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EXPERIENCES IN REGENERATING SULFATED LIMESTONE FROM FLUIDIZED-BED COMBUSTORS

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SYNOPSIS

The experiences at Argonne National Laboratory in developing a process for regenerating the partially sulfated limestone product from a fluidized-bed combustion process are described. Studies of candidate processes and the further development of the reductive-decomposition process wherein $CaSO_4$ is converted to CaO in a fluidized bed at 1100°C are discussed. Reductive decomposition reaction rates are rapid--less than 10 minutes is required for effective regeneration. A gas containing SO_2 at concentrations near 10% is produced. Stones were cycled batchwise between the combustor and regenerator to demonstrate that reactivity of the stone can be sufficiently maintained and that attrition rate of particles in the fluid bed is low. Regeneration can significantly reduce the quantity of fresh stone required in the combustion step.

NOTATION

cm	centimeter
°C	degree Celsius
dia	diameter
F	mean feed sorbent particle size, μm
hr	hour
ID	inside diameter
kPa	kilopascal
m	meter
min	minute
%	percent
R	total reducing gas concentration, %
s	second
T	operating temperature, °C
V_d	defluidization velocity, m/s
wt	weight

INTRODUCTION

The quantity of pollutants--SO_2, NO_x, and particulate solids--permitted to be released in the flue gas from boilers in the United States is now regulated. Control of SO_2 is the most difficult since NO_x release can be kept within specifications by modification of boiler equipment, and particulates can be controlled by proper choice of equipment. Currently, low SO_2 concentrations are achieved by burning low-sulfur-content fossil fuels (either naturally occurring fuels or fuels from which sulfur has been removed prior to combustion) or by combustion of high-sulfur fuels accompanied by scrubbing of the flue gas. New techniques for pollution control are being developed. In one of these, fluidized-bed combustion, coal is burned in a bed of granular particles, limestone ($CaCO_3$) or a dolomite ($CaCO_3 \cdot MgCO_3$), that are kept in suspension by an upflowing stream of combustion air. The calcium in the bed particles combines with the sulfur released during coal combustion. Development of fluidized-bed combustion systems is proceeding rapidly--a 20-MWe, atmospheric pressure combustor has been constructed (Mesko, 1976); a 20-MWe, pressurized combustor is being designed (Energy Daily, 1977).

Although the release of sulfur compounds to the atmosphere is effectively controlled by this method, the impact of quarrying large quantities of the limestone and of handling the $CaSO_4$-containing solids generated in the process must be examined more thoroughly. In the case of a typical bituminous coal containing 4% sulfur, the quantity of rejected sulfated stone can be greater than the quantity of ash that must be discarded (Johnson, 1977; Vogel *et al.*, 1974; Pope, Evans and Robbins, Inc., 1975). The rejected sulfated stone and ash can probably be used as landfill or disposed of in open pits in an environmentally safe manner (Nat. Res. & Dev. Conf., 1973; Westinghouse, 1974). Methods for commercially utilizing the material may also be developed. Studies are underway to determine if the available lime and sulfate in the reject stone can be used for agricultural purposes (Minnick, 1977) or as a component in the manufacture of cement blocks (Westinghouse, 1974). The quantity of reject that can be used in these applications is uncertain and, since a large quantity may have to be disposed of, options for reducing the quantity

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of stone used in the process should be examined. Five options are available, as follows:

1. Since stones vary in reactivity (Vogel *et al.*, 1977), use only the reactive stones. However, reactive stones may be unavailable within an economic distance of the combustion plant.

2. Modify nonreactive stones by changing the porosity, thereby increasing the quantity of sulfur that can be captured. Two methods have been demonstrated--(1) a slow calcination of the stone (O'Neill, 1976) and (2) salt addition (Pope, Evans and Robbins, 1975). In the slow calcination method, the stone would probably be precalcined in a separate vessel specially constructed for this purpose. In the second method, additives NaCl, Na_2CO_3, Na_2SO_4, KCl, and $CaCl_2$, have effectively increased the utilization of the calcium by 25 to 200% (Johnson, 1977). The chlorides of sodium and potassium appear to be the most effective. If the porosity of a stone before treatment is satisfactory for collecting sulfur [pores of a size larger than 0.3 μm are the effective collectors of the sulfur oxide (Potter, 1969)], the treatment may change the pore structure unacceptably. Studies have started at ANL to determine the possible corrosive effects of these additives on metals present in the boiler and ancilliary equipment.

3. Tailor-make a synthetic stone that has the porosity characteristics for good sulfur oxide sorption and which can be reused, *i.e.*, can be regenerated by a process to be described later. The best synthetic sorbent developed, containing 20% CaO impregnated on alumina, was about 60% as reactive as Greer limestone, one of the more reactive naturally occurring limestones (Snyder, 1977). Preparation of synthetics is expensive, ∿\$200/tonne, and unless a cheaper preparation method can be developed, this option may not be feasible.

4. Adjust boiler operating conditions using higher bed temperatures, lower gas velocities, and longer particle residence times, which will help utilize more of the calcium in the particle. These conditions, however, often conflict with other requirements for the boiler or the process and generally cannot be applied.

5. A fifth method is to regenerate the sulfated stone for reuse in the combustor, which is the topic of this paper.

SELECTION OF THE REGENERATION PROCESS

Thermodynamic and kinetic information were obtained from the literature on processes for converting calcium sulfate to calcium oxide (Swift, 1976). Of the processes examined, thermal decomposition of the calcium sulfate was not considered to be a viable process because of the high temperature, >1200°C, needed to obtain a high concentration of SO_2 in the off-gas. At this temperature, ash and sulfated stone would fuse to form unusable clinkers.

Another process, studied in laboratory scale equipment, consisted of two steps. CaS produced in the first step by reacting $CaSO_4$ with a reducing gas at ∿870°C is reacted with steam/CO_2 at ∿560°C to produce $CaCO_3$ and H_2S. Cyclic processing by alternate sulfation and regeneration showed that the extent of regeneration of the $CaSO_4$ decreased significantly in succeeding cycles (Vogel, 1972). Attempts to understand the mechanism and to develop the process further were abandoned when it became necessary to select a process for larger-scale development. Selected for further development was the reductive decomposition process in which $CaSO_4$ is heated in a fluidized bed to ∿1100°C in the presence of reductant gases. The products are CaO, which is reused in the combustion step, and a SO_2 containing off-gas, which can be processed for its sulfur content. Calcium sulfide can also form in the bed, but its concentration is maintained below 0.5% by circulating particles into an oxidizing zone of the bed where CaS is converted to $CaSO_4$.

EQUIPMENT

Figures 1 and 2 illustrate the Process Development Unit (PDU) combustion and regeneration systems used in this investigation. The combustor is 15-cm ID and approximately 3.4 m high. The regenerator consists of a nominal 20-cm-dia pipe, refractory-lined to an ID of 7.5 cm in the early experiments and to 10.8 cm in later experiments. Bubble-type gas distributor plates are flanged to the bottom of each reactor and accommodate fluidizing-air inlets, solids feed and removal lines, and thermocouples for monitoring the bed temperatures. In each system, the coal and sorbent are metered separately to a single pneumatic transport line which discharges these solids into the fluidized bed above the gas distributor plate. Expanded-bed heights of ∿0.9 m in the combustor and ∿46 cm in the regenerator are maintained with overflow pipes.

MATERIALS

The two sorbents tested were Tymochtee dolomite and Greer limestone. The dolomite contained ∿50 wt % $CaCO_3$, 39 wt % $MgCO_3$, and 2.1 wt % Si as received. The limestone contained 41.2 wt % CaO, 32 wt % CO_2, and 4.3 wt % Si. The nominal size distribution of each limestone was -14 +30 U.S. mesh in most, but not all, experiments.

Arkwright mine, Pittsburgh seam coal contained ∿2.8 wt % S, ∿7.7 wt % ash, and ∿2.9 wt % moisture and had a heating value of 7,600 kcal/kg and an average particle size of 320 μm.

In cyclic studies with Tymochtee dolomite, Triangle coal, a high-volatile, bituminous coal with a high-ash fusion temperature, 1390°C, was combusted in the regenerator. It contained 1.0% S and 9.4 wt % ash.

Sewickley coal, as received, contained ∿4.3

wt % S, 12.7 wt % ash, and 1.1 wt % moisture and had a heating value of 7,200 kcal/kg. Particle size range was -6 +14 mesh.

DEVELOPMENT OF THE REDUCTIVE DECOMPOSITION PROCESS

Methane gas was used in early experiments and coal in later experiments as a source of the reducing gases for the reaction. Coal is considered attractive since it is cheaper than methane. Also, it would be available at the combustion plant. The initial experimental work using methane reductant was carried out in a 7.5-cm-dia regenerator and generally with a 0.46-m-high bed. The results showed that the use of a shallower bed (0.46 m instead of 0.76 m), a lower fluidizing gas velocity (0.67 m/s instead of 0.92 m/s), and higher reaction temperature (1100°C instead of 1010°C) generally increased both the extent of regeneration and the SO_2 concentration in the effluent gas (Montagna & Lenc, 1977). Attrition losses ranged from 5 to 15% of the solids processed. Partial agglomeration of the bed particles occurred when the bed temperature was higher than 1100°C, the reducing gas concentration was greater than 5%, and when also the fluidization velocity was inadequate.

In the major experimental effort, using coal as the source of the reducing agent, the effects of solids residence time (7-35 min), regeneration temperature (1000-1100°C), and pressure (115-153 kPa) on the extent of calcium oxide regeneration and the SO_2 concentration in the off-gas were investigated in a 10.8-cm-dia regenerator (Montagna & Swift, 1977). The extent of regeneration improved at higher bed temperature and with longer particle residence time. Calculated results using an equation developed for regenerating sulfated Tymochtee dolomite using Triangle coal have been plotted in Fig. 3 (the data have been extrapolated for bed temperatures above the maximum temperature used in these experiments, 1100°C). Studies with sulfated Greer limestone/Arkwright coal have shown that extent of regeneration of the limestone is about the same as for the dolomite at similar operating conditions (Vogel *et al.*, 1977).

The SO_2 concentration in the off-gas increased at higher temperature, at shorter solids residence time, and at lower pressure. Typically, the SO_2 concentration in the off-gas ranged from 8-10%. Calculated concentrations obtained from an equation developed using the experimental results from the Tymochtee dolomite and Triangle coal experiments are plotted in Fig. 4. The reaction rate is rapid at ~1100°C and, with a few percent reducing gas in the bed, production rates greater than a half-tonne per day were achieved.

Bed defluidization velocity, *i.e.*, minimum velocity required to prevent particle agglomeration, was studied in a statistical experiment performed with Greer limestone and Sewickley coal (Montagna & Nunes, 1977). The effects on defluidization velocity of bed temperature (1050 and 1100°C), total reducing gas concentration (2.5 and 5.0%) and feed sorbent particle size range (-10 +30 mesh and -14 +30 mesh) were determined. Defluidization velocities in this study ranged from 0.9 to 1.6 m/s. Defluidization velocity as a function of temperature and reducing gas concentration is shown in Fig. 5 along with minimum fluidization velocities. The effect of particle size is minimal. A least-squares fit of the results is the basis for the following equation:

$$V_d = 4.05 - 3.61 \times 10^{-3}T - 2.6R + 2.54 \times 10^{-3}TR + 5.26 \times 10^{-4}F \qquad (1)$$

CYCLIC STUDIES

The feasibility of the regeneration process depends on the ability to recycle the sorbent a sufficient number of times without loss of sorbent reactivity for either sulfation or regeneration and without severe decrepitation of the particles. If either requirement is not met, the sorbent makeup rate will be too high to justify regeneration.

Two series of experiments were performed to evaluate the effects of repeated utilization on the reactivity and attrition resistance of two stones--Tymochtee dolomite and Greer limestone. Each series consisted of ten combustion/regeneration cycles. Arkwright coal was used in the experiments made with Tymochtee dolomite and Sewickley coal in the Greer limestone experiments. In the dolomite series of experiments the combustion was done at elevated pressure (8 atm) coupled with regeneration at atmospheric pressure. In the limestone studies, combustion at 3 atm pres. simulated combustion at atmospheric pressure (the $CaCO_3$ calcines at this pressure as it does in atmospheric pressure combustion), and regeneration was done at atmospheric pressure.

Cyclic Sorbent Life Study with Tymochtee Dolomite

Conditions in the combustion step were a 900°C bed temperature, a 810 kPa system pressure, a constant CaO/S mole ratio of 1.5 (ratio of unsulfated calcium in sorbent to sulfur in coal), ~17% excess combustion air, a 0.9 m/s fluidizing gas velocity, and a 0.9 m bed height.

The regeneration step of each cycle was performed at a system pressure of 158 kPa, a bed temperature of 1100°C, a fluidizing gas velocity of 1.2 m/s, a fluidized-bed height of ~46 cm, and a solids residence time of ~7.5 min.

Changes in reactivity of the sorbent from cycle to cycle were reflected in changes in the SO_2 levels in the flue gas of the combustor (Vogel *et al.*, 1976, Sept. 1976, Dec.

1976). Fresh sorbent was not added during the test.

Sulfur Acceptance and Release. Sulfur dioxide levels increased from ~330 ppm in cycle 1 to ~950 ppm in cycle 10 (see Fig. 6). This represents a decrease in sulfur retention from ~88% in cycle 1 to ~55% in cycle 10. It appears that the reactivity of the sorbent for sulfur retention decreased linearly with combustion cycle over the 10-cycle experiment.

There was no apparent loss in regenerability over the ten utilization cycles. The extent of CaO regeneration based on solids analysis varied from 67 to 80%. The SO_2 concentration in the dry off-gas varied from 6 to 9%.

Sorbent Makeup Requirements to Meet EPA Sulfur Emission. Based on the data from the cyclic combustion/regeneration batch experiment, the sorbent makeup rate which would be required in a continuous recycle operation to meet the EPA sulfur emission limit was estimated.

Adaptation of a procedure developed by Nagier (Nagier, 1964) resulted in an analytical expression for the age distribution of the combustor charge as a function of makeup rate assuming a continuous recycling of solids between the regenerator and combustor.

The result of combining the data in Fig. 6 with the expression is presented in Fig. 7. As an example of using Fig. 7, an α of ~0.2 (makeup CaO/total CaO) indicates that a makeup CaO/S ratio of ~0.27 and a total CaO/S ratio of ~1.5 are required for a sulfur retention of 75%. In comparison to the once-through CaO/S ratio of ~0.93 for 75% sulfur retention, the makeup of 0.2 for a cyclic process corresponds to an estimated savings of 78% of the fresh limestone requirements.

Particle Porosity Changes. It has been reported that most sulfation takes place in larger pores and that pores smaller than 0.3 μm are relatively easy to plug. During sulfation of CaO, the pores shrink as a result of molecular volume changes.

The porosity of sulfated dolomite was relatively unaffected by number of cycles, although the sulfur content decreased from ~10 wt % in the first cycle to ~7 wt % in the tenth cycle. However, the porosity of the regenerated dolomite consistently decreased with each cycle, as did the sulfur content of the regenerated stones. As a result of this decrease in porosity with use, effectiveness of the sorbent as an SO_2 acceptor decreased.

Coal-Ash Buildup. Based on silicon enrichment of samples, coal-ash buildups were calculated. After the tenth cycle, it was found that for every 100 g of starting dolomite, ~13 g of coal ash had accumulated in the sorbent. Photomicrographs clearly reveal that even the once-sulfated stones were beginning to be coated with coal ash.

A petrographic examination revealed the buildup of a vitreous crust surrounding most of the particles. X-ray diffraction analyses of the crust revealed the presence and accumulation of $Ca(Al_{0.7}Fe_{0.3})_2O_5$ with increasing number of cycles.

Electron microprobe analyses also confirmed the existence of the coal-ash shell. The ash which encapsulated the particle was strongly enriched with iron but contained very little sulfur. Sulfur profiles in scans of regenerated particles indicate that nearly complete regeneration occurred. Therefore, the presence of a coal-ash shell did not prevent sulfur from escaping during regeneration.

Attrition and Elutriation Losses. Sorbent losses for each cycle are given in Table 1. Although the first cycle combustion loss was quite large, losses during the remaining combustion-regeneration cycles were reasonably small, averaging about 8% per cycle. The lower losses during regeneration can probably be attributed to the very short solids residence time (~7.5 min) in this reactor, as compared with the much longer solids residence time (~5 hr) for sulfation in the combustor.

Table 1. Attrition and Elutriation Losses for Tymochtee Dolomite during Combustion and Regeneration in the Cyclic Utilization Study.

Cycle No.	Loss During Combustion (wt %)	Loss During Regeneration (wt %)
1	16	1.9
2	4	1.7
3	5	3.0
4	3	1.2
5	3	3.5
6	6	3.7
7	4	2.0
8	7	2.6
9	6	0.9
10	4	1.3

Cyclic Sorbent Life Study with Greer Limestone

The combustion conditions were a 308-kPa system pressure, 855°C bed temperature, ~17% excess combustion air, a 1.0 m/s fluidizing gas velocity, a 0.9 m bed height, and a constant sulfur retention of ~84% by the sorbent. In this study, in which the concentration of SO_2 in the flue gas was held constant by adding limestone as required (in the dolomite cyclic study, the CaO/S ratio was held constant), changes in sorbent reactivity were reflected in changes in the CaO/S ratio required to achieve the constant concentration (in the dolomite cyclic study, SO_2 retention was the dependent variable of reactivity).

The nominal operating conditions during the regeneration step in each cycle were a system pressure of 128 kPa, a bed temperature of 1100°C, a fluidizing-gas velocity of ~1.2 m/s, a total reducing gas concentration of ~3.0% in the dry off-gas, and a fluidized-bed height of ~46 cm. The residence time of the sorbent was nominally 7 min (Vogel, *et al.*, Mar. 1977).

Sulfur Acceptance During Combustion. The cyclic calcium utilization (*i.e.*, the percentage of CaO that was sulfated during each combustion step in the cycle) and the calcium present as $CaSO_4$ in the sulfated sorbent product at the end of each combustion half cycle are shown in Fig. 8. The calcium utilization decreased from ~30% in the first cycle to ~9% in the tenth cycle. Thus, in order to maintain a constant sulfur retention of 84%, it was necessary to increase the CaO/S ratio (which was ~2.9 during the first combustion cycle) by a factor of ~3 over the ten cycles. This loss of reactivity agrees closely with the loss of reactivity observed for the experiments with Tymochtee dolomite.

Sulfur Release During Regeneration. Results for the regeneration step of the ten cycles were similar to those for the Tymochtee experiments. The SO_2 concentration in the dry off-gas varied from 6 to 9%. The regenerability of the limestone remained acceptable in all ten cycles ranging from 49 to 73%.

Porosity of Sorbent. Porosity effects were essentially the same as those observed in the Tymochtee series of experiments.

Coal-Ash Buildup. In the tenth cycle, for every 100 g starting limestone, ~25 g of coal ash had accumulated, higher than in the Tymochtee dolomite experiment. Arkwright coal, however, which was used in the dolomite experiment, contains less ash, 7.7 wt %, than does Sewickley coal, 12.7 wt %.

Limestone particles from the first cycle were observed to contain some adhered coal ash. Particles from the tenth-cycle appeared to have more adhering ash than the first-cycle particles. However, not all particles were encapsulated with coal ash, as was the case with particles from the cyclic dolomite experiments. Many of the tenth-cycle limestone particles were visually identical to first cycle particles, which would indicate that the ash layer thickness was not increasing.

Attrition and Elutriation of Particles. The limestone losses caused by attrition were ~2.0% during each regeneration step. During sulfation, the loss was ~20% in the first cycle and steadily decreased to ~4% per cycle in the final cycles. The larger attrition loss in the first sulfation step can be attributed to calcination. In subsequent cycles, the resistance of the particles to attrition increased because of (1) sulfate hardening and (2) the partial sintering which occurs at the regeneration temperature.

The losses during sulfation were slightly higher in the dolomite experiment. However, combustion conditions differed in the two series of experiments. The Greer limestone was fully calcined at the system pressure of 307 kPa and the bed temperature of 855°C, whereas the Tymochtee dolomite was not fully calcined at 810 kPa and 900°C.

The combined losses average ~10% per cycle. The makeup rate would have to be at least ~10% to replenish losses and a makeup rate greater than 10% will be required to maintain the SO_2-sorption reactivity of the fluidized-bed solids.

ACKNOWLEDGMENTS

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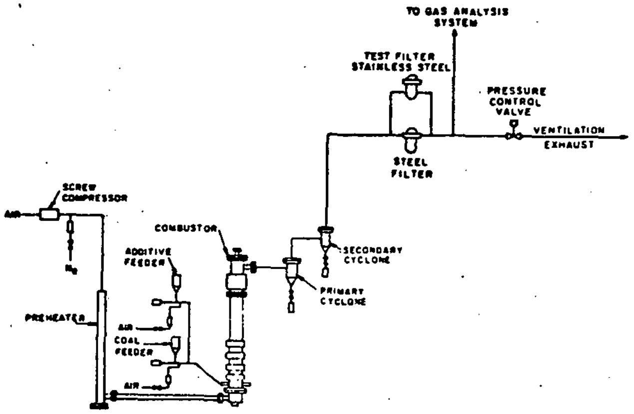

Fig. 1. Simplified Equipment Flowsheet of Fluidized-Bed Combustion Process Development Unit and Associated Equipment

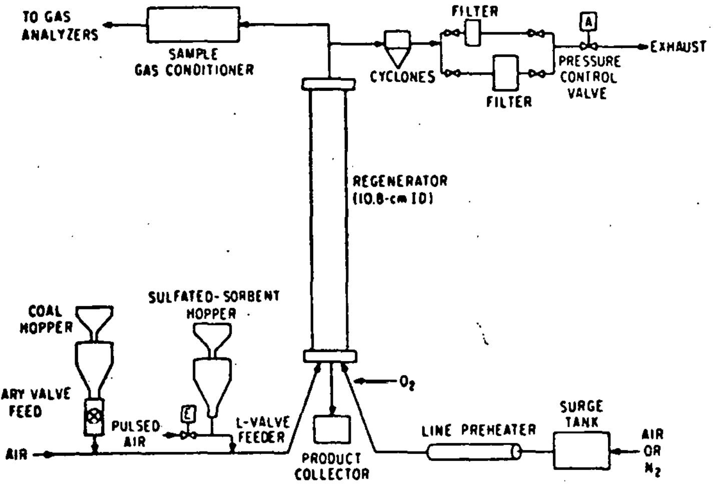

Fig. 2. Experimental Sorbent Regeneration System

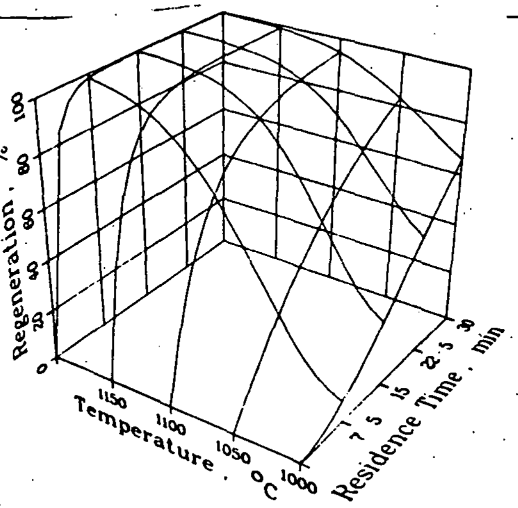

Fig. 3. The Extent of CaO Regeneration for Tymochtee Dolomite as a Function of Temperature and Residence Time

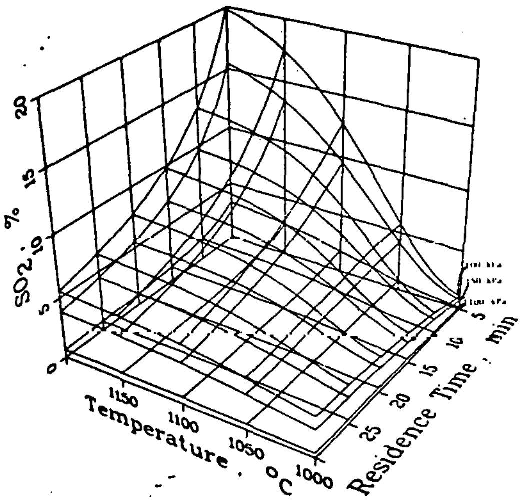

Fig. 4. SO_2 Concentration in Off-Gas from Regeneration of Sulfated Tymochtee Dolomite

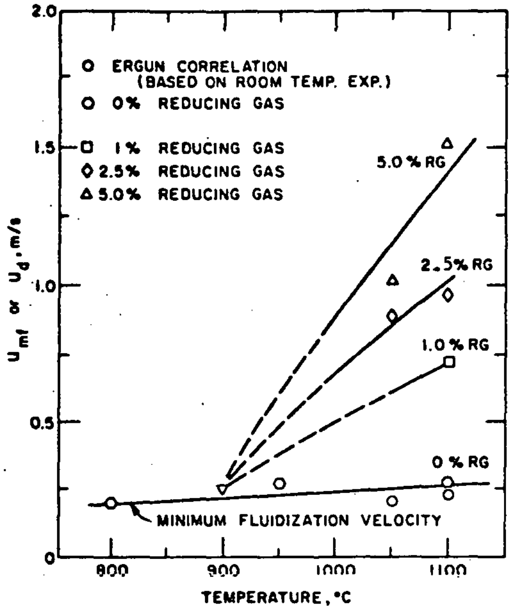

Fig. 5. Defluidization and Minimum Fluidization Velocity vs. Temperature

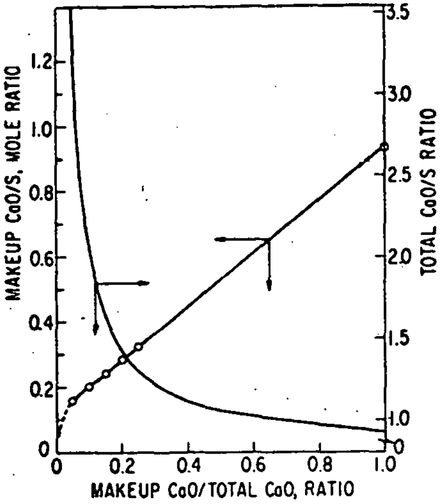

Fig. 7. Calculated Makeup and Total CaO/S Ratios Required to Achieve 75% Sulfur Retention as a Function of the Makeup CaO to Total CaO Ratio. Sulfation Conditions: Temp, 871°C; Pres, 810 kPa; Sorbent, Tymochtee dolomite.

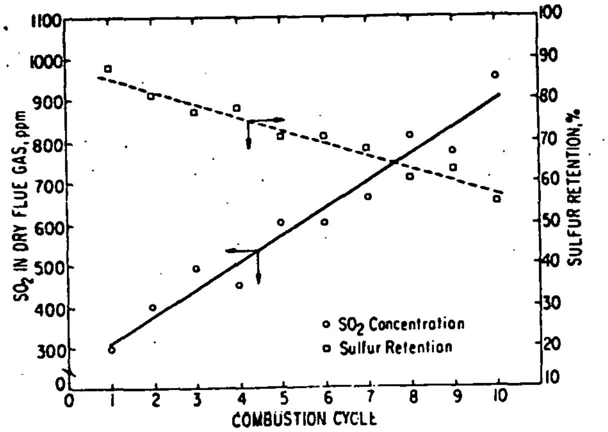

Fig. 6. Sulfur Retention in Bed and SO_2 Concentration in Flue Gas as a Function of Cycle Number

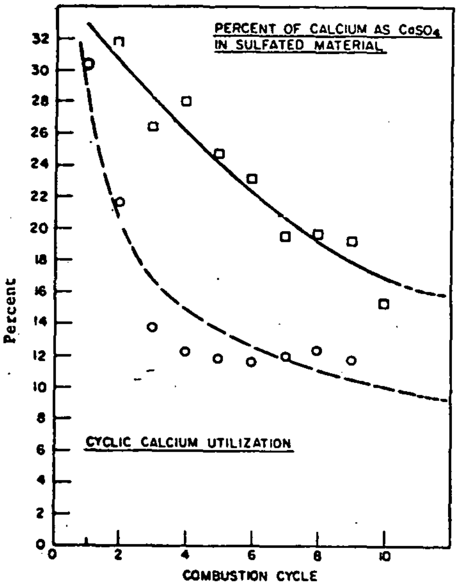

Fig. 8. Cyclic Calcium Utilization and Calcium Present as $CaSO_4$ for Greer Limestone at 84% Sulfur Retention