REGENERATIVE PROCESS FOR DESULFURIZATION OF HIGH TEMPERATURE COMBUSTION AND FUEL GASES

QUARTERLY PROGRESS REPORT NO. 7
OCTOBER 1 - DECEMBER 31, 1977

MASTER

PROCESS SCIENCES DIVISION
DEPARTMENT OF ENERGY AND ENVIRONMENT

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Abstract

A method of pretreating limestone for enhancement of its utilization in fluidized-bed combustion has been found and is under further development. The method entails spraying of the stone with an aqueous solution of $\text{Fe}^{++}/\text{Fe}^{+++} \text{SO}_3^{--}/\text{SO}_4^{--}$ before it is fed to the combustor. One percent of iron coated on the stone approximately doubles the rate of SO_2 sorption. Fe_2O_3 not only catalyzes the rate, but also enhances the sorption capacity of the stone.

The Brookhaven Regenerative Process, i.e., regenerating lime from sulfate with coal ash in a kiln-type reactor, is under further development. The results continue to show that a temperature of 1000°C is feasible for regeneration as compared with the temperature of 1100°C which is required by the fluidized-bed processes.

A commercial high-temperature insulation product containing primarily CaSiO_3 has been tested for SO_2 sorption. The rate and capacity were both higher than those of the reagent-grade CaSiO_3 although the reason for this effect is not established.

The mechanisms of the basic and common reactions taking place in the regeneration systems are being studied. It has been shown that gaseous intermediates do exist in the reaction system: $\text{CaS} + 3\text{CaSO}_4 \rightarrow 4\text{CaO} + 4\text{SO}_2$. Evidence has been gathered to show the occurrence of several other reactions between CaS and SO_2 and between CaO and SO_2 under the conditions common to the regeneration systems.

Coal ash has been found as a good binder to pelletize fine-sized sorbents. The iron oxide in the ash also acts as a catalyst for SO_2 sorption. The good binding property is attributed to the SiO_2 in the

ash. Fine CaCO_3 pelletized with coal ash showed the catalytic effects. This method was suggested to and applied by Exxon investigators for pelletizing calcium aluminates cement powder with very good results.

Two conceptual AFBC process flow diagrams and corresponding mass and energy balances have been prepared. One flow sheet depicts a once through sorbent system (System I); the other, a regenerative system consisting primarily of an AFBC, a regenerator, and a sulfuric acid plant (System II). A process comparison of the two systems and a rough analysis of sulfuric acid market potential are also presented.

Regenerative Process for Desulfurization of High
Temperature Combustion and Fuel Gases

Quarterly Progress Report No. 7
October 1-December 31, 1977

A. Calcium Silicates as Regenerable Sorbents

Figure 1 shows the sulfation rate of a Fibreboard material. The material is a commercial product which contains primarily CaSiO_3 . The material was manufactured as a high-temperature insulation material and supplied by Fibreboard Corporation (Fruita, Colorado). Sulfation rates of reagent-grade CaO (Mallinckrodt) and CaSiO_3 (ROC/RIC) are also compared in the figure. These samples were of powder form. The sulfation rate of CaSiO_3 plateaus at about 30% completion, whereas the sulfation rate of the Fibreboard material can proceed to a higher level of greater than 40% completion. The higher capacity of the Fibreboard material may be due to its probably higher porosity and/or the impurities.

B. Utilization of Coal Ash as a Binder for Sorbent and as a Catalyst

To utilize the catalytic effect of coal ash on SO_2 absorption and possible formation of reactive calcium silicates, reagent CaCO_3 or CaSiO_3 were mixed with coal ash and pelletized. Also, SiO_2 which is abundant in coal ash is a known good binding agent. The coal ash contained 54.7% SiO_2 , 21.0% Fe_2O_3 , and 15.5% Al_2O_3 by weight. The sample mixture was pelletized with a Carver hydraulic press at 20,000 psi. The sample mixture contained a 50/50 wt % CaCO_3 or CaSiO_3 and coal ash. Figure 2 shows the sulfation rates of the pellets for CaCO_3 , CaCO_3 mixed with coal ash, CaSiO_3 , and CaSiO_3 mixed with coal ash.

The pellets were crushed and sieved to 16/20 Tyler mesh in size and were calcined before sulfation. The rates of the mixtures were higher than those of the reagents alone. Higher capacity was also seen for the mixture. The sulfation rate of CaCO_3 is increased by more than three times with coal ash. Practically, the sulfation rate should be compared to the amount of SO_2 sorbed/mass of total sorbent because of the weight of the inert materials should also be taken into account. Figure 3 shows the same sulfation result based on per unit total weight. In fact, the sulfation rate of CaCO_3 mixed with coal ash is still somewhat higher on this basis, i.e., the inert coal ash may be considered to be equivalent to CaO .

The idea of using coal ash as a binder for pelletizing fine-size sorbent was also suggested to workers at Exxon Research and Engineering Company. They have shown that with the calcium aluminate cement, on a one-to-one weight basis of coal ash and the cement, the sulfation rate was tripled.

C. Mechanisms of the Lime Regeneration Reactions

The following two-step regeneration reaction mechanism for CaSO_4 regeneration is known when using such reductant materials as C and CO:

That is, a quarter of the CaSO_4 is first rapidly converted to CaS and subsequently three quarters of CaSO_4 react with the CaS to form CaO and SO_2 .

We have previously reported that for CaSO_4 regeneration with H_2 , two distinct slopes on the TGA curve indicated the two-step reaction mechanism, i.e.,

In this two-step reaction mechanism, the second common step is the rate-controlling step. That is, three moles of CaSO_4 react with one mole of CaS to form CaO and SO_2 . The experiments described below were designed to understand the reaction mechanism of the second step which is an apparent solid-solid reaction and to provide preliminary information whether this apparent solid-solid reaction involves any gas intermediates.

A CaS pellet and a CaSO_4 pellet, separated by quartz beads (about 2 mm thick), were put into a Mettler TA-1 reactor. The samples were heated at a rate of $25^\circ\text{C}/\text{min}$ to 900°C or 1100°C in a flowing nitrogen atmosphere and measured gravimetrically. The pellets (1.3-cm diameter) were proportioned according to stoichiometric molar ratio $3\text{CaSO}_4:1\text{CaS}$. The results were compared with that of the thermal decomposition of a CaSO_4 pellet in conjunction with a dummy alumina pellet replacing the CaS pellet under identical conditions. The weight loss of the $3\text{CaSO}_4/\text{CaS}$ pellets were significantly greater than the thermal decomposition of the

($3\text{CaSO}_4/\text{Al}_2\text{O}_3$) pellets at both 900°C and 1100°C (Figures 6 and 7). These results indicate that the reaction indeed involves gaseous intermediates. Furthermore, at 900°C $\text{CaS} + 2\text{O}_2 \rightarrow \text{CaSO}_4$ is a favorable reaction. Since the weight loss of $3\text{CaSO}_4/\text{CaS}$ pellets was more than that of the CaSO_4 pellet, it is unlikely that O_2 serves as an intermediate gas.

To understand the product distribution in the reacted sample pellets, we adopted the simple and quick technique used previously by Professor Wen and coworkers.⁷ When a few drops of Thymolphthalein indicator (pH 9.3-10.5) were applied to the surface of the 900°C and 1100°C product pellets, the color of both CaSO_4 and CaS product pellets immediately turned to distinct blue. This indicated that the solid product throughout the outer surfaces of both the CaSO_4 and CaS pellets was CaO . We are examining the products further by slicing the pellets in both longitudinal and radial directions so that a complete picture of the CaO distribution can be obtained. Such results would shed more light on the reaction mechanism of the reaction system.

At above 1000°C the following reactions are thermodynamically feasible:

Equilibrium constants have been calculated for some of these reactions and are listed in Table I.

Equilibrium partial pressures of the sulfur vapor can be calculated from the values of K. The form of sulfur is assumed to be dimeric. The partial pressures of the monomeric sulfur can be simply calculated by taking the square roots of the P_{S_2} values.

The calculations show that indeed all of the above reactions are feasible if the sulfur evolves as monomeric molecules. Some of the reactions are not feasible if dimers are evolved. We do have preliminary evidences showing that elemental sulfur is formed in these reactions. More results will be reported later for this complex system.

D. Enhancement of Lime Utilization in Fluidized-Bed Combustion with Iron Catalysts

In the known technology of fluidized-bed combustion of coal the porous particles of limestone are used as the bed material for SO_2 sorption and the sorption rate is rather slow. A new process is being studied which involves coating or impregnating the limestone particles with iron oxide. The impregnated stone is shown to be more reactive towards SO_2 sorption. One of the previously known catalytic processes for FBC is by the addition of salt (NaCl). However, we have shown that about 60% of the chloride winds up in the gas phase and thereby corrodes the combustor and pollutes the atmosphere. Moreover, in our previous TGA studies, with the addition of NaCl, the catalytic effect is pronounced only below $850^\circ C$ and has no effect above $900^\circ C$. The applicability of the iron catalyst can cover a wider temperature range. More significantly, for the same weight concentration of NaCl and Fe_2O_3 , Fe_2O_3 is more effective than NaCl.

The impregnation involves mixing an aqueous solution of iron sulfate or sulfite with the limestone before it is fed to the combustor. The iron compounds are instantaneously (decomp. temp. of $\text{Fe}_2(\text{SO}_4)_3$ is 460°C) decomposed into Fe_2O_3 upon being fed to the combustor and thereafter catalyze the SO_2 sorption reaction.

The rates of sulfation of Greer lime and limestone particles coated or impregnated with iron oxide are compared in Figure 4 based on atmospheric TGA under identical conditions. This figure includes the sulfation of a calcined Greer limestone, precalcined Greer limestone impregnated with Fe_2O_3 , uncalcined Greer limestone impregnated with Fe_2O_3 and precalcined Greer limestone physically mixed with Fe_2O_3 or NaCl . The stone was 16/20 Tyler mesh in size and the sulfation gas contained 0.25% SO_2 , 5% O_2 , and 5% steam in N_2 . The figure shows that in all cases the sulfation rate of Greer limestone with Fe_2O_3 is higher than that of Greer limestone alone and an increase in the amount of Fe_2O_3 impregnated increases the rate of sulfation as well as the extent of completion. The sulfation rate of precalcined Greer limestone impregnated with Fe_2O_3 is much higher in all cases. The rate of uncalcined Greer limestone impregnated with Fe_2O_3 is also seen higher but is somewhat reduced in magnitude. The rates of precalcined Greer limestone physically mixed with about the same wt% of Fe_2O_3 or NaCl are only slightly higher than that of Greer limestone alone.

The sulfation rates at 10 atm for Greer lime and Greer lime impregnated with Fe_2O_3 are compared in Figure 5. Unlike the atmospheric TGA results, the rate at 10 atm for Greer lime impregnated with Fe_2O_3 is only slightly higher than that of Greer lime alone. This is reasonable

because at 10 atm the iron catalyst increases the chemical rate but the pore diffusion rate is decreased by approximately ten fold, and a less pronounced catalytic effect is observed as shown in Figure 5. This result also indicates that the iron catalytic effect is a chemical effect rather than a pore-enlargement effect.

E. Kiln Regeneration Process

Work on investigating the performance of the kiln regeneration process is continuing from the last quarter (Report No. 6). The specific process is to react the sulfated lime with fly ash, both from the fluidized-bed combustor (FBC), and with the unburnt carbon in the fly ash being used as the reductant. The basic reaction is:

which proceeds in the following two sequential steps:

Both the sulfated Greer limestone and the fly ash of Sewickley coal were supplied by Argonne National Laboratory from their 6-inch combustor. The fly ash contains 12.5% carbon, 5.24% S, 14.6% $\text{SO}_4^{=}$, and 7.24% $\text{CO}_3^{=}$, while the sulfated Greer contains 32.1% Ca^{++} , 15% $\text{SO}_4^{=}$ (for 16/20 mesh), 1.28% Fe^{+++} , 23.9% $\text{CO}_3^{=}$ and 11.9% SiO_2 . The sizes used in the regeneration were 200/270 Tyler mesh for the fly ash and 16/20 mesh for the sulfated stone. The apparatus and experimental procedures of the rotary kiln reactor were described in the previous report (No. 6).

In the regeneration process, three important factors must be considered: (1) rates of regeneration, (2) SO_2 concentration in the

gas phase, and (3) the reactivity of the regenerated absorbents. The first two factors depend upon the operating variables, e.g., gas, velocity, temperature, solid feed rate, etc., while the third factor depends solely on the reaction temperature. This report will present the effects of kiln temperature and gas velocity on both regeneration rate and SO_2 concentration. Also, cyclic sulfation-regeneration results using a fluidized bed sulfator and a rotary kiln regenerator to test the reactivity of the regenerated material are presented.

(1) Temperature Effects

Regeneration experiments have been conducted at temperatures ranging from 950°C to 1050°C and with Ar flow rates of 10 SCCM (9.5 cm/min). In all these experiments four grams of the sulfated stone were used. The off gases were found to be predominantly SO_2 , CO_2 , and Ar. The temperature effect on the SO_2 concentration was measured using a low carrier gas velocity (10 SCCM). Results of the SO_2 fraction and CO_2 fraction at various times are given in Figures 8 and 9, respectively. These figures clearly indicate that reaction (1) is a two-step reaction, and reaction (3) is the slower rate step, and this phenomenon is more obvious at lower temperatures; e.g. $T = 950^\circ\text{C}$.

As mentioned, the "kiln temperature" indicated in this report was measured at the center line of the kiln near the head of the regeneration zone. After elaborate temperature measurements, with both thermocouples and an optical pyrometer, temperature gradients were detected in both the axial and the radial directions of the kiln. The temperature increased by 15 to 20°C along the center line in the gas passage direction

and the temperature of the quartz wall was about 15°C higher than that at the center line. Results on the SO₂ concentrations should, therefore, be studied with the understanding of the non-uniformity of the temperature distribution.

Figure 8 gives the history of the SO₂ concentration of the off gas at three kiln temperatures. The results clearly indicate that the thermodynamic equilibrium partial pressures of SO₂ (cf. Figure 6 in Report No. 6) were reached at a gas velocity of about 9.5 cm/min.

It should be mentioned here that the SO₂ partial pressure measured in previous experiments (Report No. 6), which showed lower than the thermodynamic limit were found to be due to the temperature nonuniformity in the reactor. In these experiments, the temperatures at the exit end of the reactor were about 50°C lower than that at the center of the regeneration zone. This effect results in causing lower SO₂ partial pressure.

(2) Velocity Effect

The dependence of the SO₂ concentration on the carrier gas velocity was measured at 1000°C with Ar flow rates ranging from 10 SCCM (9.5 cm/min) to 150 SCCM (142 cm/min).

Figure 10 shows that increasing carrier gas flow rate decreases the SO₂ concentration. From the data shown in Figure 10, the approximate curves of the overall extent of regeneration as a function of time at different flow rates were calculated. These results are compared with the limiting regeneration rates measured in the TGA system (wt: 100 mg, flow rate: 500 SCCM) in Figure 11. It is clear that the regeneration rate is suppressed by the SO₂ concentration in the gas

phase. By increasing the carrier gas flow rate, the regeneration rate is increased. From these figures, one can see that high regenerability with short solid residence time and with high SO_2 concentration in the off gas can be obtained from this regeneration process. For example, under the operating condition with 50 SCCM flow rate, more than 80% of the sulfated material was regenerated in 30 min and an average of 7% SO_2 concentration in the flue gas over this time period was obtained. However, the operating conditions would have to be optimized considering a trade-off between the higher SO_2 concentration and a shorter solid residence time.

(3) Reactivity of the Regenerated Sorbents

To test the reactivity of the regenerated material, cyclic sulfation/regeneration experiments have been conducted. Sulfation rates were measured in a 30-mm fluidized-bed sulfator, while regeneration took place in a rotary kiln reactor. The apparatus of the fluidized bed sulfator is shown schematically in Figure 12.

The fluidized bed was 30-mm ID, 8-cm long with a 40-mm ID, 20-cm long free board and a quartz fritted plate as the gas distributor. Solid samples were loaded to the bed and were fluidized with a simulated combustion gas. The gas was first preheated to 600°C by passing through a 20 ft heated coil and was raised to the operating temperature in the fluidized bed from the heat supplied by the furnace. After finishing each experiment, the SO_4^{2-} and CaS contents in the solid samples were measured.

The CaS content in the solid was determined from the weight gain of the solid sample in a 20% oxygen atmosphere at 950°C . For the CaSO_4

content, two different methods were compared: the ASTM wet chemical and thermal decomposition methods. It was found that the weight loss of the solid samples in N_2 flow in the temperature range of $1100^{\circ}C$ to $1200^{\circ}C$ correspond (within 3%) to the SO_3 content (of $CaSO_4$) determined by the ASTM method. In this study, the thermal decomposition method was, therefore, adopted for the purpose of time saving. A high temperature TGA system was used accordingly to measure both the contents of CaS and $CaSO_4$ in the solid samples. About 60 mgs sample was used for each analysis. The reactivity of the regenerated lime for sulfation was determined based on the fractional uptake of SO_3 after 5 hours of sulfation time. Also, in order to compare with the reactivity of the raw sorbent, Greer lime was used as the starting material. The experimental conditions for both sulfation and regeneration are shown in the following.

Sulfation

Temperature: $850^{\circ}C$

Starting material: Greer lime (precalcined at $900^{\circ}C$)

weight: 10 grams

size: 16/20 mesh

Superficial velocity: 5 ft/sec

Gas composition: SO_2 : 0.25%, O_2 : 5%, N_2 balance

Time: 5 hrs

Regeneration

Temperature: $1000^{\circ}C$

Material: Sulfated Greer + coal ash (size 200/270 mesh)

Time: 2 hours Flow rate (Ar): 100 SCCM

After each sulfation/regeneration run, a small portion (about 60 mg) of the sample with size 16/20 mesh was taken out for analysis of the contents of CaSO_4 and CaS . Also, to assure having a large degree of regeneration, the regeneration period was kept for two hours. The results of the SO_3 content in the solid sample for the eight cycles are given in Figure 13.

This figure shows that for all the regeneration cycles, a very high degree of regeneration can be reached (88-100%). It was also found that the regenerated stone did not contain any CaS . This indicated that the regeneration reaction was completed in all the cycles. This high degree of regeneration is very encouraging for a regeneration process.

It should be emphasized here that the 2-hr regeneration time used was only to ensure complete regeneration of lime so we could study the sulfation characteristics in a more meaningful way. In practice, however, the regeneration time can be substantially shortened. For example, based on the integrated amounts of SO_2 evolved, over 80% regeneration was accomplished in 1/2 hr at a flow of 50 SCCM.

The regeneration results at 950°C ³ performed in the TGA indicated the existence of CaS in the solid absorbent after 4 hours of regeneration. The difference in the solid content, compared with the results obtained in this study, is very likely due to the difference in reaction temperatures. Since reaction (3) was found to be strongly temperature dependent with about 62 Kcal/mole activation energy, by increasing the temperature from 950°C to 1000°C , the reaction rates become 2.7 times higher. Thus, the second step reaction could be completed in a shorter time. Other factors such as the extent of sulfation of the sorbent and the sources of carbon material may also affect the reaction rates.² Snyder et al.⁴ have found that by using

H₂ as the reductant at about 1100°C, the only product was CaO whereas below 900°C, the product was all CaS. These results are in line with the above discussion and the fact that reaction (2) has a lower temperature dependence, as observed by Turkdogan and Vinters.²

Figure 13 also shows a slight decrease in SO₂ absorption ability of the regenerated lime in eight cycles. To further test the regenerated sorbent, portions of the regenerated samples were sulfated in a TGA system. These results are shown in Figure 14 indicating approximately 10% decrease in reactivity. The detrimental effect of this temperature on the reactivity of the lime sorbent is believed to be lower than the temperature at 1100°C. For example, the dolomite regenerated at 1100°C was found to be 50% lower than the material at 900°C.³

Attrition experiments were performed to compare the strength of the regenerative lime with that of the fresh lime. The samples compared were the regenerated lime after eight cycles, which contained 3 wt. % of SO₃, and the fresh lime precalcined at 900°C, both 16/20 Tyler mesh in particle size. They were fluidized with nitrogen gas in a fluidized-bed for 5 hours at 850°C with 5 ft/sec superficial gas velocity. Results of the size distribution of the attrituted samples are shown in Table II. It is seen that the regenerated lime has a much higher strength than the calcined lime. This is because the regenerated lime contained SO₄⁼ and some silicates as will be shown later; both would increase the strength of the material. Also, the regenerated material has been treated at higher temperatures (1000°C) than the fresh lime (at 900°C). The strength of the regenerated material would thus be higher. More direct comparisons on the attrition characteristics are being made.

(4) Product Analysis

Besides the regeneration reactions, many other reactions did indeed also take place in the kiln regenerator. The reactions between CaO and the various minerals in the coal ash are well known to the material scientists. For example, silicates, ferrites, ferrates, aluminates, ferro-silicates, etc. can all be formed at below 1000°C. We have found earlier that Fe_2O_3 catalyzes the sulfation reaction of CaO, because it catalyzes the oxidation of SO_2 to SO_3 .⁶ These reactions are presently under investigation, however, some preliminary results will be presented here.

The sulfation rates were compared of a raw Greer lime and a kiln-regenerated lime (1000°C kiln temperature) from the partially sulfated Greer lime from Argonne's FBC. The kiln regenerated lime showed higher reactivity and absorbed about 30% more SO_2 in 150 minutes than the raw lime.

X-ray diffraction analysis and atomic absorption methods were used to determine the concentrations of the major impurities (Si, Fe, and Al) in the limestone particles. For these analyses, samples of Greer limestone particles (16/20 mesh) were screened after each sulfation/regeneration experiment and the free coal ash and finer particles were sieved out. X-ray diffraction showed that calcium silicates in Greer limestone are present as β -dicalcium silicates form. It has been reported in our laboratory that β -dicalcium silicate is a reactive form towards SO_2 .⁵ The β -dicalcium silicate was not present in Argonne's once sulfated Greer limestone while it was present in an appreciable amount as detected by x-ray after regeneration of this sample in our kiln. Also found in all the Greer limestone samples was alpha quartz.

From the x-ray diffraction intensities, the amount of alpha quartz also increased in the kiln regenerated sample. Results of the atomic absorption analyses showed that Si, Fe, and Al all increased in the kiln regeneration. The concentrations were increased from: 14.50% Si; 0.85% Fe, and 1.90% Al in the Argonne sulfated stone to: 14.9% Si; 1.16% Fe, and 2.14% Al in the kiln regenerated Argonne stone. Although these analyses were preliminary in nature and may not be representative because only a 100 mg sample was used for an analysis, possible catalytic effects due to the minerals may be the cause of the observed increase in the sulfation reactivity of the kiln regenerated stone.

(5) Summary

Results of regeneration of the sulfated lime in a kiln using fly ash as the reductants have been presented in this report. Because of the low gas flow required in this process, high SO_2 concentration can be obtained at relatively low temperatures in comparison with the fluidized bed regeneration process. This high regenerability in a reasonably short solid residence time, the less detrimental effect of temperature on the reactivity of the regenerated sorbent and potentially less solid attrition make the kiln regeneration process look promising. The kiln regenerator may also serve the function of the carbon burn-up cell and thus could replace it.

Although these results are preliminary, they do seem to indicate that the kiln regeneration process can remedy the shortcomings of the fluidized bed, one-step reductive decomposition process for lime regeneration. To further develop this process, extensive studies on the effects of the process variables must be investigated. Furthermore, the kinetics and mechanism of the apparent solid-solid regeneration reaction, which is currently under

investigation in our laboratories, must be understood. With the knowledge of the reaction kinetics, mathematical modeling of the kiln regeneration process, for both batch and continuous operation will be made to evaluate the process.

F. Process Design and Evaluation Studies

Introduction

The purpose of these studies is to begin to apply the laboratory-derived process chemistry data to the development of full-scale systems. With this approach, critical design factors and the need for additional process data are identified early, as well as the relative merits of the competing systems.

Two conceptual process flow diagrams were prepared (Figures 15, 17, and 19), one for a once through sorbent/carbon burnoff cell system (System I); the other, for a regenerative sorbent system based on reducing CaSO_4 with carbon in a roaster (kiln) type apparatus (System II). Mass and energy balances were also prepared for each system, for a feed rate of 1 ton/hr (dry basis) of Illinois No. 6 coal (Figures 16, 18, and 20). The bases of the subject flow sheets and the assumptions made in preparing the mass and energy balances are presented in Table III.

Process Description of System I (once through sorbent)

Coal is fed to the atmospheric fluidized bed combustor (AFBC) concurrently with fresh limestone and recycled calcium oxide from the carbon burnoff cell (BOC). The lime feed rate is set in proportion to the coal feed so as to maintain a calcium to sulfur molar ratio of 2.5. Air is pumped to the AFBC by a blower to fluidize the solids contained

in the AFBC and to furnish oxygen (20% excess) to the bed. The air is preheated prior to entering the bed by heat exchange with the hot gaseous effluent of the combustor.

In the combustor, which operates at about 1550°F, limestone is calcined to calcium oxide and the coal oxidized, generating a net quantity of energy which is absorbed by banks of tubes for power generation. Ninety percent of the carbon contained in the coal is oxidized to CO₂ at this point. All of the other principal bed reactions are assumed to go to completion. About 80% of the sulfur dioxide produced in the bed reacts with calcium oxide to form calcium sulfate. Solids consisting primarily of calcium sulfate, calcium oxide, and stone ash are continuously withdrawn from the combustor to maintain a constant bed level, and are sent to waste disposal. Residual sulfur dioxide along with other gaseous effluents and entrained particulates exit the AFBC at the top and flow to a cyclone. The particulates consist of fly ash, unburned carbon, and attrited solids.

The gases exiting the AFBC are drawn through a cyclone (above), an electrostatic precipitator and an air preheater by an exhaust blower, which discharges the cleaned gas stream to the atmosphere via a stack. The solids collected by the cyclone are fed to a carbon burnoff cell (BOC) to recover energy values (carbon) contained in the particulates while the solids collected by the electrostatic precipitator are sent to waste disposal.

The carbon which enters the BOC is burned with 25% excess air at a conversion efficiency of about 90%. The burnoff cell operates in much the same way as the AFBC but at a temperature of about 2000°F. About 17% of the total limestone feed to the process is fed to the BOC, the remaining to

the AFBC described above. The lime (now CaO) that is withdrawn from the BOC is recycled to the AFBC. The BOC gaseous effluent passes through a cyclone and then combines with the gaseous effluent of the AFBC cyclone. The combined stream flows through an electrostatic precipitator and is discharged to the atmosphere as described above. The solids collected by the BOC cyclone as well as by the precipitator are sent to waste disposal.

The various solids effluent streams described above are combined and cooled from about 1250°F to 300°F by cooling water, in an indirect cooler, and transported to waste disposal. The solids consist primarily of fly ash, calcium oxide, calcium sulfate, stone ash, and small amounts of unburned carbon.

Process Description of System II (regenerative system)

Coal and a combined stream of makeup limestone and recycled calcium oxide (from the regenerator) are concurrently fed to the AFBC. The total feed of limestone and recycled calcium oxide is set to maintain a calcium to sulfur molar feed ratio of 2.5. Air is pumped to the AFBC by a blower to fluidize the solids contained in the AFBC and to furnish oxygen (20% excess) to the bed. The air is preheated prior to entering the bed by heat exchange with the hot gaseous effluent of the combustor.

In the combustor, which operates at about 1550°F , the makeup limestone is calcined to calcium oxide and the coal oxidized, generating a net quantity of energy which is absorbed by banks of tubes for power production. Ninety-seven and one half percent of the carbon contained in the coal is oxidized to CO_2 at this point. All of the other principal bed reactions are assumed to go to completion. About 80% of the sulfur dioxide generated in the bed reacts with calcium oxide to form calcium sulfate. Solids

consisting primarily of calcium sulfate, calcium oxide and stone ash are continuously withdrawn from the combustor to maintain a constant bed level and are fed to the regenerator. Residual sulfur dioxide along with other gaseous effluents and entrained particulates exit the AFBC at the top and flow through a primary cyclone. The solids collected by the cyclone are recycled back to the AFBC while its gaseous effluent is fed to a second stage cyclone. The recycled solids consist of carbon, fly ash, calcium oxide, and stone ash.

The gases which exit the primary cyclone are drawn through a secondary cyclone (above), an electrostatic precipitator and an air preheater by an exhaust blower, which discharges the cleaned gas stream to the atmosphere via a stack. The solids collected by the second stage cyclone and the precipitator, and the calcium sulfate effluent stream of the AFBC are combined and fed to a roaster type regenerator (similar to a kiln without a combustion system), along with preheated dry air from the H_2SO_4 plant. The regenerator operates at atmospheric pressure and at temperatures between 1832 and 1922°F.

In the regenerator, calcium sulfate is reduced to calcium oxide by carbon contained in the solids feed. Additional carbon is burned to carbon dioxide to provide the necessary energy for driving the calcium sulfate reduction reaction, which is endothermic. The solids feed to the regenerator contains enough carbon to meet the requirements of both reactions. Oxygen (air) is fed to the regenerator at a rate just sufficient to satisfy the stoichiometry of the carbon combustion reaction. The air supply must be dry in order to maintain a moisture-free gas feed to the sulfuric acid plant, to prevent corrosion from occurring in the plant equipment.

The solids (CaO) effluent of the regenerator is screened to remove fines, and transported to the AFBC for reuse. The gaseous effluent, rich in SO_2 , is drawn through a cyclone, an air preheater and an electrostatic precipitator by a blower, which compresses the cleaned gas stream to about 5 psig and feeds it to the sulfuric acid plant. The particulates captured in the cyclone and precipitator are combined with the fines from the regenerator screen and fed to an indirect cooler. The combined stream is cooled by cooling water from about 1750°F to 300°F and then transported to waste disposal. The solids consist primarily of fly ash, attrited calcium oxide, stone ash, and small amounts of unburned carbon.

Dry air is mixed with the cleaned, dry gaseous effluent from the regenerator so that the combined stream of air and gases contains an equal number of moles of oxygen and sulfur dioxide. The resulting concentration of SO_2 in the mixture is about 8.6 volume percent. The combined stream flows through an economizer, where it is heated by hot product gases from the first stage of the SO_2 to SO_3 converter, and into the converter. In the converter, SO_2 reacts with oxygen to form SO_3 in four stages (i.e., four layers of catalyst) and about 98% conversion of SO_2 to SO_3 is effected. The hot conversion gases are cooled between stages and after leaving the fourth stage pass through a waste heat boiler and a cooler before entering the sulfur trioxide absorbing tower.

The conversion gases flow upward through the absorbing tower, where sulfur trioxide is absorbed by 98% sulfuric acid recirculated from the bottom of the absorber, and to the atmosphere. The absorbing acid, since

it is continuously becoming more concentrated, is diluted with weaker acid from the air drying tower (see below) and with water to maintain its strength at about 98%. The recirculated and product acids are also cooled to remove heat produced in the absorber. The product acid is collected in a storage tank and transferred to tank trucks or cars for shipping, as required.

Dry air is supplied to the process by means of a blower and a drying tower. Ambient air is pumped through the drying tower by the blower and is dried by contacting 98% sulfuric acid supplied by the SO_3 absorber. Diluted drying acid is concentrated by mixing with the acid bottoms of the absorbing tower and is returned to the drying tower after cooling. A portion of the dried air is fed to the SO_2 to SO_3 converter; the remaining portion, to the sorbent regenerator described above.

Process Discussion

System I (once through sorbent system) is modeled after the Rivesville Plant and may be considered a first generation AFBC system. It is based on data appearing in the literature and on information received from the Foster Wheeler Development Corporation,⁸ with some modification. System II (regenerative) depicts an improved system that can achieve a carbon conversion efficiency of 97.5% in the AFBC and which has the capability of regenerating sulfated calcium oxide. Although System II is somewhat more speculative than System I, there is experimental evidence indicating that a carbon conversion efficiency of 97.5% (and even greater) can be achieved by recycling the solids collected in the AFBC primary cyclone back to the fluid bed. The assumed regeneration capability is based on data developed by BNL on TGA and small scale batch rotary kiln experiments.⁹ At regenerator operating temperatures between 1832°F (1000°C) and

1922°F (1050°C), SO₂ concentrations in the kiln exhaust gases as high as 22 volume percent have been achieved. The 22% concentration is close to the thermodynamic limit (calculated) of the controlling regeneration reaction, at a temperature of 1922°F, and therefore reaction rates would tend to decrease as this concentration is approached. Further work in this area is currently underway.

The concentration of SO₂ in the exhaust gases for the System II regenerator is calculated to be about 15% when feeding stoichiometric quantities of air (see process description above). However, if it is necessary to operate at a lower concentration, nitrogen rich gas from the SO₃ absorber (H₂SO₄ plant) could be recycled to the regenerator. Operating at lower concentrations, however, would effect the economics of the sulfuric acid plant because larger equipment would be required for the same sulfur recovery. Another important factor effecting the cost of the sulfuric acid plant is the dryness of the regenerator gaseous effluent (which is the feed to the sulfuric acid plant). It has been assumed in this study that the solids feed to the regenerator contains no free moisture and very little hydrogen and therefore that the regenerator gaseous effluent is moisture free. If this were not the case, additional purification equipment would be required upstream of the SO₂ to SO₃ converter. Again, the economics of the sulfuric acid plant would be affected but not the technical feasibility of operation.

The total emissions of gaseous pollutants from both Systems I and II would be, based on current data, within current environment emission limits. In the case of System II, however, further explanation is required. If the AFBC and H₂SO₄ plants are considered to be a power generating complex,

the total emissions of SO_2 from the complex would be less than the limiting value of 1.2 lb SO_2 /MMBTU. If the AFBC portion of the plant was considered separately, it too would meet SO_2 emission regulations. However, the sulfuric acid plant standing alone would not conform to current SO_2 emission standards for new sulfuric acid plants, unless the single contact/single absorption (SC/SA) process (depicted in the sulfuric acid plant of System II) was replaced with a double contact/double absorption (DC/DA) process. The DC/DA process differs from the SC/SA process principally in that it has an intermediate SO_3 absorption tower added ahead of the final conversion stage of the SO_2 to SO_3 converter. Estimates of the additional cost for building a new sulfur burning DC/DA plant range from about the same investment¹⁰ (which does not appear to be a realistic estimate) up to 13% more than for a SC/SA plant.¹¹ Since the primary function of System II would be to generate power, not H_2SO_4 , and since the sulfuric acid plant can be considered a pollution abatement device, it was assumed that the AFBC in combination with the SC/SA sulfuric acid process would be considered a single entity (i.e., a power generating system) and treated as such.

A process comparison between Systems I (once through) and II (regenerative) is presented in Table IV. The table is self-explanatory, however, it is worth mentioning that the limestone requirements and the quantity of solid wastes produced by System I are substantially greater than for System II, that is, about 15 times more limestone is required and about 3 times more solids are produced. Furthermore, the solid wastes from System I are principally comprised of calcium compounds whereas the solids from System II are principally fly ash. These factors are important to the economics and environmental impact of operation. Also

of significance is the fact that although the overall carbon conversion efficiency of System I is greater than for System II, the energy conversion efficiency of System I is lower than for System II. This reversal occurs because System II requires less energy to preheat and calcine makeup limestone than System I and also because the carbon required to satisfy and drive the regeneration reactions of System II is available in the collected solids from the AFBC secondary cyclone and downstream precipitator. Thus, more energy is available for power production purposes. The energy required to drive blowers, material handling equipment, pumps, etc. is roughly estimated to be about the same for both systems. Note that a net quantity of steam is produced by the sulfuric acid plant which could be used to drive some of the equipment of System II.

Market Potential of Generated Sulfuric Acid

Based on data appearing in the MOPPS Phase I report (ERDA, June 1977) on the anticipated energy contribution of AFBC's in the year 2000, the quantity of sulfuric acid that would be produced by a System II plant has been estimated (Table V). For an energy production of 4.6^* Quads, about 17.5×10^6 tons/year of sulfuric acid would be generated. The current usage of sulfuric acid by the US is about 35×10^6 tons/year while the usage of sulfuric acid in the year 2000 is projected (BNL) at greater than 55×10^6 tons, based on current use patterns. Thus, it appears that there may be an outlet for AFBC derived sulfuric acid.

* Which is about 10 to 15% of the total anticipated demand for coal energy by the US in the Year 2000.

Future Process Studies

Our next task with regard to the subject processes is to determine the economic viability of regeneration. Subsequent studies will be directed towards developing processes for converting regenerator SO_2 to elemental sulfur rather than to H_2SO_4 .

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Discussions and guidance provided by Dr. Andrej Macek of the US Department of Energy are appreciated. Samples of the sulfated limestone and the fly ash were kindly supplied by Argonne National Laboratory. The CaSiO_3 insulation material was offered by Mr. K. S. Horr of Fibreboard Corporation. We also wish to thank Mr. Henry Phillips of the Foster Wheeler Development Corporation for supplying us with useful AFBC process information.

References

1. G. J. Vogel et al., "A Development Program on Pressured Fluidized-Bed Combustion", Annual Report, Argonne National Laboratory, Argonne, Ill., ANL/ES-CEN-1016 (1976).
2. E. T. Turkdogen and J. V. Vinters, Trans. Inst. Mining & Metallurgy, in press (1977).
3. R. T. Yang, M. S. Shen, and M. Steinberg, "A Regenerative Process for Fluidized-Bed Combustion of Coal with Lime Additives", BNL Report 22782, Brookhaven National Laboratory, Upton, New York (1977).
4. R. B. Snyder, W. I. Wilson, G. J. Vogel, and H. A. Jonke, Proc. 4th Intern. Conf. FBC, Mitre, McLean, Va., Dec. 1975.
5. R. T. Yang, et al., "Regenerative Desulfurization of Hot Combustion and Fuel Gases", Quarterly Reports Nos. 5 and 6, Brookhaven National Laboratory, Upton, New York, April 1-September 30, 1977.
6. R. T. Yang, M. S. Shen, and M. Steinberg, Env. Sc. Tech., in press.
8. H. Phillips, private communication, Foster Sheeler Development Corp., Livingston, N. J. (1977).
9. R. T. Yang, et al., Regeneration of Lime-Based Sorbents in a Kiln with Solid Reductants, Proceedings of the 5th Inter. Conf. on FBC, Washington, D.C., December 12, 1977, in press.
10. Atmospheric Emissions from Sulfuric Acid Manu. Processes, US Dept. Health, Education, and Welfare, Cincinnati, Ohio (1965).
11. J. G. Kronseder, "Economics of High Conversion Sulfuric Acid Plants", AIChE 61st Annual Meeting, Los Angeles, Calif. (December, 1968).

Table I

$2\text{CaS} + \text{SO}_2 \rightarrow 2\text{CaO} + 3/2\text{S}_2$			
<u>Temp. °K</u>	<u>ΔG, kcal/rx.</u>	<u>RT, kcal</u>	$K = \frac{(\text{S}_2)^{3/2}}{(\text{SO}_2)}$
1255.38	22.417	2.4944	0.125×10^{-3}
1366.5	20.618	2.7152	0.5037×10^{-3}
1477.6	18.695	2.9360	0.1716×10^{-2}
$\text{CaS} + 2\text{SO}_2 \rightarrow \text{CaSO}_4 + \text{S}_2$			
<u>Temp. °K</u>	<u>ΔG</u>	<u>RT</u>	$K = \frac{\text{S}_2}{(\text{SO}_2)^2}$
1255.38	6.206	2.4944	0.8308×10^{-1}
1366.5	10.94	2.7152	0.1779×10^{-1}
1477.6	15.33	2.9360	0.540×10^{-2}
$4\text{CaO} + 6\text{SO}_2 \rightarrow 4\text{CaSO}_4 + \text{S}_2$			
<u>Temp. °K</u>	<u>ΔG</u>		$K = \frac{\text{S}_2}{(\text{SO}_2)^6}$
1255.38	-20.01		3047
1366.5	2.524		0.3947
1477.6	23.93		0.289×10^{-3}
$3\text{CaS} + \text{CaSO}_4 \rightarrow 4\text{CaO} + 2\text{S}_2$			
<u>Temp. °K</u>	<u>ΔG</u>		$K = (\text{S}_2)^2$
1255.38	38.63		0.188×10^{-6}
1366.5	30.30		0.142×10^{-4}
1477.6	22.06		0.5456×10^{-3}
$\text{CaS} + 3\text{CaSO}_4 \rightarrow 4\text{CaO} + 4\text{SO}_2$			
<u>Temp. °K</u>	<u>ΔG</u>		$K = (\text{SO}_2)^4$
1255.38	26.22		0.272×10^{-4}
1366.5	8.416		0.4507×10^{-1}
1477.6	-8.6		18.712

Table II

Size Distribution of the 8th Cycle Regenerated Lime
and Fresh Lime after 5 Hours of Fluidization at 850°C

Size (Tyler Mesh)	Weight Percentage	
	Regenerated lime	Fresh lime
16/20	86.1	30
20/24	13.1	20.8
24/60	0.3	14.7
60-	0.5	34.5

Table III

Flow Sheet Bases and Assumptions

- Coal Feed (dry basis): Illinois No. 6 - 70.56% C, 10% Ash,
10% O, 5% H, 3.33% S,
1.11% N
- Operating Conditions: FBC - 1550°F
BOC - 2000°F
Regenerator - 1832 to 1922°F
- Calcium to Sulfur Ratio: 2.5 moles Ca/mole S
- SO₂ Retention: 80%
- Excess Air: FBC - 20% based on actual combustion requirements
BOC - 25% based on actual combustion requirements
- Attrition: 16% of fresh limestone feed
5% of recycled CaO
1% in regenerator
- Carbon Combustion Efficiency: FBC - 90% once through system (without recycle)
- 97.5% regenerative system (with recycle)
BOC - 90%
- Heat Loss from Equipment: None assumed
- CO Formation: None assumed
- Sorbent Activity Loss: No appreciable loss assumed.

Table IV

Comparison between Once Through Sorbent System
and Regenerative System

	System I <u>Once Through</u>	System II <u>Regenerative</u>
1. Carbon combustion efficiency (%):	98.5	97.5
$\left[\frac{\text{lb carbon combusted}}{\text{lb carbon feed}} \times 100 \right]$		
2. Energy conversion efficiency (%):	89.4	90.9
$\left[\frac{\text{net heat output fr. FBC \& BOC/lb dry coal}}{\text{HHV of coal}} \times 100 \right]$		
3. Limestone feed		
a) lb lime/lb dry coal feed:	0.310	0.021
b) tons/hr (for 200 MWe plant at $\eta = 37\%$):	22.5	1.5
4. Solid wastes		
a) total lb solids/lb dry coal feed:	0.374	0.119
b) lb fly ash and carbon/lb dry coal feed:	0.116	0.106
c) lb lime and sulfate/lb dry coal feed:	0.258	0.013
d) total tons/hr (200 MWe)	27.2	8.6
5. Gaseous emissions		
a) lb SO ₂ /MM BTU:	1.047	1.134*
b) lb NO _x /MM BTU:	0.591	0.591
c) lb particulates/MM BTU:	0.094	0.098
6. 98% H ₂ SO ₄ produced		
a) lb acid/lb dry coal feed:	--	0.082
b) tons acid/hr (200 MWe):	--	6.0

*Includes SO₂ emissions from H₂SO₄ plant.

Table Y

Market Potential for Generated H_2SO_4

1. Anticipated energy contribution by AFBC in the Year 2000 (basis: MOPPS Phase 1 report - ERDA, June 1977)

a) Industrial	3.2 Quads
b) Generating	1.4 Quads
	<u>4.6*</u> Total

2. Tons coal required per year: 213×10^6
3. Tons H_2SO_4 (98%) produced per year: 17.5×10^6
4. Current H_2SO_4 usage (US): 35×10^6 tons/year
5. Projected H_2SO_4 usage (Year 2000): $> 55 \times 10^6$ tons/year
6. Current H_2SO_4 usage for fertilizer production: $\sim 44\%$ of total consumption

* Which is about 10 to 15% of the total anticipated demand for coal energy by the US in the Year 2000.

Figure 1. Sulfation rates at 850°C with 0.25% SO_2 and 5% O_2 in N_2 . $\square$ Fibreboard powder; $\bullet$ powdered $CaSiO_3$ (ROC/RIC, 99.75%); Δ powdered reagent CaO (Mallinckrodt).

Figure 2. Sulfation rates of 16/20 mesh pellets at 900°C with 0.25% SO₂ and 5% O₂ in N₂. ○ CaCO₃; ● CaCO₃ mixed with coal ash; □ CaSiO₃; ■ CaSiO₃ mixed with coal ash (1 to 1 mixture by wt).

Figure 3. Sulfation rates of 16/20 mesh pellets per unit mass of CaCO₃ and CaCO₃ mixed with coal ash (1 to 1) at 900°C with 0.25% SO₂ and 5% O₂ in N₂. The ordinate is based on 25 mg of calcium oxide.

Figure 4. Comparison of sulfation rates of 16/20 mesh Greer lime with various amounts of iron catalyst at 900°C in 0.25% SO₂, 5% O₂, 5% steam and a balance of N₂.

Figure 5. Comparison of sulfation rate between Greer lime (with 0.56% inherent Fe) and Greer lime impregnated with 1.35% Fe at 10 atm and 900°C in 0.25% SO₂, 5% O₂, 5% steam and balance of N₂.

Figure 6. Comparison of rate at 900°C between reaction of CaSO_4/CaS pellets (▲) and decomposition of CaSO_4 pellet (●) in N_2 flow, with 0.645 gr CaSO_4 pellet and 0.09 gr CaS pellet.

Figure 7. Comparison of rate at 1100°C between reaction of CaSO_4/CaS pellets (▲) and decomposition of CaSO_4 pellet (●) in N_2 flow, with 0.645 gr CaSO_4 pellet and 0.09 gr CaS pellet.

Figure 8. Temperature effect on the partial pressure of SO₂ in the kiln regenerator; gas flow rate (Ar), 10 SCCM. T_c = 1050-1070°C (□), T_c = 1000-1020°C (Δ), T_c = 950-970°C (○). T_c was measured along the center of the reactor tube. Four grams of sulfated Greer lime (16/20 mesh) from Argonne's FBC were used.

Figure 9. Partial pressure of CO₂ from the kiln regenerator. Gas flow rate (Ar): 10 SCCM. T_c = 1000-1020°C (Δ), T_c = 950-970°C (○). Four grams of sulfated Greer lime (16/20 mesh) from Argonne's FBC were used.

Figure 10. Gas flow on the SO_2 concentration at $T_c = 1000-1020^\circ C$ from the kiln regenerator; flow rates (Ar); 10 SCCM (Δ), 50 SCCM ($\square$), 150 SCCM ($\circ$). Four grams of sulfated Greer lime (16/20 mesh) from Argonne's FBC were used.

Figure 11. Overall extent of regeneration versus time at $T_c = 1000-1020^\circ C$; flow rate: 50 SCCM ($\square$), 150 SCCM ($\circ$), limiting regeneration rate from TGA measurement (Δ) (N_2 : 500 SCCM, sample weight: 100 mg). Four grams of sulfated Greer lime (16/20 mesh) from Argonne's FBC were used.

Figure 12. Schematic diagram of fluidized-bed sulfator.

Figure 13. Extents of sulfation and regeneration of Greer lime from the cyclic sulfator (S) and regenerator (R). Conditions are shown in text.

Figure 14. Comparison of the sulfation rates between fresh lime and regenerated lime at $T = 900^{\circ}\text{C}$, SO_2 : 0.5%, O_2 : 5%, N_2 : bal. Sample: precalcined lime (□), 2nd cycle regenerated lime (Δ), 4th cycle regenerated lime (○), 8th cycle regenerated lime (∇).

Figure 15. System I - AFBC of coal once thru sorbent system.

PRINCIPAL REACTIONS

Overall Carbon Combustion Efficiency = 98.5%
 LB Solid Wastes/Lb Coal Feed (Dry) = 0.3738
 Gaseous Emissions:
 $SO_2 = 1.047 \text{ LB/MMBTU}$
 $NO_2(NO_x) = 0.591 \text{ LB/MMBTU}$
 Particulates = 0.094 LB/MMBTU

BASIS: 1 ton per hour coal feed (dry basis)

Stream No. Description	1 Coal Feed	2 Lime Feed (Total)	3 Lime Feed (FBC)	4 Lime Feed (BOC)	5 Transf. Sorbent	6 FBC Solids Effl.	7 Air To FBC	8 Air To FBC	9 FBC Gaseous Effl.	10 Prim. Cycl. Effl.	11 Prim. Cycl. Solids	12 Air To BOC	13 Air To BOC	14 BOC Gaseous Effl.	15 BOC Cycl. Effl.	16 BOC Cycl. Solids	17 Electr. Precip. Feed	18 Electr. Precip. Effl.	19 Electr. Precip. Solids	20 Total Air Feed	21 Gases To ATM	22 Total Solids Effl.	23 Cooled Solids Effl.
Carbon	1611.2								161.1	7.1	134.0			13.4	1.3	12.1	8.4	0.4	8.0		0.4	20.1	20.1
Fuel Ash	200.0								212.5	10.6	201.9			201.9	20.2	181.7	30.8	1.6	29.2		1.6	210.9	210.9
Sulfur	66.6																						
Hydrogen	100.0																						
Oxygen	200.0						4,677.5	246.2	820.6	820.6		40.2	361.8	80.4	80.4		901.0	901.0		5,325.7	901.0		
Nitrogen	22.2						15,396.8	810.4	16,224.8	16,224.8		132.3	1,191.0	1,323.3	1,323.3		17,548.1	17,548.1		17,530.5	17,548.1		
Water	61.9	7.4	6.2	1.2			200.7	10.6	1,179.4	1,179.4		1.7	15.6	18.5	18.5		1,197.9	1,197.9		228.6	1,197.9		
Carbon Dioxide									4,847.8	4,847.8				480.3	480.3		5,328.1	5,328.1			5,328.1		
Sulfur Dioxide									26.6	26.6							26.6				26.6		
Nitr. Oxides									15.0	15.0							15.0				15.0		
Calc. Carbonate		520.3	433.6	86.7					40.8	2.0	38.8			46.6	4.7	41.9	6.7	0.3	6.4		0.3	197.8	197.8
Calc. Oxide					40.8	149.5															226.5	226.5	
Calc Sulfate					12.9	226.5			12.9	0.6	12.3			14.8	1.5	13.3	2.1	0.1	2.0		0.1	92.3	92.3
Stone Ash		92.4	77.0	15.4		77.0																	
Total(Lb/Hr)	2,061.9	620.1	516.8	103.3	53.7	453.0	20,275.0	1,067.2	23,521.5	23,134.5	387.0	174.2	1,568.4	2,179.2	1,930.2	249.0	25,064.7	25,019.1	45.6	23,084.8	25,019.1	747.6	747.6
Temp.(°F)	77	77	77	77	2000	1550	620	100	730	730	730	100	620	730	730	730	730	730	730	77	310	1250	300

Figure 16. MB-AFBC of coal once thru sorbent.

Figure 17. System II - AFBC of coal regenerative sorbent system kiln process.

PRINCIPAL REACTIONS

Overall Carbon Combustion Efficiency = 97.5%
 LB Solid Wastes/LB Coal Feed (Dry) = 0.1191
 Gaseous Emissions:
 $\text{SO}_2 = 1.134 \text{ LB/MMBTU}^*$
 $\text{NO}_x(\text{NO}_2) = 0.591 \text{ LB/MMBTU}$
 Particulates = 0.098 LB/MMBTU

BASIS: 1 ton per hour coal feed (dry basis).

* Includes H_2SO_4 Plant Emissions.

Stream No. Description	1 Coal Feed	2 Lime Makeup	3 Lime Recycle	4 Lime Feed	5 FBC Solids Effl.	6 Air To FBC	7 FBC Gaseous Effl.	8 Prim Cyclone Effl.	9 Recycle Solids	10 2nd Cyclone Effl.	11 Solids To Regn.	12 Elect. Precip. Effl.	13 Elect. Precip. Solids	14 Gases To ATM	15 Dry Air To Regn.	16 Regr. Gas. Effl.	17 Fines To Disposal	18 Cyclone Effl.	19 Collect Solids	20 Air Feed	21 Collect Solids	22 SO_2 To H_2SO_4 Plant	23 Ash To Disposal
Carbon	1,411.2						353.0	35.3	317.7	10.6	24.7	0.3	10.3	0.3		0.6	1.7	0.2	0.4		0.2	Trace	2.3
Fuel Ash	200.0						2,125.0	212.5	1,912.5	63.8	148.7	1.9	61.9	1.9		52.7	157.9	15.8	36.9		15.6	0.2	210.4
Sulfur	66.6																						
Hydrogen	100.0																						
Oxygen	200.0					5,262.4	877.1	877.1		877.1		877.1		877.1	60.5					5,262.4			
Nitrogen	22.2					17,322.1	17,339.7	17,339.7		17,339.7		17,339.7		17,339.7	199.1	199.1		199.1		17,322.1		199.1	
Water	61.9	0.5		0.5		225.8	1,188.2	1,188.2		1,188.2		1,188.2		1,188.2						225.8			
Carbon Dioxide							5,060.3	5,060.3		5,060.3		5,060.3		5,060.3		119.9		119.9				119.9	
Sulfur Dioxide							26.6	26.6		26.6		26.6		26.6		106.6		106.6				106.6	
Nitr. Oxides							15.0	15.0		15.0		15.0		15.0									
Calc. Carbonate		34.8		34.8			167.0	16.7	150.3	5.0	11.7	0.2	4.8	0.2		4.8	14.5	1.4	3.4		1.4	Trace	19.3
Calc. Oxide			271.9	271.9	181.4																		
Calc. Sulfate					226.5																		
Stone Ash		6.2	86.2	92.4	87.1		53.0	5.3	47.7	1.6	3.7	0.1	1.5	0.1		1.5	4.6	0.5	1.0		0.5	Trace	6.1
Total (LB/Hr)	2,061.9	41.5	358.1	399.6	495.0	22,810.3	27,204.9	24,776.7	2,428.2	24,587.9	188.8	24,509.4	78.5	24,509.4	259.6	485.2	178.7	443.5	41.7	22,810.3	17.7	425.8	238.1
Temp. (°F)	77	77	1832	1666	1550	590	730	730	730	730	730	730	730	310	1800	1832	1832	1832	1832	77	800	934	300

Figure 18. MB-AFBC of coal regenerative sorbent system-kiln proc.

Figure 19. System II - AFBC of coal regenerative sorbent system sulfuric acid plant.

PRINCIPAL REACTIONS

*Estimated to be within environmental emission regulation of 0.15 LB of H_2SO_4 mist per ton of H_2SO_4 produced.

Stream No. Description	1 SO ₂ Feed	2 Amb. Air	3 Compr. Air	4 Air To Reg'r	5 Air To Convert.	6 Convert Feed	7 Convert Feed (Heated)	8 1st Stg Prod.	9 2nd Stg Feed	10 2nd Stg Feed	11 2nd Stg Prod.	12 3rd Stg Feed	13 3rd Stg Prod.	14 4th Stg Feed	15 4th Stg Product (SO ₃)	16 Absorb Feed	17 Gaseous Effl.	18 Absorb. Bottoms	19 Recycle Acid	20 Water	21 98% H ₂ SO ₄	22 Collect Solids	23 Absorb. Acid	24 Drying Acid	25 98% H ₂ SO ₄ PProd
Carbon	Trace					Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace		Trace	Trace	Trace	Trace	Trace
Fuel Ash	0.2					0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		0.2	0.2	Trace	Trace	Trace
Oxygen		113.8	113.8	60.5	53.3	53.3	53.3	34.2	34.2	34.2	28.3	28.3	28.3	27.2	27.2	27.2	27.2	48.0	44.4	27.7	120.1		77.4	39.5	3.2
Nitrogen	199.1	374.6	374.6	199.1	175.5	374.6	374.6	374.6	374.6	374.6	374.6	374.6	374.6	374.6	374.6	374.6	374.6								
Water		4.9	4.9																						
Sulfur Dioxide	106.6					106.6	106.6	30.1	30.1	30.1	6.5	6.5	3.0	3.0	2.2	2.2	2.2								
Carbon Dioxide	119.9					119.9	119.9	119.9	119.9	119.9	119.9	119.9	119.9	119.9	119.9	119.9	119.9								
Sulfur Trioxide								95.6	95.6	95.6	125.1	125.1	129.5	129.5	130.5	130.5	Trace								
H ₂ SO ₄																		3,953.3	1,933.7		5,887.0	Trace	3,793.4	1,933.7	159.9
CaO	Trace					Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace		Trace	Trace	Trace	Trace	Trace
Stone Ash	Trace					Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace		Trace	Trace	Trace	Trace	Trace
Total (LB/HR)	425.8	493.3	493.3	259.6	228.8	654.6	654.6	654.6	654.6	654.6	654.6	654.6	654.6	654.6	654.6	654.6	654.6	4,001.5	1,978.1	27.7	6,007.3	0.2	3,870.8	1,973.2	163.1
Temp. (°F)	934	77	139	122	122	650	770	1112	996	806	905	806	833	801	806	122	122	187	136	77	187	187	122	122	122

Figure 20. MB- H_2SO_4 plant regenerative sorbent system-kiln proc.

Distribution;

A. Macek, FE/DOE (25)
W. E. Winsche, BNL
K. C. Hoffman, BNL
B. Manowitz, BNL
D. H. Gurinsky, BNL
M. Steinberg, BNL
R. T. Yang, BNL (5)
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, DOE (BNL)
R. Smol, BNL
D. B. Henschel, EPA
J. W. Jones, EPA
F. Princiotta, EPA
H. B. Levine, Jaycor
F. B. Hill, BNL
C. L. Steen, BNL