed reactor (TG) systems. The SO₂ sorption abilities of a di-calcium silicate and a mono-calcium silicate have been demonstrated. First kinetic data and the related observations on the two studies are included in this report.

A. Regenerative Process Using Carbon for Lime Regeneration

Introduction

The basic chemistry of this process involves two reactions:

The equilibrium partial pressure of SO₂, P_{SO_2} , is given as a function of temperature in Figure 1. It is assumed that no O₂ or CO₂ is added or subtracted from the system. Under this circumstance, the partial pressure of SO₂ can reach about 10 atm at about 950°C. This presents an ideal process possibility for regeneration of CaO in either the atmospheric or pressurized fluidized bed combustion system. It also indicates possible isothermal sulfation (combustion)-regeneration operations and a possible mode of operation of regeneration in which large amounts of other gases can be allowed in the regenerator without violating the thermodynamic feasibility. The remainder to be tested are: 1. kinetics of reaction (1) and (2) under various conditions and 2. recyclability. The question of recyclability includes mainly the reactivity and the strength of the regenerated CaO.

Reaction (2) has been used for making sulfuric acid from calcium sulfate minerals (gypsum or anhydrite) in the cement-sulfuric acid process as early as 1918.² Some mechanistic studies were undertaken recently at US Steel.³

The reactions considered in the US Steel studies are:

Reaction (3) was found to be faster than (2) and (2) is only an overall reaction of (3) and (4)

Not considered in the US Steel studies are the two reactions which we found to be also important:

To apply reaction (2) for regeneration of CaO in the fluidized bed combustion technology, the crucial question is on the SO₂ sorption activity of the regenerated CaO, as well as on the kinetics of the cyclic systems involving reactions (1) and (2). The experimental program in this report was designed to answer these questions.

Experimental

The rates of regeneration and sulfation were measured gravimetrically. Detailed experimental and calculation procedures and the apparatus used for the measurements have been described elsewhere.^{4,5} A platinum sample holder was used in the experiments. The total amount of sample mixture for regeneration was about 0.1 gram containing 2 CaSO₄ : 1 C (molar) in all cases. Gas was passed over the packed sample surface at about 250 cc/min (STP) which corresponded to a velocity of 2 cm/sec. The composition of the gas mixture for sulfation was: 4% SO₂, 10% O₂, 2.9% H₂O and the balance N₂. Straight N₂ was used for regeneration. The gases used were of the following grades:

SO₂: anhydrous (99.98%), N₂: prepurified (99.996%) and O₂: commercial (99.5%). Nitrogen was passed through a Supelco Carrier Gas Purifier (Supelco, Inc.) to remove residual O₂ and H₂O to eliminate the reaction $C + O_2 \rightarrow CO_2$ during regeneration. Coconut charcoal (Fisher Scientific), 5% volatile and 1% ash, was used in all the regeneration experiments. The rate of regeneration is independent of the type of carbon used.³ CaSO₄ was obtained by sulfating Greer limestone to 80% at 900°C. The size of CaSO₄ was 16/20 Tyler mesh (850-1000 microns) which is similar to that used in fluidized-bed combustion. The size of coconut charcoal was 200/250 Tyler mesh. The Greer limestone was kindly supplied by Argonne National Laboratory.

A General Electric automatic powder diffractometer and a powder camera were used for x-ray diffraction analyses of the reaction products.

Results and Discussion

Cyclic, isothermal sulfation and regeneration reactions were tested at 950°C using Greer limestone. The stone was 16/20 Tyler mesh in size and was calcined before the first sulfation cycle. One hundred milligrams of limestone was the starting weight. Ten cycles were run which included rate measurements of ten sulfation and nine regeneration experiments. In the first regeneration, only about half of the CaSO₄ was regenerated to CaO. About the same amount of CaO was regenerated in all the subsequent cycles. Hence about 40 mg of CaO was sulfated in the first sulfation experiment and about 20 mg of CaO was sulfated in all the following cycles. Furthermore, in each regeneration, there was a small amount of CaS left on the surface layer, the weight of which was about 10% of the available CaO for sulfation. The amount of CaS was determined by, prior to sulfation

in each cycle, oxidizing it with 20% O_2 in N_2 and the weight gain in this process was taken to be the O_2 consumed by CaS to form $CaSO_4$. The oxidation was very rapid; it took several minutes to complete the reaction. To summarize, before sulfation in the 2nd to 10th cycles, the shelled structure of a regenerated (and oxidized) particle is (proceeding from the outermost layer): a thin layer of $CaSO_4$, a thick layer of CaO followed by a layer of $CaSO_4$ of about the same thickness and CaO in the core. This picture has not been experimentally identified and was rather drawn from the knowledge of the state of the art.

With the above picture in mind, we can now proceed to discuss the results shown in Figures 2 and 3. The sulfation results are summarized in Figure 2. Each experiment actually lasted for 4-5 hr while only the initial 40 minutes were shown. The times for 70% completion of sulfation for the ten cycles are tabulated in Table 1. From these results, the first emminent conclusion is that there was no tendency for the sorbent reactivity to decay after ten cycles. The thin $CaSO_4$ layer coated on the regenerated sorbent did not seem to affect the rate, the initial rate, in sulfation.

Also in Figure 2, the rate of the first sulfation, i.e., sulfation of the virgin sample, was about half of the rate of the 2nd-9th cycles. This difference was not real because in the rate calculations, the amount of the available CaO for the first cycle sulfation was about double that of the other cycles. The rate would have been the same had the rate been expressed as the amount of SO_2 sorption per unit exterior surface (or per particle) per unit time.

Before the regeneration experiments, the sulfated sample was intimately mixed with fine particles of carbon at a ratio of 2 $CaSO_4$:1C. The mixed sample was heated up to 950°C at 15°C/min in an N_2 flow. Slight weight loss

was incurred before the final temperature of 950°C was reached. No attempt was made of suppressing the reaction during the heating-up period (or time $< t = 0$) by using SO_2 and O_2 because both oxidants can react with carbon. It should also be noted that in the first regeneration experiment, when more carbon was used, the reaction product was predominantly CaS , as shown by the x-ray diffraction analysis. This result is in agreement with that of Turkdogan and Vinters.³

Results of the nine regeneration experiments are summarized in Figure 3. The temperature profile (or history) is inserted on top of the weight loss curves. Before discussing the results, a brief review of the mechanism of reaction (2) is in order. It has been shown³ that the reaction proceeds in two steps. The first step is the reduction (3) of sulfate in the outer layer by carbon into sulfide until the carbon is all burnt off. Reaction (4), which is slower than the reduction reaction, is subsequently the predominant reaction. The amount of carbon present is consequently critical in determining the products. Going back to Figure 3, the actual weight loss was plotted against time because it would be meaningless to plot the percentage conversion to CaO owing to the two stage nature of the reaction. Each reaction proceeded for 4-5 hrs for nearly complete regeneration with the initial 30 minutes shown in Figure 3. The shape of the curves is very much conformative to the two-step mechanism; a rapid weight loss due to the reduction followed by a slow weight loss due to reaction (4). Two interesting observations were made: (1) the reduction rate increased with the number of cycles significantly and (2) the rate of the slower reaction (4) decreased slightly with the number of cycles. The reduction reaction was completed in about 5-10 min. in the second cycle and about

2 to 4 min. in the ninth cycle. Rates of the $\text{CaS} + 3 \text{CaSO}_4$ reaction for the nine cycles are shown in Table 2. A gradual but slight decrease in the rates is seen.

Figure 4 shows the comparison of regeneration with and without 2.9% steam. Steam increases the reduction rate but it is not clear at the present time whether it affects the rate of the second stage (reaction (4)).

A final note is that, by unsophisticated testing methods, the regenerated lime particles appeared to be as strong (if not more) as the starting material. Sophisticated testing will be conducted later.

B. Regenerative Process Using Silica for Silicate Regeneration and Sulfation with Silicates

Introduction

The basic chemistry and some preliminary kinetic data have been described in the previous reports.¹ The previous data were obtained by using practical (or impure) samples; the samples were coal ash and various CaSO_4 . The thermodynamic feasibility of using silicates (mono-, di-, and tri-calcium) for sorption of SO_2 and $1/2 \text{O}_2$ has also been reported.¹ It is desirable to understand the basic phenomena and kinetics underlying these reactions. We, therefore, as a first step, demonstrated the kinetic feasibility of sulfation of the silicates using pure systems. In this report, the first kinetic data are presented by the following reactions:

Experimental

Apparatus

The apparatus used was a Cahn R-100 microbalance. Details of the reactor system will be described elsewhere. In brief, the reactor was made of a quartz tube (35 mm diameter) with the solid sample holder placed in the central portion supported by the platinum hang-down wire from the balance beam. The reactor was heated with a resistance heating furnace and the temperature was controlled based on a thermocouple located within a few mm from the solid sample. Gas flow in the reactor was downward and the inert carrier gas (N_2 or Ar) was preheated to temperatures near the reaction temperature with a preheater outside the reactor. The preheater was a quartz tube packed with crushed alumina chips and was heated with a tubular resistance furnace. Gas flow rate was $703 \text{ cm}^3/\text{min}$ (STP) which corresponded to a velocity of about 5 cm/sec passing over the solid sample. The sample holder was a flat disk made of alumina (15 mm in diameter).

Measurement and calculation procedures were the same as described previously.^{4,5}

Materials

Monocalcium silicate was supplied by Research Organic/Inorganic Chemical Corporation. Its purity was assayed at 99.75%. Particle size used in this work was 16/20 Tyler mesh.

Dicalcium silicate was prepared by heating a mixture of $2 \text{ CaO} + 1 \text{ SiO}_2$ at 1400°C for 2 1/2 hrs in Ar.

CaO: passing 200 Tyler mesh; Mallinckrodt Company; over 98% purity (1% MgO and other salts, 0.1% SO_4 ; 0.1% Fe, etc.) SiO_2 : passing

200 Tyler mesh; chromatographic grade silica gel supplied by MCB Company. The first attempt for forming the dicalcium silicate at 1100°C was unsuccessful as shown by the x-ray diffraction analyses. For the 1400°C experiments, a graphite (H-451 nuclear graphite) crucible was used as the sample holder. The slow Argon flow (50 cc/min STP) was of ultra-high purity and was further purified of O_2 and H_2O with a drying agent and copper turnings held at 500°C. The x-ray diffraction analysis showed that two major species were existent: gamma calcium ortho silicate (γ - Ca_2SiO_4) and alpha calcium silicate (α - Ca_3SiO_5). Weak lines of CaO and SiO_2 were also present in the diffraction pattern. The dicalcium species was definitely identified but the identification of the tricalcium species was not completely certain. Further experiments will be performed at lower temperatures, e.g., 1200-1300°C (with water vapor), to form predominantly dicalcium silicate.

The gases used were of the following grades: SO_2 ; anhydrous (99.98%), N_2 ; prepurified (99.996%) and O_2 , commercial (99.5%).

Results and Discussion

The monocalcium silicate had a purity of 99.75%. However, upon heating a weight loss of about 20% occurred consistently. The weight loss started at about 100°C and prolonged to about 300°C. This loss is interpreted as the moisture content; hydrate and water adsorbed. The "dehydrated" sample was subject to sulfation experiments. Rates of sulfation were measured with a gas with the composition: 1.42% SO_2 , 1.42% O_2 and balance N_2 . Total pressure was atmospheric and not controlled.

The results are summarized in Figure 5. Curve A was the rate of sulfation of monocalcium silicate at 950°C. A direct comparison with

the sulfation rate of Greer limestone has not been made because the SO_2 and O_2 concentrations were different. It is known that the initial rate of sulfation (a measure of the intrinsic reactivity) of lime is approximately proportional to the SO_2 partial pressure to the 0.7th power.⁶ Using this relationship and the rate data for sulfation of Greer limestone (with the same particle size and same temperature) with 4% SO_2 (Fig. 2), the intrinsic reactivity towards SO_2 of the monocalcium silicate is about 40% higher than that of the calcined Greer lime. This result is, of course, encouraging in the utilization of the silicate for desulfurization.

Curve B shows the rate data at 900°C. Curve C shows the results also at 900°C with a gas containing 2.5% water vapor and 1.42% SO_2 and O_2 each in N_2 . The water vapor does indeed increase the sulfation rate. More important, the rate is increased not only in the initial period, where the chemical rate predominates, but also in the later period, where diffusion of SO_2 and O_2 is complete with the chemical rate. This indicates that besides the chemical rate being increased by water vapor, the diffusion of SO_2 and O_2 through the sulfated layer is also increased.

Curve D in Figure 5 shows the rates of sulfation of the dicalcium silicate (and the other components) at 900°C (with the same gas composition, without water vapor). The rates are lower than that with the monocalcium-silicate. The results were calculated based on 100% dicalcium silicate in the synthesized compound. Therefore, the actual rate could be higher if the actual composition were considered. Nevertheless, comparing curves B and D, and recalling that size in D was smaller than that in B, it is concluded that the reactivity of the dicalcium species is lower than that

of the monocalcium species, and that they are perhaps in the same order of magnitude.

C. Materials Preparation and Testing

1. Coal ash generator with controlled unburnt carbon

A small fluidized bed was constructed for this purpose. The reactor was made of stainless steel, 1 3/4 inches in diameter and 8 inches in height. The temperature of the bed is controlled by an electric tubular furnace outside the bed for supplying the heat and by a water cooling coil immersed inside the bed for cooling. By controlling the temperature and the length of time of combustion, coal ash with various amounts of unburnt carbon can be generated.

2. Attrition or particle strength test

Procedures for testing the attrition characteristics and particle strength of the amount of mgs of sample are being developed. For example, 5 gms of sea sand (or fused alumina) particles (they are quite spherical) of size -6 +10 mesh are mixed with 50 mg of the sample under testing. The size of the sample is smaller, e.g., -16 +20 mesh. The mixed material is fluidized with N₂ in a small quartz bed at a precontrolled temperature for a certain period of time. The sample was subsequently separated by sieving. Blank tests with sea sand alone are also run. Size distribution of the attrited sample is analyzed with microscopy. The results will give indications of the attrition characteristics under the fluidized bed combustion conditions.

D. Micro- and Semi-Pilot Plant Studies

The apparatus will be small (micro-) and its operation will be batch-wise (semi-).

This phase of work includes a small fluidized bed, such as the one described in Section C for combustion/sulfation and a roasting device (such as a rotary or stationary kiln) for regeneration.

This work is already underway in our laboratory and the results of these studies will be important in assessing the applicabilities of all the results from the static TGA reactors to any larger scale operations.

The regenerative process using carbon for CaO regeneration will be first tested in this phase. Testing on silicates and coal ash-containing systems will await further understanding of the actual reactions involved.

Conclusions and Work Planned

1. Regeneration with carbon appears to be a promising process. The SO₂ sorption ability of the regenerated lime showed no sign of weakening after ten cycles.

2. This regenerative process offers the following advantages over the reductive process with CO or H₂:

- (a) the requirement of carbon is cut in half,
- (b) lower temperature regeneration or perhaps isothermal sulfation/regeneration is possible,
- (c) less deactivation problems due to less sintering, and
- (b) less attrition because that fluidized bed operation is not required.

3. More experiments on the effects of temperature and steam concentration on regeneration are being planned. The carbon source will include chars and the unburnt carbon in fly ash.

4. Monocalcium silicate appeared to be more reactive to SO₂ and O₂ than both calcined Greer limestone and dicalcium silicate. Studies of the

SO₂ sorption ability of the various silicates will be continued. Studies on the regeneration reactions and cyclic sulfation/regeneration of the silicates will be initiated.

5. Studies on the interactions of fly ash with the sulfated limestone will be continued. Fly ash with some unburnt carbon appears to be the most promising candidate proposed in our regenerative processes.

6. Procedures of attrition test of mgs amount of sample under simulated FBC conditions are being developed. A device for generating coal ash with the controlled amount of unburnt carbon has been constructed. A micro-, semi-pilot plant is being constructed and testing of processes A, B, and combined A and B will follow.

7. Economic and process studies will be initiated, with emphasis on comparisons between the non-regenerative and the various regenerative processes. Work on kinetic and process modeling will be initiated. Kinetic modeling will afford interpretations of the kinetic data and process modeling will be used to predict, if possible, the behaviors of the scaled-up systems.

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Table 1. Time for 70% sulfation of the available lime in regenerated stone using carbon. Sulfation at 950°C and 4% SO₂ and 10% O₂ in N₂.

<u>Cycle No.</u>	<u>Time, min.</u>
1	--
2	35
3	24
4	28
5	23.5
6	25
7	22
8	26
9	28.5
10	22.5

Table 2. Rate of the CaS + 3 CaSO₄ reaction in regeneration as a function of number of cycles (950°C).

<u>Cycle No.</u>	<u>Weight loss in 2 hours, mg (from 30 min. to 2 1/2 hrs)</u>
1	11.2
1	10.6
2	10.1
3	10.8
4	9.6
5	9.85
6	8.9
7	9.65
8	7.5
9	8.3

Figure 1. Thermodynamic equilibria in the regenerative desulfurization process using carbon for regeneration.

Figure 2. Cyclic sulfation of calcined Greer limestone (-16 + 20 Tyler mesh) at 950°C and 1 atm. Gas composition: 4% SO₂, 10% O₂ in N₂. Numerals indicate the order of cycles.

Figure 3. Cyclic regeneration with carbon at 950°C and 1 atm ($\text{CaSO}_4/\text{C} = 2$). Amount of CaSO_4 to be regenerated in each cycle was about 60 mg. Numerals indicate the order of cycles.

Figure 4. First cycle regeneration with carbon at 950°C with and without 2.9% steam. Both with 4% SO₂ and 10% O₂ in N₂.

Figure 5. Rate of sulfation of mono- and di-calcium silicates with 1.42% SO₂, 1.42% O₂ in N₂ at 1 atm. A. Mono- at 950°C. B. Mono- at 900°C. C. Mono- at 900°C with additional 2.5% H₂O in gas. D. γ - Ca₂SiO₄ at 900°C.

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