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FLUIDIZED-BED REGENERATION OF SULFATED DOLOMITE FROM A COAL-FIRED FBC PROCESS BY REDUCTIVE DECOMPOSITION

by

John C. Montagna, Gerhard J. Vogel,
Gregory W. Smith, and Albert A. Jonke

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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Chemical Engineering Division

April 1977

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TABLE OF CONTENTS

TABLE OF CONTENTS (Contd.)

LIST OF FIGURES

LIST OF FIGURES (Contd.)

LIST OF TABLES

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ABSTRACT

A fluidized-bed, reductive decomposition process has been developed for regenerating $CaSO_4$, a product of fluidized-bed combustion. The effect of process operating variables on the extent of regeneration and on SO_2 levels in the off-gas has been determined, and a process model has been proposed.

SUMMARY

A process for regenerating spent SO_2 sorbents has been developed on a PDU scale. Tymochtee dolomite that had been sulfated during fluidized-bed combustion of coal is regenerated (reductive decomposition of $CaSO_4$ to CaO and SO_2) by the incomplete combustion of either methane or coal in a fluidized-bed reactor.

In the first investigation (methane was the fuel used), the effects of the operating variables (temperature, fluidizing gas velocity, fluidized-bed height, solids residence time, and total reducing gas concentration in the effluent) on the regeneration of CaO and on the buildup of CaS were examined. It was found that:

1. Deeper beds resulted in poorer regeneration because of unfavorable bed geometry.
2. Increasing the fluidizing-gas velocity adversely affected regeneration.
3. Higher regeneration temperatures increased the extent and the rate of regeneration. However, dolomite that had been regenerated at a lower temperature was more reactive during subsequent sulfation.
4. In preliminary regeneration experiments, 5 to 15% of the sulfated dolomite (calcium basis) was lost, mainly by attrition. Solids residence time ranged from 18 to 30 min.
5. Electron microprobe analysis of the regenerated particles suggested a two-stage particle desulfurization mechanism. In the first stage, the sulfated core shrinks relatively rapidly (reaction limited); in the second stage, the residual sulfur is removed more slowly (diffusion limited).
6. Concentrations of SO_2 in the dry off-gas ranged from 0.8 to 7.3%.
7. The extent of regeneration ranged from 21% to 89%.
8. In experiments performed with $\sim$3% total reducing gas in the effluent, $\leq$0.1% sulfide was found in steady state regenerated dolomite samples; with $\sim$15% reducing gas in the effluent, sulfide concentrations in the products were of the order of 0.3-0.7%.

In the second investigation (coal was the fuel used), the effects of solids residence time (7-35 min), regeneration temperature (1000-1100°C), and system pressure (115-153 kPa) on (1) the extent of regeneration to CaO and (2) the SO_2 concentration in the off-gas were investigated. The extent of regeneration improved at higher temperatures and longer solids residence times. A regeneration of $\sim$70% was accomplished at 1100°C with a solids residence time of $\sim$7 min. The SO_2 concentration in the dry off-gas increased at higher temperature (to >10% in the dry off-gas at 1100°C), at shorter solids residence time (bed weight/mass feed rate), and at lower pressure.

The results from these experiments were analyzed statistically, and an equation for the extent of CaO regeneration as a function of (1) sorbent residence time in the reactor and (2) regeneration temperature was obtained. This equation was used in the third section of this report in a mass and energy constrained model for the regeneration process, and a preliminary process sensitivity analysis has been performed. The fuel burden of sorbent regeneration when a 3 wt % S coal is burned in a power generation system has been estimated at 2-3%.

INTRODUCTION

The current national goal, to become less dependent on foreign energy resources, is heavily dependent on increased utilization of domestic high-sulfur coal. To this end, fluidized-bed combustion of coal is currently being developed for electric power and/or steam generation. In the fluidized-bed coal combustion process, high-sulfur coal is combusted in a fluidized bed (∿900°C) of a sulfur-accepting sorbent. Natural calcium-based stones such as limestones and dolomites are receiving primary consideration as sulfur-accepting sorbents (sulfur reacts with calcium to form $CaSO_4$). The primary reasons are their acceptable reactivity, their low costs, and their bountiful supply throughout the United States.

Approximately one tonne of natural stone will be sulfated for every four tonnes of coal (∿3 wt % S) combusted. In a 1000-MW electric power plant (70% capacity factor), ∿2000 tonnes of stone per day will be sulfated. If the stone is used only once, this will generate large amounts of sulfated stone for disposal. Multicyclic utilization of the stones by regenerating the CaO is a potentially attractive alternative which would greatly reduce the quantity of solid waste that must be disposed of. Based on present dolomite or limestone cost, the feasibility of using a sorbent regeneration process in FBC power generation will depend on the cost of regeneration and on the environmental impact of the solid waste.

A conceptual power-generating facility utilizing fluidized-bed coal combustion and sorbent regeneration systems is schematically represented in Fig. 1. Steam is removed from the boiler and is expanded in turbines to generate power. The flue gas (off-gas) from the boiler meets EPA chemical emission requirements. After the sulfated sorbent is transferred to the regenerator and regenerated, this sorbent is combined with fresh sorbent (to compensate for losses due to attrition and changes in reactivity) and is recycled to the boiler. The SO_2-rich off-gas from the regenerator is treated in a sulfur recovery plant.

For sulfur recovery, a process that uses coal as a reductant is recommended, such as the Foster-Wheeler RESOX process.[1] It is recommended that the off-gas from the sulfur recovery step be recycled to the boiler and thus eliminate tail gas processing from the sulfur recovery step. (The gas volume throughput in the regenerator is much smaller than that in the boiler.) An added advantage of this gas recycle is that any trace elements devolatilized during regeneration of the sorbent would not be emitted to the atmosphere since trace elements would leave the regeneration system only in solid streams.

A sorbent regeneration process is being investigated in which $CaSO_4$ is reductively decomposed in a fluidized bed at temperatures of ∿1100°C. The heat and the reductants required are produced by incomplete combustion of coal in the fluidized bed of sulfated stone. Two solid-gas reactions by which regeneration occurs are:

$$CaSO_4 + CO \rightarrow CaO + CO_2 + SO_2 \quad (1)$$

$$CaSO_4 + H_2 \rightarrow CaO + H_2O + SO_2 \quad (2)$$

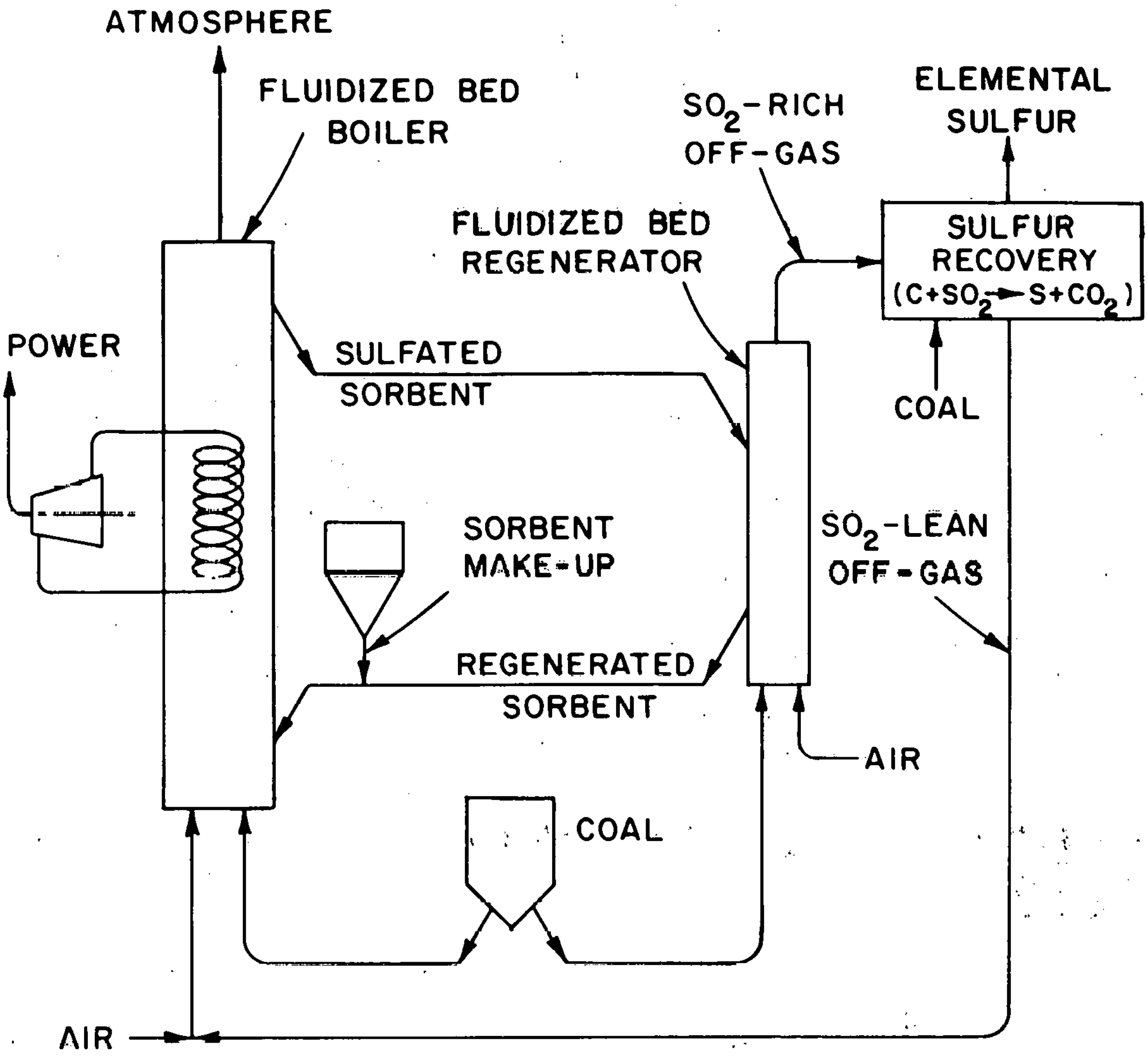

Fig. 1. Conceptual fluidized-bed coal combustion power-generating facility having sorbent-regeneration and sulfur-recovery capabilities.

At lower temperatures and under more highly reducing conditions, the formation of CaS is favored:

$$CaSO_4 + 4CO \rightarrow CaS + 4CO_2 \qquad (3)$$

$$CaSO_4 + 4H_2 \rightarrow CaS + 4H_2O \qquad (4)$$

When there is an oxidizing zone at the bottom of the fluidized bed (where the fluidizing gases, O_2 and N_2, are introduced), the buildup of CaS is minimized. The buildup of large amounts of CaS is undesirable because it prevents the reductive decomposition of $CaSO_4$ and generates regeneration process solid waste (*e.g.*, solids collected from off-gas) which cannot be disposed of without further processing.[2]

The feasibility of a sorbent regeneration process will depend on (1) the ability to regenerate the stones and to generate an SO_2-rich off-gas which can be treated in a sulfur recovery process, (2) the reactivity of the regenerated sorbent during subsequent sulfation (coal combustion) cycles, and (3) decrepitation of the sorbent at acceptable levels. A fresh sorbent makeup rate of 10-20% and an SO_2 concentration in the off-gas of 8-10% appear to be technically feasible and economically acceptable. The requirements for a process have not yet been optimized; they will become better established as development work progresses.

The effects of key variables on the regeneration of CaO in Tymochtee dolomite have been evaluated in two separate investigations. This report is arranged in four sections. The first section contains the results obtained in an early investigation in which methane was used as the fuel. The second section contains the results obtained in an investigation in which coal was used as the fuel. In the third section, a mass and energy constrained model for the regeneration process is given; it has been used to make a preliminary process sensitivity analysis. The fourth section contains the conclusions.

I. REGENERATION OF TYMOCHTEE DOLOMITE USING METHANE AS THE FUEL

In the first investigation, both the heat and the required reducing gases for the regeneration reactions were generated by incomplete combustion of methane in a fluidized bed of partially sulfated dolomite. The effects of operating variables (temperature, fluidizing-gas velocity, fluidized-bed height, solids residence time, and total reducing gas concentration in the effluent gas) on the regeneration of $CaSO_4$ to CaO and on the buildup of CaS were examined.

Experimental

The regeneration system (Fig. 2) consisted of a 7.62-cm-ID (3-in.-dia) fluidized-bed reactor (regenerator), a peripherally sealed rotary feeder for metering solids transported into the regenerator, and the off-gas solids-cleanup system. Another component was an electrically heated pipe heat exchanger used to preheat some of the fluidizing gas and for preheating air (used in startup only) to ∿500°C. The pressurized, fluidized-bed reactor was lined with a 6.35-cm-thick castable refractory and encased in a 20.3-cm (nominal 8-in.-dia) Schedule 40 pipe (Type 316 stainless steel), approximately 2.29 m (7 1/2 ft) long, with its entire length contained within a 30.5 cm-dia (nominal 12-in.-dia) Schedule 20 carbon steel pipe. Differential thermal expansion of the inner and outer pipes was accommodated by the use of packing glands on lines entering the bottom flange of the unit.

The experimental procedure consisted of first preheating the reactor and its bed of sulfated dolomite to ∿430°C (800°F) with external wall heaters and preheated air. Kerosene was then combusted in the fluidized bed under oxidizing conditions to increase the temperature of the bed to ∿870°C (1600°F), which is well above the auto-ignition temperature of methane. Methane was then fed in the place of kerosene and the fluidized bed was heated to ∿982°C (1800°F), at which temperature reducing conditions were established. The

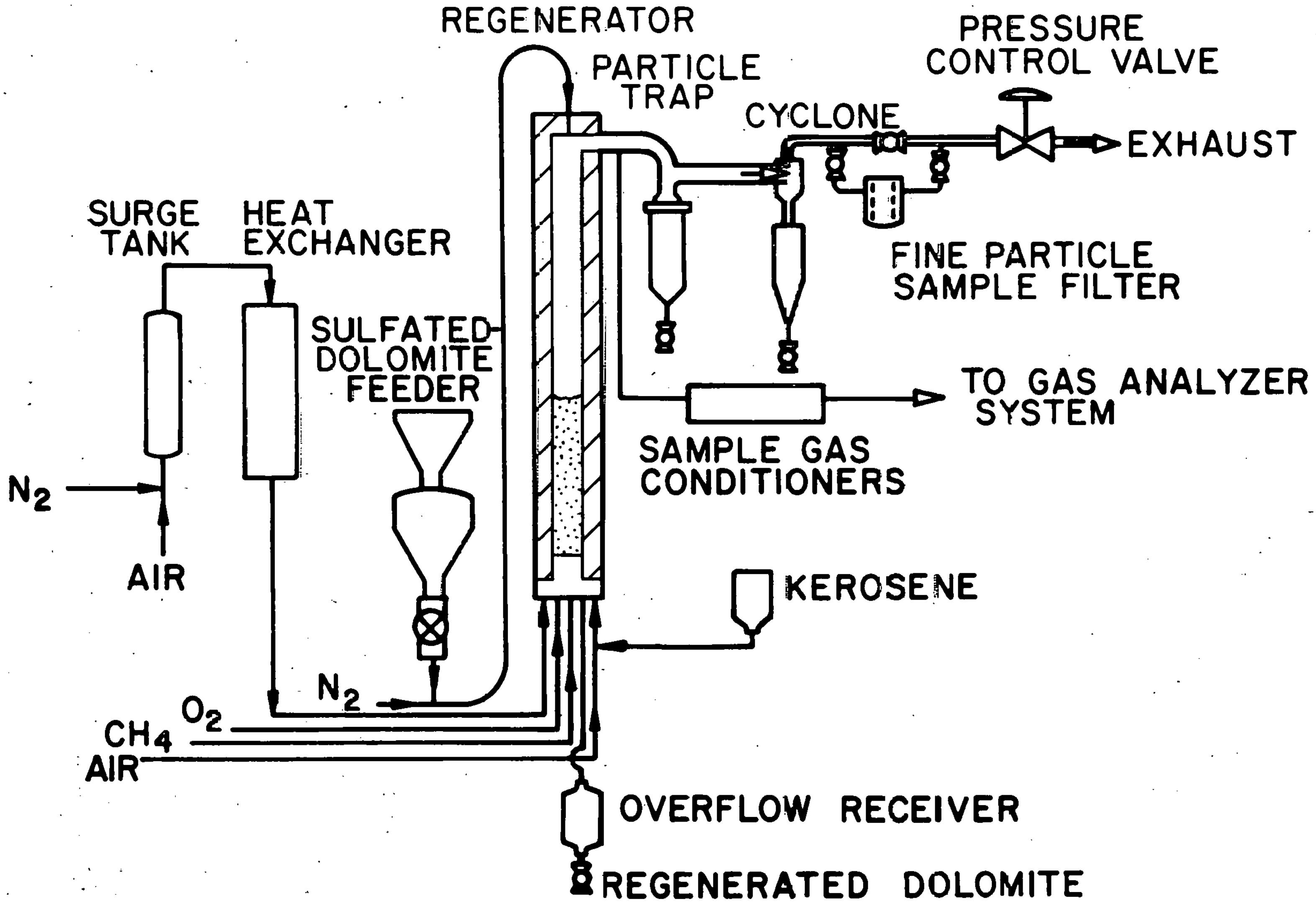

Fig. 2. Schematic diagram of the fluidized-bed regeneration system.

fluidizing gas was a mixture of nitrogen, oxygen, and methane. A multipoint injection system was used rather than a single injection point, to obtain lower local temperatures at the injection points. Oxygen and nitrogen were metered separately to produce the proper oxygen requirement in the reactor without changing the fluidizing-gas velocity. The final reducing conditions and operating temperature were approached slowly.

In this investigation, methane was combusted to generate both the heat and the reducing gases required for the reductive decomposition of $CaSO_4$ in sulfated Tymochtee dolomite at ∿1010-1100°C. The combustion reactions that dominate in the two zones of the fluidized bed are:

$$\text{Oxidizing Zone:}\quad CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O \qquad (5)$$

$$\text{Reducing Zone:}\quad CH_4 + O_2 \rightarrow CO + H_2 + H_2O \qquad (6)$$

Excess methane served as a reductant as did CO and H_2. Methane was injected into the fluidized bed of the reactor through multiple injection points at locations beginning at 15 cm and ending at 25 cm above the gas distributor plate (Fig. 3). The location of methane injection was not varied throughout this investigation.

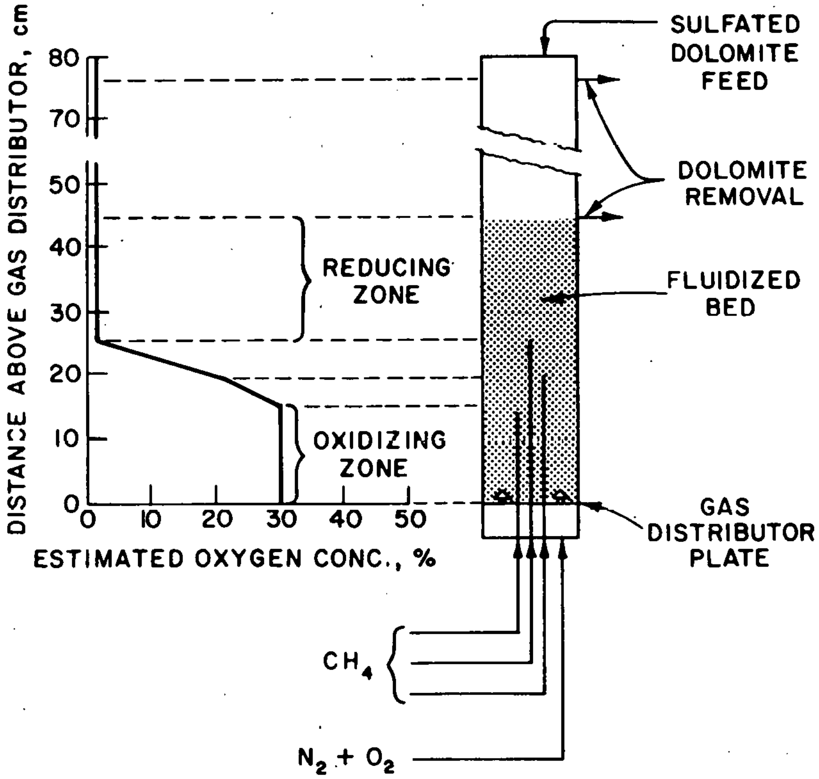

Fig. 3. Schematic diagram of the regeneration reactor used for the experiments with CH_4 and the expected axial oxygen concentration profile.

Sulfated dolomite was transported pneumatically from the storage hopper to the reactor and continually dropped onto the fluidized bed. Regenerated dolomite was continually removed from the bed through an overflow pipe. The fluidized-bed height was controlled by the location of the overflow pipe opening (see dolomite removal, Fig. 3) which was either 0.46 m or 0.76 m above the gas distributor. Solid samples taken over a 30-min steady state period were analyzed by techniques having an accuracy of ∿5%. Steady state was assumed to exist when (1) all off-gas measurements were constant and (2) over 90% of the initial bed material had been replaced (assuming backmixed solids flow).

In each experiment, a portion of the off-gas stream was continually removed, dewatered, and analyzed for SO_2, NO, CH_4, CO, and O_2: the gas was intermittently analyzed for CO_2. In addition, steady state off-gas samples were analyzed for H_2S, H_2, and trace gases COS and CS_2, using a mass spectrograph.

The Tymochtee dolomite that was regenerated contained 10.2 wt % S as $CaSO_4$ (none as $MgSO_4$), 22.2 wt % Ca, and a nominal size distribution of -14 +45 mesh. In its virgin state, it contained 50 wt % $CaCO_3$ and 39 wt % $MgCO_3$. It was sulfated during the combustion of Arkwright (bituminous) coal which contained 2.82 wt % S. The methane fuel used during regeneration was tank pressurized ∿99% CH_4.

Results and Discussion

The percent regeneration of CaO was calculated from chemical analyses of the steady state products. It was based on the sulfur to calcium ratios in (1) the sulfated dolomite feed and (2) the steady state product after regeneration. These calculated regeneration percentages are compared in Table 1 with the percentages based on off-gas analyses. The latter values are calculated from the ratios of the total sulfur released into the off-gas stream to the total sulfur contained in the sulfated dolomite feed. The gas volumetric changes in the fluidizing gas caused by the combustion and regeneration reactions were estimated. These estimates and the gas feed rate were used to calculate the off-gas flow rate (see Table 2). The sulfur regeneration values obtained by chemical analysis of the regenerated products generally agreed, within analytical accuracy, with the values calculated from off-gas analyses. The solids residence time was calculated as the ratio of the mass of the sorbent in the fluid bed to the feed rate of the sulfated sorbent.

The concentrations and rates of the feed and effluent gases are given in Table 2. Total reducing gas concentration is the sum of the concentrations of CO, H_2, and excess CH_4 in the wet off-gas. The concentrations of minor gas constituents, CS_2 and COS, in the off-gas ranged from 100 to 500 ppm. The water concentration in the off-gas for these experiments, in which methane was combusted, was high. When other fuels (such as coal) having a lower hydrogen content are used for regeneration, the water content of the effluent gas is lower.

Table 1. Design and experimental conditions, chemical analyses of regenerated products, and regeneration results

Reactor ID, 7.62 cm Pressure, 184 kPa
Additive, Sulfated Tymochtee dolomite (10.2 wt % S)

	Design Conditions									
Exp.	Temp., °C	Sorbent Feed Rate, kg/hr	Residence Time, min	Bed Height, m	Total Reducing Gas in Effluent, vol %	Fluidizing Velocity, m/sec	Elutr. Calcium[a] x 100 / Feed Calcium, %	Sulfide (S^{2-}) in Regenerated Products, %	Measured in SO_2 Effluent, % dry	CaO Regeneration, (%)[b]/(%)[c]
1	1040	2.72	30	0.46	3	0.67	5	0.1	4.0	70/76
1R1	1040	2.72	30	0.46	3	0.73	15	<0.1	3.6	65/72
1R2	1040	2.72	30	0.46	3	0.76	13	<0.1	2.9	60/58
3	1040	4.54	18	0.46	15	0.79	12	0.3	5.7	70/79
4	1095	4.54	18	0.46	3	0.76	9	<0.1	7.3	83/89
5	1040	4.54	30	0.76	15	0.82	--	0.7	4.4	61/79
9A	1040	2.72	30	0.46	3	0.91	--	<0.1	1.5	40/40
7	1040	4.54	30	0.76	3	0.76	15	<0.1	3.3	43/36
8	1010	2.72	30	0.46	3	0.70	14	<0.1	0.78	15/21
9[d]	1040	2.72	30	0.46	3	0.76	11	<0.1	1.7	58/55

[a] Only elutriated particles larger than 15 μm were monitored.
[b] Based on flue gas analysis.
[c] Based on chemical analysis of regenerated dolomite samples.
[d] The feed was sulfated dolomite that had previously been partially regenerated (∿5.8 wt % S) in FAC-1 and FAC-1R1.

Table 2. Rates and concentrations of the feed and effluent gases.

	Feed Gas					Effluent Gas (wet)								
Exp.	Rate, L/min[a]	N_2	O_2	CH_4	O_2/CH_4	Rate, L/min[a]	CH_4	CO	H_2	O_2	SO_2	H_2S	CO_2	H_2O
			%							%				
1	75.9	51.8	31.4	16.8	1.9	82.4	1.7	0.8	0.6	0.3	3.0	<0.07	16	25
1R1	81.4	57.8	27.7	14.5	1.9	87.7	1.7	0.5	0.6	0.1	2.6	0.02	16	27
1R2	85.5	58.7	26.7	14.6	1.8	91.0	1.9	0.4	0.6	0.1	2.3	0.02	15	22
3	88.2	42.4	33.3	24.3	1.4	100.5	11	1.7	1.5	0.06	4.1	0.6	20	28
4	80.7	43.6	37.0	19.4	1.9	93.3	1.0	1.6	0.9	0.03	5.3	0.3	23	27
5	90.8	42.5	33.9	23.6	1.4	104.4	10	1.7	1.4	∿0.2	3.5	0.6	23	22
9A	102.9	67.6	21.4	11.0	1.9	90.3	2.0	0.4	0.5	0.1	1.3	0.03	12	14
7	93.6	49.0	33.8	17.2	2.0	83.6	1.7	0.3	0.3	0.1	2.7	0.03	20	20
8	78.2	62.4	24.5	13.1	1.9	105.5	2.0	0.4	0.3	0.4	0.7	<0.04	13	17
9	83.0	60.5	26.3	13.2	2.0	88.6	2.2	0.3	0.3	0.3	1.3	0.03	13	23

[a] At 101.3 kPa and 22.8°C.

Effect of Fluidized-Bed Height. The bed height was varied by changing the height of the solids removal standpipe (see Fig. 3). This did not affect the height of the oxidizing zone; only the reducing zone height in the fluid bed changed. The results of Exp-3 and Exp-5 (performed at the same sulfated dolomite feed rate, Table 1) were compared. It was found that increasing the nominal fluidized-bed height from 0.46 m to 0.76 m (which increased the solids residence time from 18 min to 30 min) did not improve the extent of CaO regeneration.

At a constant solids residence time (∿30 min), increasing the fluidized bed height from 0.46 m (Exp-1R2) to 0.76 m (Exp-7) had a more pronounced effect on the extent of regeneration--decreasing it ∿20%.

The absence of a beneficial effect of increased fluidized-bed height may have been due to the formation of larger gas bubbles in deeper beds causing more segregation of the gas phase from the well-fluidized phase, especially near the top of the bed. Transport of the reducing gases from the gas phase to the well-fluidized phase would become increasingly difficult; and this could reduce the extent of conversion (the reactions are relatively fast). Also, poorer mixing in a deeper bed could prevent the sulfated dolomite from circulating throughout the entire bed, so that reaction would occur only in the upper, more segregated portion of the fluidized bed (the feed solids were dropped on the top of the fluidized bed). This would result in the actual solids residence times in a deeper bed being shorter than calculated.

Effect of Fluidizing-Gas Velocity. The effect of fluidizing-gas velocity on regeneration was evaluated by comparing the results of four experiments in which the sole variable was fluidizing-gas velocity (Fig. 4). As the gas velocity was increased from 0.67 m/sec to 0.91 m/sec, CaO regeneration decreased from 76% to 40%. In a study by Martin *et al.*[3] on the reductive decomposition of gypsum in a 25.4-cm-dia (10-in.-dia) fluidized bed, the optimum fluidizing-gas velocity (for decomposition) was found to be about 0.6 m/sec. However, the effect of fluidizing-gas velocity was reported to be small.

In this study, fluidizing-gas velocity had a meaningful effect in the investigated velocity range. The relatively small internal diameter (7.62 cm) of the fluidized-bed reactor probably enhanced the detrimental effect of gas velocity, lowering the fluidization quality.

At higher fluidizing-gas velocities, the proportion of the gas in the bubbles in the fluidized bed increased and the transport of gases from the bubble phase to the well-fluidized phase was hampered. Also, solids mixing was less effective at high fluidizing velocities because of the unfavorable bed geometry (a ratio of bed height to bed diameter of 6 or 10).

Effect of Regeneration Temperature on Regeneration and Resulfation of Tymochtee Dolomite. The effect of regeneration temperature (ranging from 1010 to 1095°C) on the regeneration of dolomite was evaluated in five experiments. The results are given in Fig. 5. In these five experiments, regeneration

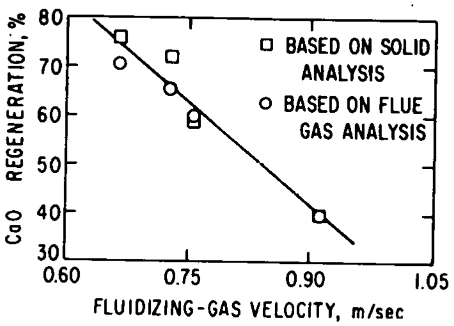

Fig. 4. The effect of fluidizing-gas velocity on CaO regeneration for sulfated Tymochtee dolomite.

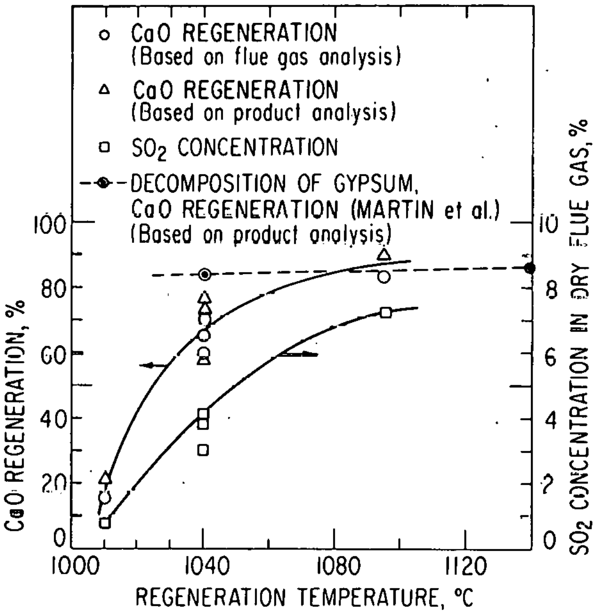

Fig. 5. Effect of temperature on CaO regeneration for sulfated Tymochtee dolomite.

temperature was the only variable except that the solids residence time was 18 min instead of 30 min in the experiment at 1095°C. As the temperature was increased from 1010°C to 1095°C and the solids residence time remained constant or decreased, CaO regeneration (based on analysis of the regenerated product) increased from 21% to 89%, and the SO_2 concentration in the dry off-gas increased from 0.8% to 7.3%.

The temperature dependence of the regeneration of sulfated Tymochtee dolomite in these experiments was compared (see Fig. 5) with similar results obtained by Martin *et al.*[3] In that investigation, the reductive decomposition of gypsum was studied, with carbon the reductant in a 25.4-cm-dia fluidized bed (solids residence time of ∿90 min). The results agree at the higher temperature where the rate of decomposition is fast and most of the conversion occurs in the first few minutes of the reaction.

Porosity measurements of samples (-25 +35 mesh particles) at several process steps have been made (Fig. 6) to evaluate the effect of regeneration temperature on the quality of the regenerated dolomite as a SO_2-acceptor. Porosity was measured as the extent of penetration of mercury as a function of pressure. The cumulative pore volumes (mercury penetration) per 0.5 g of sorbent as a function of pore diameter are given (Fig. 6).

Curve A represents the pore size distribution of fully calcined virgin dolomite that was calcined at 900°C for 2 hr in a furnace (preated to 900°C) in a 20% CO_2-80% air environment. The pore volume for pores 0.4 μm and larger was found to be 0.1 cm^3/0.5 g. As reported by Hartman and Coughlin,[4] most sulfation takes place in the larger pores ($\geq$0.4 μm). Pores smaller than ∿0.4 μm are relatively easy to plug and therefore contribute little to the extent of sulfation. The pore distribution of fully calcined virgin dolomite was compared with that of sulfated and regenerated dolomite because dolomite is fully calcined during regeneration.

Curve B represents the pore volume distribution of dolomite that was sulfated (10.2 wt % S) in coal combustion experiments at 900°C; this sulfated dolomite was used as the feed for the regeneration experiments. The pore volume for pores 0.4 μm and larger was found to be 0.045 cm^3/0.5 g. In contrast to the pore volume distribution of the calcined material, the pores of the sulfated material were severely plugged by sulfation. The pores shrink during sulfation of CaO as a result of changes in molecular volume.

Curves C and D illustrate the pore volume distribution of dolomite that was regenerated at 1040°C or 1095°C. At the higher regeneration temperature, the volume of the larger pores ($\geq$0.4 μm) was greater. On the basis of this result, the sulfation reactivity of dolomite regenerated at the higher temperature was expected to be greater.

Sulfation experiments with the regenerated samples and the calcined dolomite sample were performed in a thermogravimetric analyzer. The results are given in Fig. 7. It was found that the higher regeneration temperature did not improve the reactivity of the dolomite with SO_2. Rather, the dolomite that was regenerated at 1095°C was found to have a lower reactivity than the dolomite regenerated at 1040°C and the precalcined dolomite.

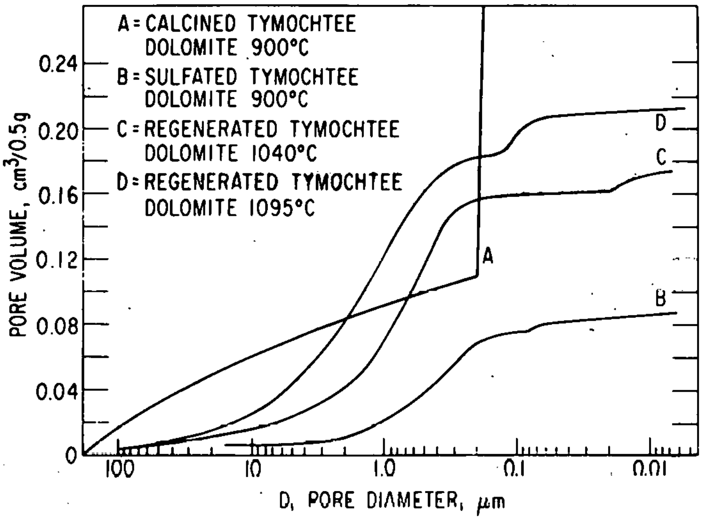

Fig. 6. Pore distributions of dolomite samples from different process stages.

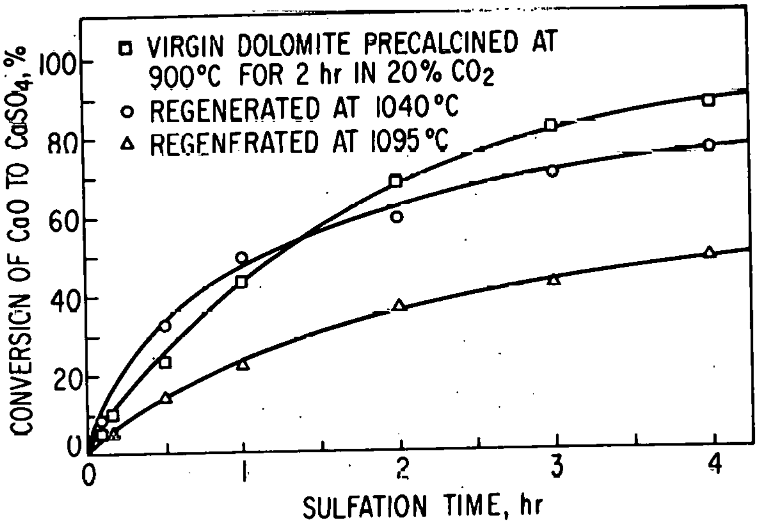

Fig. 7. Sulfation reaction data obtained with a thermogravimetric analyzer at 900°C, 0.3% SO_2, and 5% O_2.

Although higher regeneration reaction rates were obtained at the higher regeneration temperature, the potential detrimental effect of high regeneration temperatures on the reactivity of the dolomite in subsequent sulfation cycles requires further study. A decrease in the reactivity of regenerated sorbent during cyclic exposures to high temperature was reported by Skopp *et al.*[5] In that study, the reactivity loss was presumed to be caused by loss in porosity. In this study, the sorbent's porosity increased after one cycle in the second sulfation step.

Electron Microprobe Analysis of Sulfated and Regenerated Particles. Regenerated Tymochtee dolomite particles from some of these experiments (Exp-IR2 and 4), as well as nonregenerated sulfated Tymochtee dolomite particles, were analyzed with an electron microprobe to determine the effect of regeneration on the sulfur concentration profiles in individual particles. The radial distributions of calcium, magnesium, and sulfur were measured. A random sample of particles was screened; then approximately twenty nominally -20 +25 mesh particles were mounted in epoxy and machined to remove the equivalent of one-half of the nominal diameter of a typical mounted particle (~400 μm). A thin gold layer (~50 angstroms) was sputtered on the machined surface to enhance the conductivity of the mounts. Apatite (38.9 wt % Ca), FeS_2 (53.4 wt % S), and MgO (60.3 wt % Mg) were used as standards to calibrate the probe and to obtain a rough quantitative estimate of the local component concentrations.

The radial concentration distributions of calcium and sulfur as obtained by the electron probe for three typical sulfated particles are given in Fig. 8 (magnesium concentration profiles are not given because they are similar to those for calcium). The extent of sulfation in these particles varied because the particles had been sulfated in the continuously fed, fluidized-bed coal combustor for different periods of time (solids are back-mixed). The extent of sulfation was least for the particle represented at the top of the figure and greatest for the bottom particle. As sulfation progressed, the edge of the sulfated shell moved towards the center of the particle. The local sulfur and calcium concentrations obtained were lower than the true local concentrations because irregularities on the surfaces caused scattering of the characteristic emitted X-rays (the sample surfaces could not be machined as smooth as the calibration sample surfaces). The bulk concentrations of sulfur and calcium, obtained by wet chemical analysis of the sample from which these particles were taken, were 10.2 wt % and 22.2 wt %, respectively.

Regenerated particles from Exp-IR2 (performed at 1040°C) were chemically analyzed and found to contain 5.1 wt % S and 26.2 wt % Ca. The electron microprobe analyses of two sample particles from this experiment are given in Fig. 9. In the particle whose analysis is given at the top of Fig. 9, regeneration apparently was in an early stage, with the primary regeneration-reaction zone moving radially into the uniformly sulfated particle. Some residual sulfur (sulfur that is less accessible, probably due to diffusion limitation) is left behind the advancing primary reaction zone. The bulk of the sulfur is removed during the first regeneration stage. The particle represented by the other electron probe analysis is in a later (slower) stage of regeneration and the residual concentration of sulfur in the entire particle is relatively low.

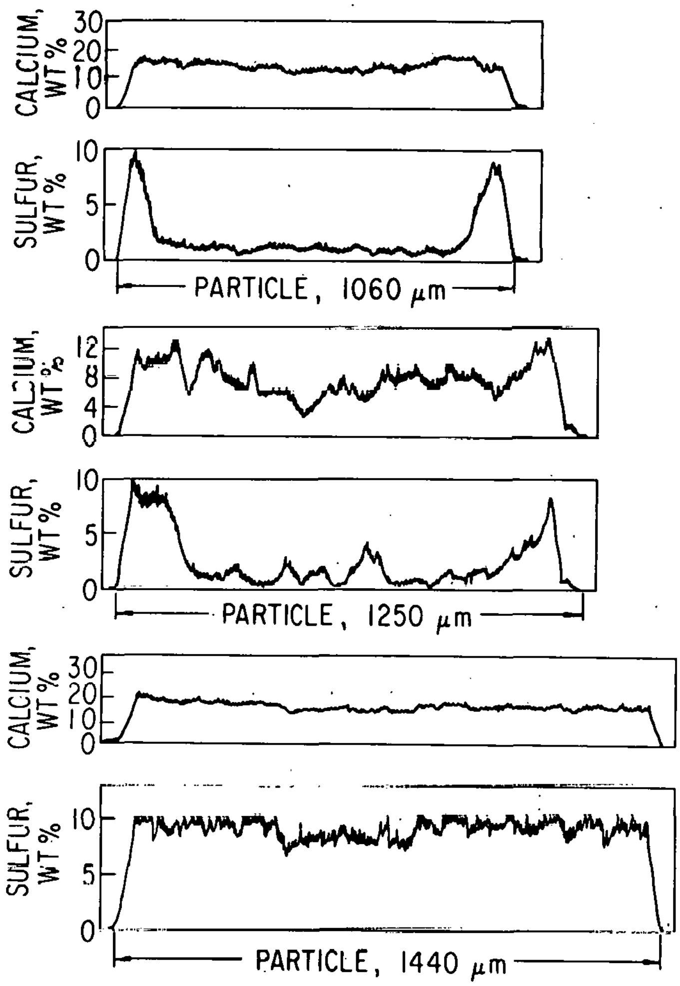

Fig. 8. Electron microprobe analyses of typical sulfated Tymochtee dolomite particles.

(Note the difference in scales for the two diagrams.) In an industrial process in which the solids residence time would be short (high solids throughput rate), probably only the first (rapid) stage of regeneration would occur. Hence, most but not all of the sulfur would be removed in an industrial regeneration process.

Electron microprobe analyses were also performed on regenerated particles from Exp-4, which was conducted at the higher temperature of 1095°C. The bulk calcium and sulfur concentrations in regenerated Tymochtee dolomite from this experiment were 30 wt % and 1.5 wt %, respectively. The electron microprobe analyses for calcium and sulfur in three particles from this experiment are shown in Fig. 10. The particle whose analysis is given at the top of

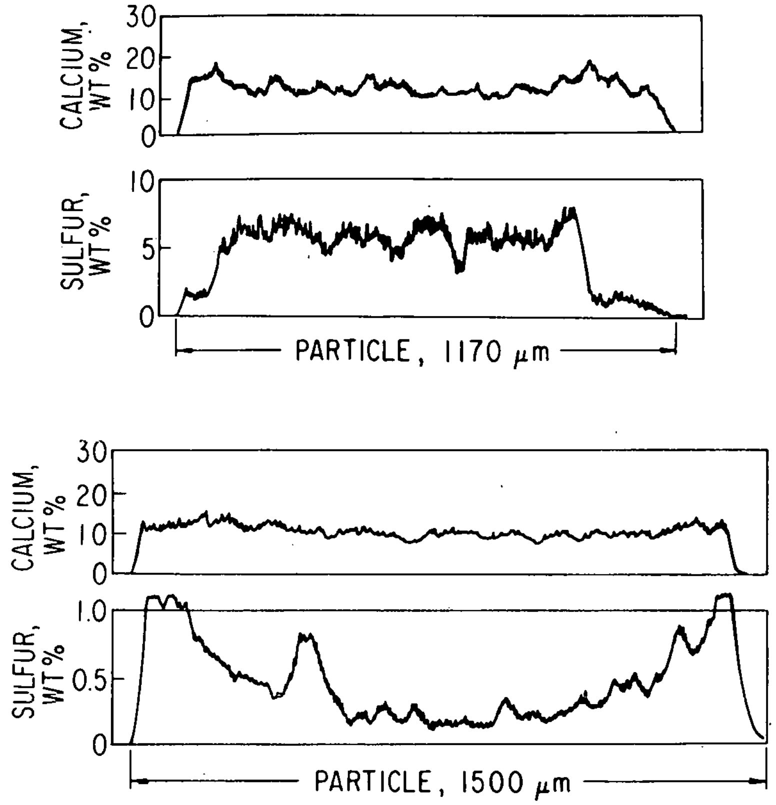

Fig. 9. Electron microprobe analysis of regenerated Tymochtee dolomite particles from Exp-1R2.

Fig. 10 appears to be near the end of the first regeneration stage; the primary desulfurization reaction zone has almost reached the center of the particle. Regeneration in the other two particles is more nearly complete. A greater extent of regeneration was observed in particles from Exp-4 than in particles from Exp-1R2 (regenerated at a lower temperature). Generally, the regenerated particles examined showed no sulfur concentration irregularities that might lead to poor utilization in subsequent sulfation cycles.

Formation of CaS. The buildup of large amounts of CaS would be detrimental to the reductive decomposition of $CaSO_4$ to CaO. The sulfide analyses of the regenerated products are given in Table 1. Of the four variables in these experiments, only reducing gas concentration in the effluent gas had an effect of sulfide buildup. Very small amounts of sulfide ($\leq$0.1%) were found in the steady state regenerated dolomite samples from all experiments performed with low reducing gas conditions (*i.e.*, with $\sim$3% total reducing gas in the effluent). With $\sim$15% reducing gas in the effluent, the buildup of CaS was enhanced--for example, in two experiments, sulfide concentrations in the products were 0.3 and 0.7%, respectively.

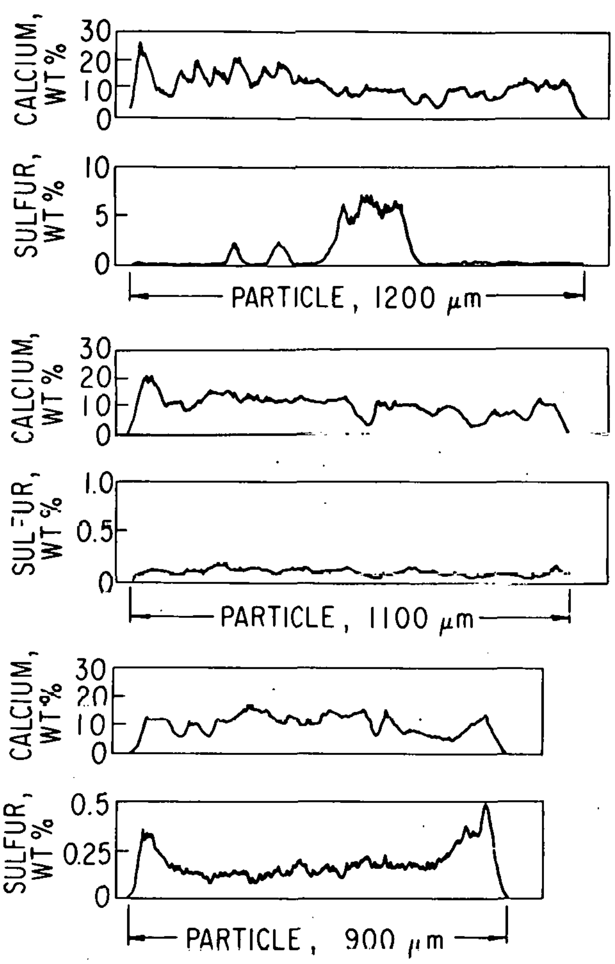

Fig. 10. Electron microprobe analysis of regenerated Tymochtee dolomite particles from Exp-4.

The obtained experimental sulfide concentrations are much lower than those predicted by the equilibrium equation (below) at the experimental off-gas conditions of these experiments.

$$1/4\ CaSO_4 + CO \rightarrow 1/4\ CaS + CO_2,\ \frac{1}{k_p} = \frac{P_{CO}}{P_{CO_2}} \tag{3}$$

At 1040°C, the maximum partial pressure ratio of CO to CO_2 (P_{CO}/P_{CO_2}) for which CaS and $CaSO_4$ coexist is 0.017. At higher partial pressure ratios, only CaS should exist at equilibrium.[6] Since the experimental values of partial pressure ratios of CO to CO_2 in the effluent for these experiments were all above 0.02, higher sulfide concentrations might be expected. The experimental results may be explained on the basis that (1) the sorbent in the fluidized-bed reactor is not at equilibrium and (2) the conditions in the fluidized bed are not reducing throughout (see Fig. 3). The fluidizing gas (N_2 and O_2) was introduced through the gas distributor, and a highly oxidizing zone was established (see Table 2) between the gas distributor and the methane injection ports, as illustrated in Fig. 3. A multipoint injection system was used, rather than a single injection point, to obtain lower local temperatures at the injection points. In the oxidizing zone, CaS was oxidized:

$$CaS + 2\ O_2 \rightarrow CaSO_4 \qquad (7)$$

$$CaS + 3/2\ O_2 \rightarrow CaO + SO_2 \qquad (8)$$

A reducing zone was established in the top portion of the fluidized bed. Solid reactants and products are circulated between the reducing and oxidizing zones, allowing CaS to be oxidized to $CaSO_4$ and this minimizes the buildup of CaS.

In related experimental investigations by others, an oxidizing zone to oxidze the CaS was purposely created above the reducing zone by adding secondary air or oxygen near the top of the fluidized bed during the decomposition of gypsum[7] and anhydrous $CaSO_4$ and sulfated limestone.[8]

Attrition and Elutriation of Sorbent. Knowledge of the extent of attrition of sorbent is of major concern in the development of a sorbent regeneration process. The physical integrity of sorbent particles may be affected by thermal stresses at the high process temperature (∿1100°C) and by molecular rearrangements within the particles due to regeneration reactions.

Losses of regenerated dolomite due to attrition and/or elutriation (including attrition during pneumatic transport) at the various conditions used in these experiments were measured. Since the sulfated dolomite was nominally -14 +45 mesh and the particles elutriated from the bed were all nominally -45 mesh (<350 μm), it was assumed that the elutriated particles were attrited fragments of the feed Tymochtee dolomite. Table 1 shows the fraction of dolomite lost during regeneration because of attrition and consequent elutriation (elutriated calcium as a percentage of feed calcium). The loss ranged from 5-15%.

Sorbent attrition was also characterized by a more direct approach; the fractional distributions of the sulfated feed and regenerated product for Exp-1 were plotted (Fig. 11, upper plot). The fractional distribution curves suggest a particle population shift to small diameters in the regenerated dolomite. This was confirmed by plotting the mass ratios from Exp-1 (*i.e.*, the calcium mass content of the product to the calcium mass content of the feed dolomite) as a function of particle diameter (Fig. 11, lower plot). Generally, all plots of fractional product-to-feed calcium ratio as a function of particle diameter showed that during regeneration, the number of larger particles (>800 μm) decreased and the number of medium-size particles (>300 and <800 μm) increased because of attrition of the larger particles.

Agglomeration of Sulfated Dolomite. Partial agglomeration of the sulfated dolomite bed occurred when a regeneration experiment was attempted with a bed temperature of 1095°C and a 15% reducing gas concentration in the effluent gas. It is believed that insufficient fluidization velocity at these conditions caused some particles to adhere to each other. This was

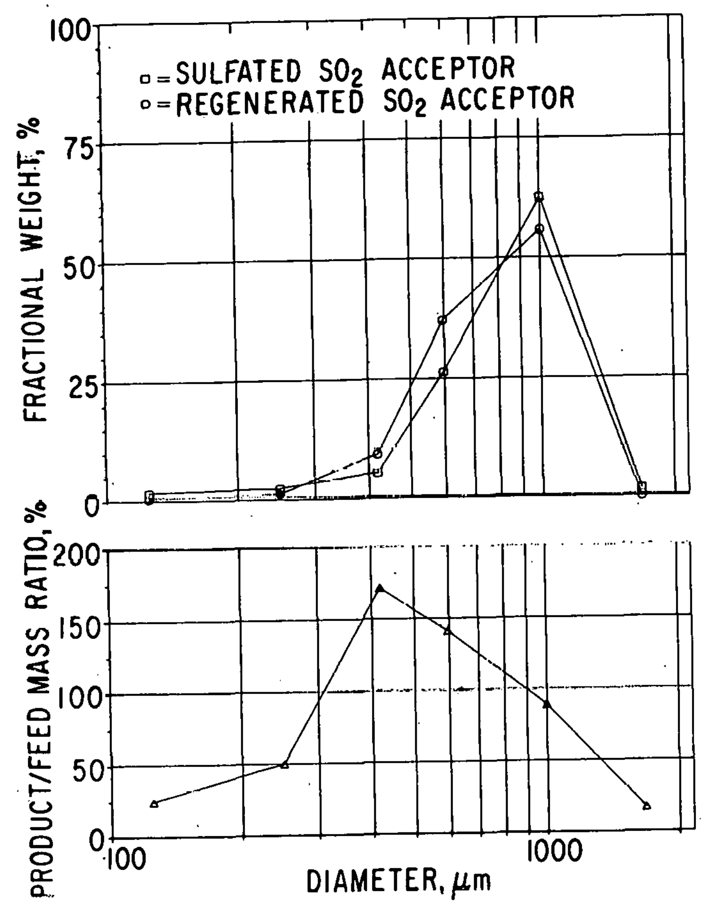

Fig. 11. Exp-1, fractional feed and product particle size distributions (upper graph). Attrition, characterized by the fractional product to feed mass ratios at different particle diameters (lower graph).

followed by further defluidization and a temperature excursion in the bed which caused the dolomite particles to fuse. (It was previously reported by Wheelock and Boylan[9] that the surface of gypsum becomes glassy during regeneration at 1250°C.) Agglomerates from this attempted experiment have been analyzed by X-ray diffraction. In the fused portion, calcium-magnesium silicate compounds (which are absent in virgin dolomite) were found. When this class of materials is pure, the melting point is ∿1300°C. The agglomeration problem is further accentuated by the presence of coal ash because at the temperature and reducing conditions of the regeneration reactor, most coal ashes soften.

II. REGENERATION OF TYMOCHTEE DOLOMITE USING COAL AS THE FUEL

At the completion of the above investigation, the PDU regeneration system (including the reactor) was modified and features were added which permit the combustion of coal. In the subsequent investigations, incomplete combustion of coal in a fluidized bed of partially sulfated dolomite generated both the heat and the required reducing gases for the regeneration reactions.

The effects of solids residence time in the reactor, regeneration temperature, and pressure on the extent of CaO regeneration in the sulfated Tymochtee dolomite, the SO_2 concentration in the dry off-gas, and the buildup of CaS were evaluated.

Experimental

The modified regeneration system used in this investigation is shown schematically in Fig. 12. The reactor ID was expanded from 7.62 cm (3.0 in.) in the previous investigation to 10.8 cm (4.25 in.), and the height of the fluidized bed (∿46 cm) was regulated by an overflow pipe that is external to the fluidized bed. The pressurized, fluidized-bed reactor was lined with a 4.8-cm-thick castable refractory. The coal and the sulfated sorbent flows were metered separately (for independent control) to a common pneumatic transport line which discharged into the fluidized bed ∿15 cm above the gas distributor, as shown in Fig. 13. Thus, two zones were formed: a highly oxidizing zone below the solid injection point, and a reducing zone above the injection point.

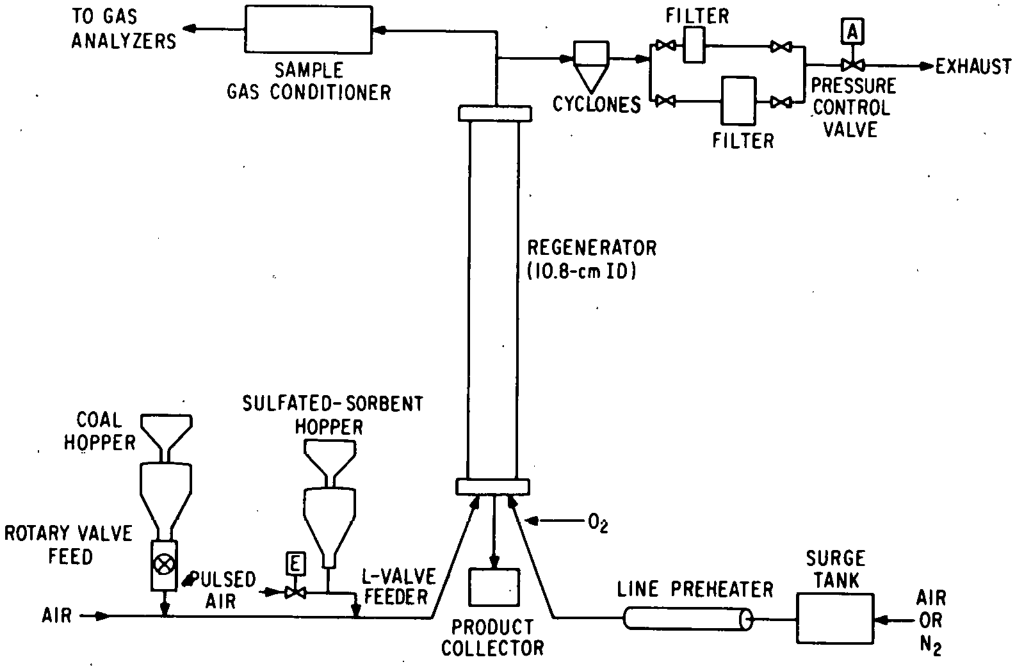

Fig. 12. Experimental sorbent regeneration system

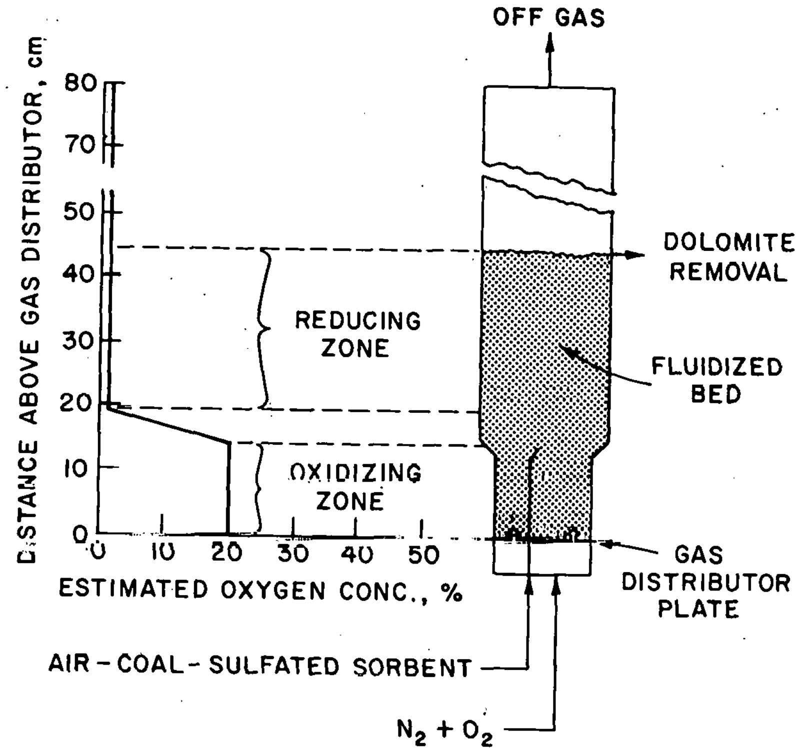

Fig. 13. Schematic diagram of the regeneration reactor used for the experiments with coal and the expected axial oxygen concentration profile.

Other components of the experimental system were similar to those used in the previous regeneration investigation described in Part I of the report. Pertinent constituents (SO_2, O_2, CO, H_2, CH_4, and NO) of the off-gas were continuously analyzed. Solids transport air constituted ∿40% of the total fluidizing gas in the reactor. The remaining fluidizing gas was a mixture of pure nitrogen and oxygen.

Oxygen and nitrogen were metered separately and mixed to produce the required oxygen environment in the reactor. Thus the oxygen requirements at different experimental conditions could be satisfied without changing the fluidizing gas velocity. Oxygen concentrations in excess of that in air were used in the feed gas in most of the reported regeneration experiments. Large amounts of heat (per unit capacity) were required to compensate for (1) the heat losses in the relatively small experimental system and (2) the heat load imposed by feeding cold sulfated sorbent to the system. In a large-scale industrial regeneration system, such heat requirements would not be encountered and oxygen enrichment of the fluidizing air would not be needed.

The Tymochtee dolomite that was regenerated contained ∿9 wt % S as $CaSO_4$ (no $MgSO_4$ present), 26 wt % Ca, 9.5 wt % CO_2, and a nominal size distribution of -14 +30 mesh before regeneration. In its virgin state, its main constituents were $CaCO_3$ (50 wt %) and $MgCO_3$ (39 wt %).

During regeneration, Triangle coal was combusted under reducing conditions. It is a Type B bituminous high-volatile coal (32.6% volatile matter, dry) and has a high ash fusion temperature (1390°C, initial deformation under reducing conditions). As received, it contains 73.5 wt % C, 9.4 wt % ash, and 0.98 wt % S.

Results and Discussion

The experimental conditions and results for thirteen experiments are given in Table 3. The experiments were performed at three temperature levels: 1000°C, 1050°C, and 1100°C. Solids residence times ranging from ∿7 min to ∿35 min were used at each temperature level.

Regeneration of CaO was calculated from chemical analyses of the steady-state products. It was based on the sulfur to calcium ratios in (1) the sulfated dolomite feed and (2) the steady state product after regeneration. These calculated regeneration values are compared in Table 3 with the values that are based on off-gas analyses. The latter values are the ratios of the total sulfur released into the off-gas stream to the total sulfur contained in the sulfated-dolomite feed. The off-gas flow rate was calculated using the feed gas rate and the model of the regeneration process (discussed in a later section) in which the gas volumetric expansion in the reactor is predicted. The concentrations and rates of the feed and effluent gases are given in Table 4. The CaO regeneration values obtained by chemical analyses of the regenerated products generally agree within analytical accuracy with the values calculated from off-gas analyses.

Effect of Solids Residence Time and Temperature on Regeneration. The extents of regeneration (based on off-gas and regenerated solids analyses) are plotted in Fig. 14 as a function of solids residence time for the three temperature levels. The solids residence time was varied by changing the solids feed rate and not by changing the reactor volume.

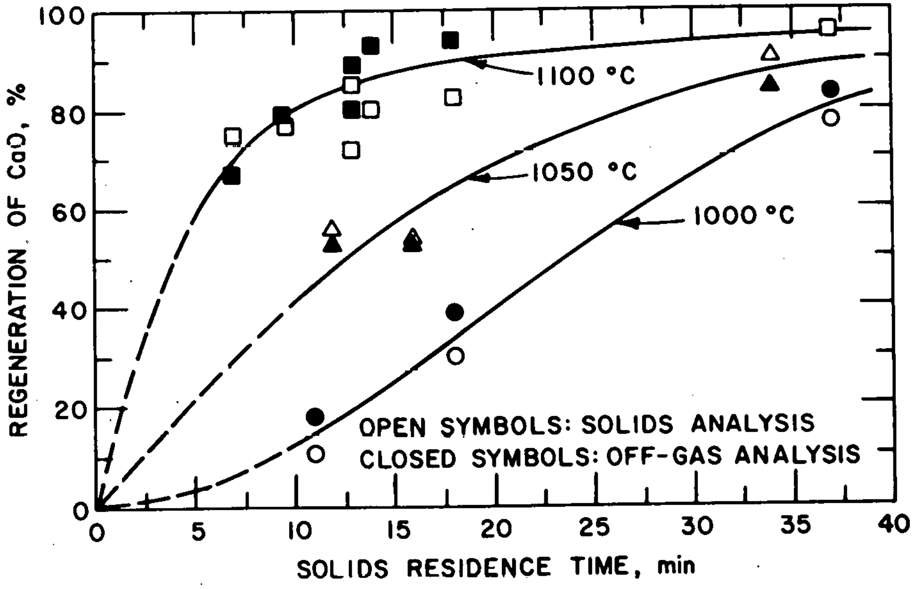

Fig. 14. Regeneration of CaO in Tymochtee dolomite as a function of solids residence time (pressure: 153 kPa).

Table 3. Experimental conditions and results for the regeneration of sulfated Tymochtee dolomite by the incomplete combustion of Triangle coal in a fluidized bed.

Nominal fluidized-bed height: 46 cm   Pressure: 153 kPa
Reactor ID: 10.8 cm
Coal: Triangle coal (0.98 wt % S) ash fusion temp. under reducing conditions, 1390°C (initial deformation)
Sorbent: (1) -14 +50 mesh, 9.0 wt % S (CS-6, -7, -8)
(2) -14 +50 mesh, 9.4 wt % S (CS-10, -11, -12)
8.5 wt % S (CS-13 thru -18 and CCS-1)

Exp.	Temperature, °C	Fluidizing-Gas Velocity, m/sec	Feed Rate, kg/hr	Solids Residence Time, min	Reducing Gas Concentration in Effluent, %	Measured SO_2 in Dry Off-Gas, %	CaO Regeneration, %[a]/%[b]
CS-6	1000	0.98	5.0	37	1.4	2.5	83/77
CS-8	1000	0.92	10.0	18	2.2	2.5	39/30
CS-17	1000	1.04	16.1	11	2.4	1.4	18/11
CS-7	1050	0.92	5.4	34	1.9	3.0	84/90
CS-16	1050	1.0	11.1	16	2.2	3.3	53/53
CS-10	1050	0.98	15.0	12	2.5	4.8	53/56
CS-15	1100	1.02	5.0	37	1.5	2	82/95
CS-14	1100	1.05	10.0	18	2.2	4.8	94/82
CS-11	1100	1.07	14.3	13	2.9	6.4	80/85
CS-13	1100	1.09	31.6	13	2.2	6.1	89/72
CS-18	1100	1.07	13.2	14	2.4	6.3	93/80
CS-12	1100	1.16	19.5	9.4	2.9	7.8	79/77
CCS-1	1100	1.43	26.4	7.0	2.7	6.5[c]	67/75

[a] Based on off-gas analysis.
[b] Based on chemical analysis of dolomite samples.
[c] The SO_2 concentration adjusted for a 1.08 m/sec fluidizing-gas velocity is 8.7%.

Table 4. Rates and concentrations of feed and effluent gases.

	Feed Gas					Effluent Gas (wet)								
Exp.	Rate, L/min[a]	Solids Transport Air, %	Tank N_2, %	Tank O_2, %	Total O_2, %	Rate, L/min	CO, %	CH_4, %	H_2, %	O_2, %	SO_2, %	H_2S, %	CO_2, %	H_2O, %
1	186.6	44.6	47.2	8.2	17.4	209.2	0.84	0.19	0.19	0.09	2.33	0.018	14.5	6.65
2	174.2	47.8	40.2	12.0	21.9	201.1	1.29	0.41	0.27	0.18	1.93	0.007	24.4	8.08
3	197.1	41.2	43.5	15.2	23.8	227.1	1.28	0.50	0.34	0.0	1.09	0.068	30.2	8.53
4	167.4	49.7	39.8	10.5	20.8	182.8	1.25	0.23	0.25	0.14	2.49	0.009	21.7	7.76
5	181.8	44.7	38.8	16.5	25.8	210.9	1.38	0.37	-	-	2.67	0.068	31.3	8.01
6	178.4	46.7	34.0	19.4	23.4	221.3	1.6	0.35	-	0	4.77	-	27.0	10.06
7	179.0	44.9	43.0	1.20	21.3	203.7	1.29	0.14	-	-	1.62	0.157	26.7	7.65
8	191.7	42.4	38.7	18.9	27.7	232.4	1.73	0.18	0.18	0.19	4.4	0.045	23.6	9.17
9	188.0	44.3	32.1	23.6	32.8	239.7	2.15	0.07	0.18	0.09	5.7	0.009	24.6	10.35
10	192.9	42.1	33.3	24.5	33.2	241.7	1.71	0.27	-	0	4.8	0.09	32.4	9.97
11	187.8	-	-	-	33.0	235.3	-	-	-	-	4.95	-	-	10.00
12	204.2	40.8	31.5	27.7	36.2	267.5	2.14	0.09	0.18	0.05	6.9	0.009	29.0	11.03
13	251.2	31.4	48.5	20.1	26.6	333.3	2.13	0.22	-	0	4.89	0.017	37.3	11.12

[a] At 101.3 kPa and 22.8°C.

At 1000°C, as the solids residence time was varied from 37 min to 11 min, the extent of regeneration decreased drastically from 77% to 11% (based on solids analyses). The SO_2 concentrations in the dry off-gas decreased from 2.5% to 1.4%. At this relatively low temperature, the rate of regeneration of CaO is low, and therefore long solids residence times are required to obtain acceptable ($\geq$50%) regeneration levels.

At 1050°C, decreasing the solids residence time from 34 min to 12 min decreased the extent of CaO regeneration from 90% to 56%. The SO_2 concentration in the dry off-gas increased from 3.0% to 4.8%. At 1100°C, the highest temperature level investigated, decreasing the solids residence time from 37 min to 7.0 min caused the extent of CaO regeneration to decrease from 95% to 75% and the SO_2 concentration to increase from 2% to 8.7%. (The SO_2 concentration for the experiment with a 7-min solids residence time [Exp. (CS-1)] was adjusted from 6.5% to 8.7% to compensate for the dilution due to the higher fluidizing-gas velocity.) Because the rate of regeneration of CaO is high at 1100°C, the extent of regeneration remained relatively high when the solids residence time was as low as 7 min.

An improved rate of $CaSO_4$ decomposition at higher temperatures ($\sim$1100°C) for the reductive decomposition of gypsum has also been reported by numerous workers, including Martin *et al.*[3] who used carbon as the reductant and Wheelock *et al.*[9] who used CO as the reductant. As expected, the oxygen requirement in the feed gas increased with (1) the sulfated sorbent feed rate and (2) the total amount of reductive decomposition, which is represented by the SO_2 concentration in the off-gas.

Regression Analysis of Regeneration Data. A best fit has been obtained by regression analysis for the experimental extent of CaO regeneration as a function of regeneration temperature and solids residence time. The equation is

$$\ln(1 - R) = A\cdot\tau + B\cdot\tau^2 \qquad (9)$$

where R = extent of CaO regeneration (*i.e.*, at complete regeneration, R = 1)
τ = particle residence time in the reactor, min
A,B = functions of temperature.

The temperature-dependent constants A and B were evaluated at the three regeneration temperature levels investigated (1000, 1050, and 1100°C) by least squares technique. From these values, a quadratic equation was obtained to represent the functional dependence of A and B on regeneration temperature as given below.

$$A \times 10^2 = -5.05 - 8.72T - 4.00T^2 \qquad (10)$$

$$B \times 10^4 = -2.94 + 18.64T + 10.65T^2 \qquad (11)$$

$$T = (t - 1050)/50 \qquad (12)$$

where t = regeneration temperature, °C

The values calculated with the model equation, Eq. 9, compare well with the experimental results. A correlation coefficient ranging from 0.96

to 0.99 was obtained for the experimental data and the results calculated from the model equation. Equation 9 with the calculated coefficients was found to be a good mathematical model of the dependence of the extent of CaO regeneration on regeneration temperature and solids residence time in the reactor for the investigated experimental range. This relationship for the rate of CaO regeneration has been used in a mass and energy-constrained model for the regeneration process to predict sorbent behavior within and outside the investigated operating range.

The extent of CaO regeneration as a function of temperature and sorbent residence time as calculated by Eq. 9 has been plotted in Fig. 15. The plot has been extrapolated to 1200°C, which is beyond the experimentally investigated temperature range of 1000-1100°C. On the basis of these predictions, it is expected that the extent of CaO regeneration would increase considerably (by ~1/3) if the temperature were increased from 1100°C to 1150°C at a solids residence time of 5 to 7.5 min. At higher temperatures, the extent of regeneration does not significantly increase above that at 1150°C.

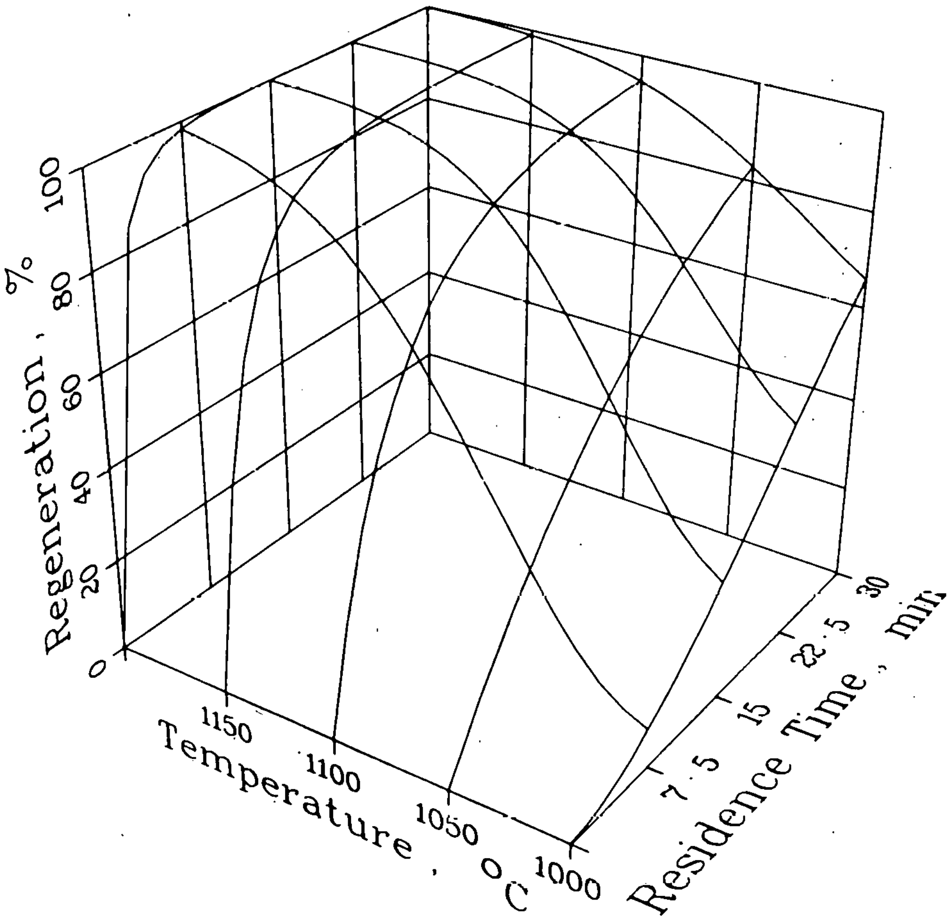

Fig. 15. The extent of CaO regeneration for Tymochtee dolomite as a function of temperature and residence time as represented by the model equation, Eq. 9.

Analysis of Variance of Regeneration Data. The series of regeneration experiments presented in Table 3 (excluding experiment CCS-1), constitutes a 3^2 factorial experimental design plus three replicate experiments. As described in the preceding section, they were designed to measure the effects of sorbent residence time in the reactor and reactor temperature on (1) the extent of CaO regeneration and (2) SO_2 concentration in the off-gas. Table 5 summarizes the design conditions for the experiments whereas the actual experimental conditions are given in Table 3.

An analysis of variance performed for the extent of regeneration as calculated from flue gas and solids analyses is summarized in Table 6. According to the F-test for significance at the $\alpha = 0.1$ level (90% confidence level), both the residence time and the temperature have a significant effect on the extent of regeneration. However, no significant difference was indicated between extents of regeneration based on the two methods of calculations: (1) by off-gas analyses and (2) by solids analyses. (This indicates that the analyses agree within analytical accuracy and that no constant difference exists between the two analytical methods.)

The validity of this analysis depends on the absence of interactions between the controlled variables. For a 3^2 factorial experimental design, the model equation is expressed by:

$$X_{ij} = \mu + \alpha_i + \beta_j + I_{ij} + \varepsilon_{ij} \tag{13}$$

where X_{ij} is the observed response, μ is the mean of all possible responses, α_i and β_j are the treatment effects, I_{ij} is the interaction effect, and ε_{ij} is the error between the observed and the expected response.

Analysis of the variance for a factorial experimental design with partial replication cannot estimate the effect of the term I_{ij}. The term I_{ij} is included in the term ε_{ij}. In addition to inflating the error mean square, the presence of an interaction can give misleading results in F-tests for significance. Comparing the error mean square (192) with the variance calculated from the replicate experiments (46) gives an indication of the extent that interaction has inflated the error mean square. Since both of these values are estimates of σ^2 (the true variance of the response data), the difference may indicate an interaction between the controlled variables.

Effect of Solids Residence Time and Temperature on SO_2 Concentration in the Off-Gas. The measured SO_2 concentrations in the dry off-gas for the experiments (Table 3) are plotted in Fig. 16. The best fit relationship (Eq. 9) for the functional dependence of CaO regeneration on solids residence time for the three temperature levels investigated was used in the model for the regeneration process (described in a later section of this report), and the SO_2 concentration in the dry off-gas was calculated for solids residence times ranging from 40 to ∿2.5 min. The calculations were made for the three investigated temperature levels, a pressure of 153 kPa, and a fluidizing-gas velocity of 1.07 m/sec. A sulfur content of 9.5 wt % was assumed for the sulfated dolomite. The calculated (predicted) SO_2 concentration in the dry off-gas are plotted in Fig. 16, together with the experimentally

Table 5. Design conditions and matrix representation for the 3^2 factorial experimental design.

Equipment: 10.8-cm-ID fluidized-bed regenerator
Fluidized-Bed Height: 46 cm
Pressure: 153 kPa
Fluidizing-Gas Velocity: 1.07 m/sec
Reducing Gas in Off-Gas: ∿2.3%

Variable	Levels of Independent Variables Level 1	Level 2	Level 3
t, Temperature, °C	1000	1050	1100
R, Residence Time, min	37	18	12

Matrix Representation of Experimental Conditions

	t_1	t_2	t_3
R_1	CS-6	CS-7	CS-15
R_2	CS-8	CS-16	CS-14
R_3	CS-17	CS-10	CS-11[a]

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[a] Three replicate (CS-12, CS-13, and CS-18) were made of this experimental condition.

Table 6. Analysis of variance of extent of CaO regeneration data, CS series of experiments.

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	Calculated F_e[a]	$F_{1-\alpha}$[b]
Residence Time	2	4011	2006	10.5	2.81
Temperature	2	5547	2774	14.5	2.81
Analytical Method	1	20	20	0.1	3.18
Error	12	2300	192		
Corrected Total	17	11878			

[a] F_e = Ratio of variable mean square to error mean square.

[b] α = 0.1 (90% confidence level).

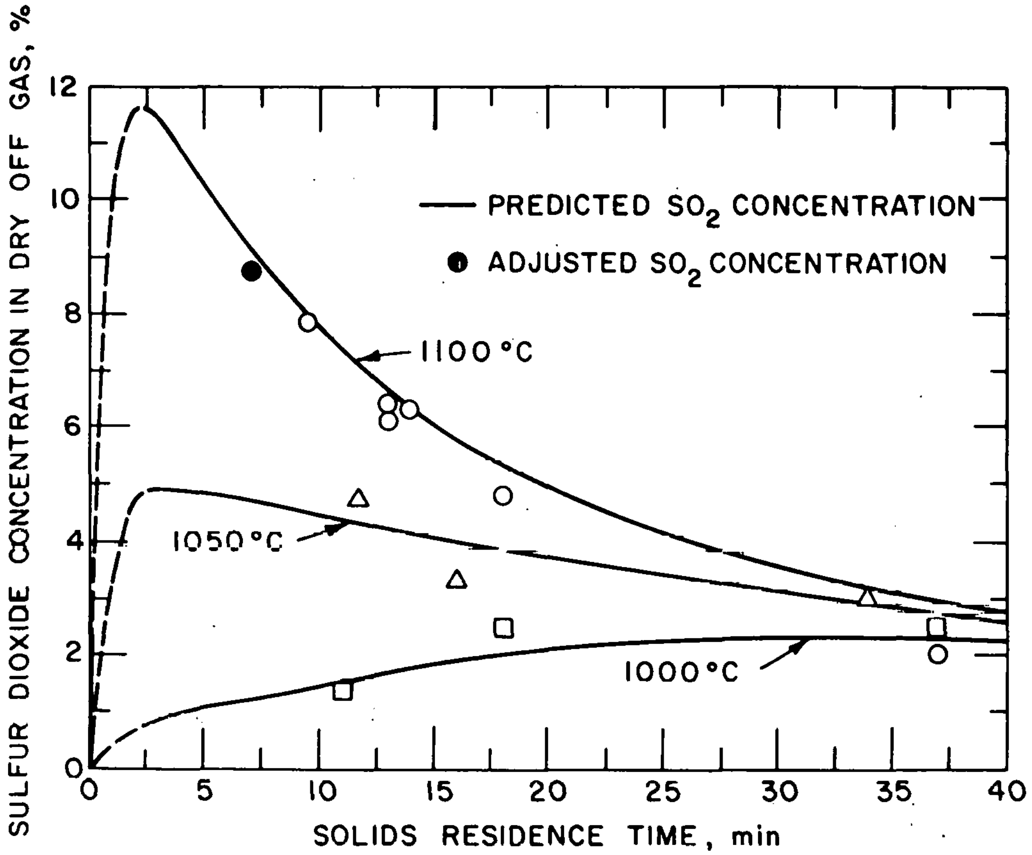

Fig. 16. Predicted and experimental SO_2 concentration as a function of solids residence time at three regeneration temperatures (pressure: 153 kPa).

obtained concentrations. The experimental and predicted SO_2 concentrations in the dry off-gas for all three temperature levels were in good agreement.

At 1000°C, the SO_2 concentration in the dry off-gas is predicted to continually decrease as the solids residence time decreases, in agreement with the experimental data. At this temperature, the regeneration rate was low. At 1050°C and 1100°C, the SO_2 concentration is predicted to be maximum at the lowest permissible solids residence time of ~2.5 min, at which point the process oxygen requirement is greater than the quantity of total fluidizing gas.

At 1100°C, much higher SO_2 concentrations were experimentally obtained and predicted. For a 5-min solids residence time (realistic), an SO_2 concentration in excess of 10% is predicted.

At 1100°C, the experimental SO_2 concentrations increased from 2% to 8.7% as the solids residence time was decreased from 37 min to 7 min. These experimental results show that for temperatures $\geq$1050°C, as the solids residence time in the reactor is decreased (*i.e.*, at higher rates of sulfated sorbent throughput), extent of regeneration is sacrificed but SO_2 concentration in the dry off-gas is increased. The possible kinetic effect of introducing room-temperature sorbent for very short solids residence times, <7 min, has not yet been evaluated.

With Eq. 9 used for the functional dependence of extent of CaO regeneration on temperature and solids residence time in the above-mentioned model for the regeneration process, the SO_2 concentrations in the dry off-gas were also predicted at three different system pressures and are given in Fig. 17. These predictions were extrapolated beyond the experimentally investigated temperature range of 1000-1100°C. The effect of pressure on SO_2 concentration is very large, as discussed below. It is predicted that with a system pressure of 1000 kPa (10 atm), SO_2 concentrations no greater than 4% can be obtained, even with regeneration temperatures as high as 1200°C and solids residence times as short as 5 min. At a pressure of 100 kPa (1 atm), SO_2 concentrations as high as 20% are predicted at regeneration temperatures up to 1200°C. However, based on the experience to date with the regeneration process at ANL and by Skopp *et al.*,[5] it is expected that regeneration temperatures in excess of 1100°C will not be feasible because of an increased tendency of the sulfated sorbent (a mixture of sorbent and residual coal ash) to agglomerate. Also, high temperatures (>1100°C) may have a detrimental effect on the reactivity of the sorbents in subsequent sulfation cycles.

Higher temperatures were found to increase both the extent of CaO regeneration and the SO_2 concentration in the off-gas. This effect of temperature agrees with previous results presented in Section I, in which methane was used as the fuel for the regeneration of dolomite by reductive decomposition. Increased SO_2 concentrations in the off-gas at higher regeneration temperatures have also been reported by Hoke *et al.*[8] for the reductive decomposition of pure $CaSO_4$ in a fluidized-bed batch regeneration. Based on the above results with Tymochtee dolomite, an industrial regeneration process should be operated at 1100°C and a solids residence time of ∿5-8 min. The SO_2-enriched off-gas from the regeneration process operated at a pressure of 100 kPa (1 atm) can be expected to contain ∿10-13% SO_2 at best, without off-gas recycle.

Effect of System Pressure on Extent of CaO Regeneration and Off-Gas SO_2 Concentration. Thermodynamically, from an equilibrium standpoint, when the system pressure is lowered, the SO_2 concentration in the off-gas will increase. In the fluidized-bed process, the SO_2 concentration in the off-gas is determined by the rate of total gas flow through the reactor and the rate of CaO regeneration in the reactor. Because the air requirements (fluidizing gas and/or combustion oxygen) and energy requirements (sensible heats of gas and solids, and the heats for the decomposition reactions) of the process are high, equilibrium SO_2 concentrations in the off-gas cannot be achieved practically. At low pressures, less fluidizing gas is required and thus the extent of dilution is reduced.

The effect of system pressure on the extent of regeneration of CaO and the SO_2 concentration in the dry off-gas has been evaluated in six experiments in which sulfated Tymochtee dolomite from the second and sixth regeneration cycles of a ten-cycle experiment was regenerated. The experimental conditions and results are given in Table 7. In experiments CCS-2A, -2B, and -2C, the pressure was ∿115 kPa or ∿75% of that in CCS-2. In the experiments at the lower pressure, decreasing solids residence time from 8.8 min to 5.3 min caused

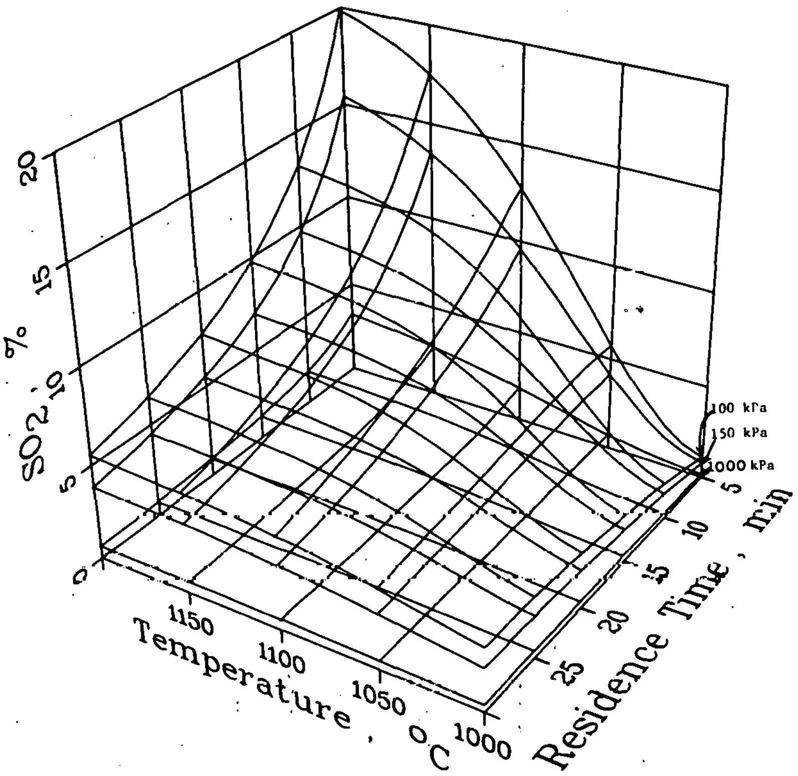

Fig. 17. Predicted SO_2 concentration in the dry off-gas as a function of solids residence time, regeneration temperature, and system pressure.

<u>Experimental Conditions</u>
Solid Feed Temp, °C: 815
Fluidizing-Gas Velocity, m/sec: 1.07
Fluidizing-Gas Feed Temp, °C: 650
Sulfur Concentration in Sorbent, %: 9.5

the extent of CaO regeneration to decrease from 80% to 60% (based on solids analysis). These results on extent of regeneration are in agreement with those obtained at the higher pressure of 153 kPa (see Fig. 14) and equivalent solids residence times. Specifically, results for CCS-2B and CCS-2 agree well.

At the lower pressure, the measured SO_2 concentration in the dry off-gas increased from 8.9% to 9.6% as the solids residence time was decreased from 8.8 min to 5.3 min. These concentrations are higher than those obtained in the higher pressure experiments (Table 3 and Exp. CCS-2). A larger difference, and a more accurate comparison between off-gas SO_2 concentrations from the lower and higher pressure experiments, would be obtained by adjusting the concentrations for a common fluidizing-gas velocity of 1.07 m/sec (the velocity used for predictions in Fig. 17) as given in Table 7. The adjusted SO_2 concentrations could then be compared with the results in Fig. 17.

Table 7. Effect of regeneration pressure on the regeneration of Tymochtee dolomite and the SO_2 concentration in the off-gas.

Nominal fluidized-bed height: 46 cm
Reactor ID: 10.8 cm
Temperature: 1100°C
Reducing gas concentration in off-gas: 3.0-3.2%
Coal: Triangle coal (0.98 wt % S)
Sorbent: -14 +30 mesh, sulfated dolomite in the second (10.7 wt % S) and sixth (9.3 wt % S) utilization cycles.

Exp.	Pressure, kPa	Fluidizing-Gas Velocity, m/sec	Solids Residence Time, min	CaO Regeneration, %	SO_2 Concentration in Dry Off-Gas, %[b]/%[c]	Minor Sulfur Compounds in Off-Gas, %		
						H_2S	COS	CS_2
CCS-2A	115	1.35	8.8	78	8.9/11.2	0.03	0.1	0.1
CCS-2B	115	1.41	7.4	69	9.5/12.5	0.04	0.1	0.1
CCS-2C	118	1.44	5.3	57	9.6/12.9	-	-	-
CCS-2	153	1.26	7.5	67	8.6/10.1	0.02	0.1	0.1
CCS-6A	125	1.22	7.5	73	10.4/11.9	0.03	0.1	0.1
CCS-6	153	1.18	7.8	75	8.7/ 9.6	0.03	0.1	0.1

[a] Based on chemical analysis of dolomite samples.
[b] Measured SO_2 concentration.
[c] Adjusted SO_2 concentration based on a constant fluidizing-gas velocity of 1.07 m/sec.

During the regeneration step of the sixth utilization cycle of the cyclic experiments, an additional experiment (CCS-6A) was performed at a reduced pressure, 125 kPa instead of 153 kPa (CCS-6). The experimental conditions and results for both of these experiments are also presented in Table 7. As a result of lowering the system pressure by ∿20% while the fluidizing-gas velocity was maintained almost constant (∿1.2 m/sec), the SO_2 concentration in the dry off-gas increased by ∿20% from 8.7% to 10.4% (the highest SO_2 concentration obtained to date). The SO_2 concentration in the off-gas increased because of less dilution at the reduced pressure.

Relatively high SO_2 concentrations (∿8%) have also been reported by Gordon *et al.*[10] for the regeneration of limestone at atmospheric pressure. Although the number of experiments in this evaluation was limited and the pressure variation was small, the system pressure was found to have a negligible effect on the rate of CaO regeneration because the SO_2 concentration in the off-gas was not near equilibrium. However, pressure has been found to affect the SO_2 concentration in the off-gas via the extent of dilution.

Formation of CaS. The sulfated dolomite before regeneration contained negligible amounts of CaS. The buildup of CaS during regeneration of Tymochtee dolomite for all experiments, including those performed at 1000°C, was found to be ≤ 0.1 wt % (S^{2-}). The investigated ranges of temperature, solids residence time, and system pressure had no significant effect on the buildup of CaS because of the existence of an oxidizing zone at the bottom of the fluidized bed, as discussed in Section I of this report.

III. MASS AND ENERGY CONSTRAINED MODEL FOR THE REGENERATION PROCESS

A first-generation mass and energy constrained model for the one-step regeneration process was developed and used to predict the effects of experimental variables on:

1. Off-gas composition (SO_2, CO_2, H_2O, *etc.*)
2. Volumetric gas changes
3. Fuel and oxygen requirements
4. Individual energy terms
5. Fuel cost and consumption of regeneration

The first phase of this work was concentrated on what occurs in the regeneration reactor. The objectives were to predict the effects of experimental variations and to use these results to guide further experimental efforts.

Model Description

A flow chart for the regeneration process model is given in Fig. 18. The input parameters consist of (1) reactor conditions and size (temperature, pressure, fluidizing gas velocity, fluidized bed depth, and reactor diameter), (2) feed stream description (feed fluidizing gas temperature, sulfated sorbent feed rate, sorbent composition, *i.e.*, sulfur and carbonate, and feed sorbent temperature), and (3) coal properties (composition, *i.e.*, carbon, hydrogen, and sulfur and heating value). The conversions in the model (extent of

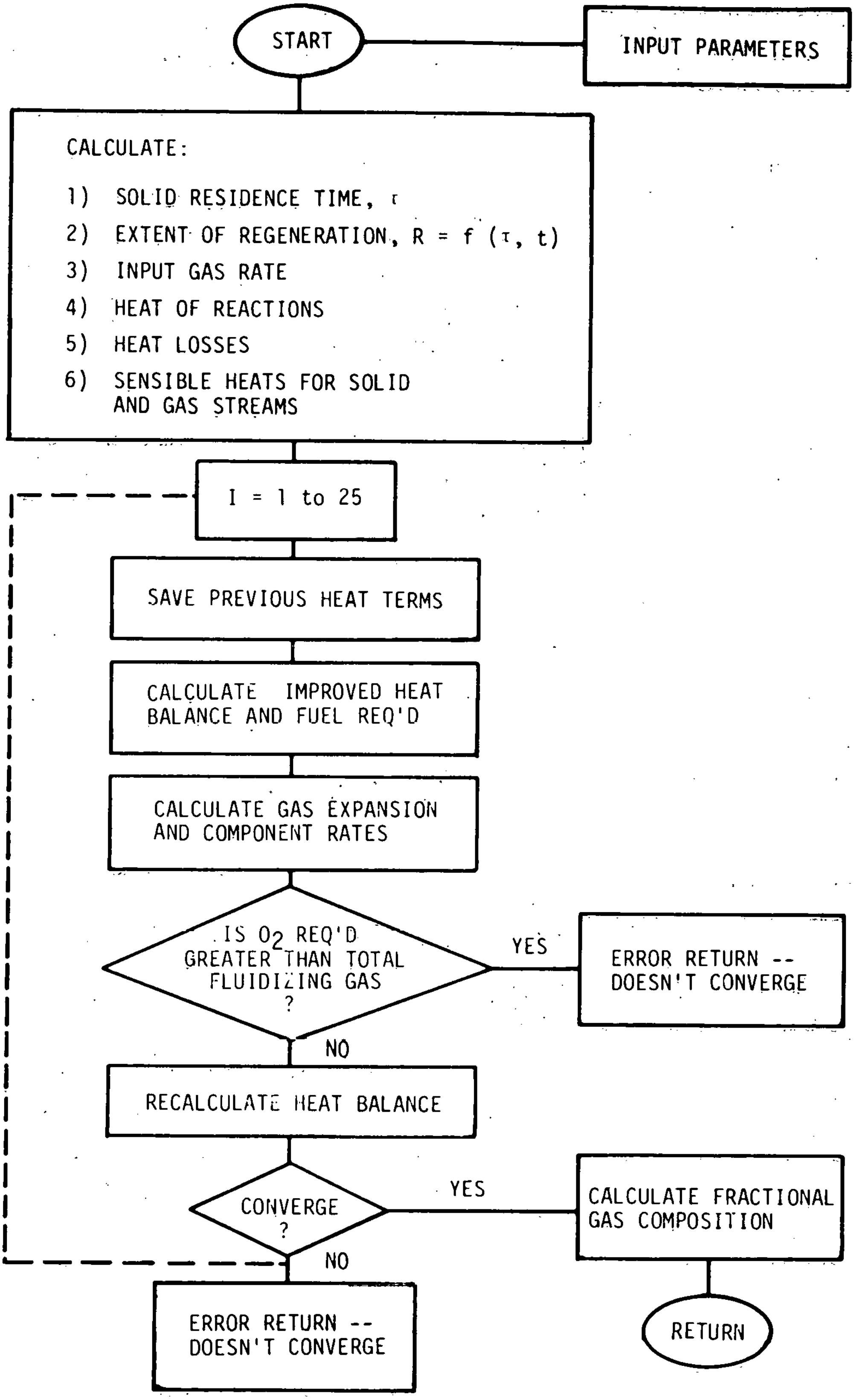

Fig. 18. Flow diagram for the regeneration process model

regeneration) are predicted from the above given (Section II) least squares best fit equation, Eq. 9, which was obtained from the experimental data in Table 1.

$$\ln(1 - R) = A\cdot\tau + B\cdot\tau^2 \qquad (9)$$

where R = fractional extent of CaO regeneration (*i.e.*, at complete regeneration, R = 1)
τ = particle residence time in the reactor, min

$$A \times 10^2 = -5.05 - 8.72T - 4.00T^2 \qquad (10)$$

$$B \times 10^4 = -2.94 + 18.64T + 10.65T^2 \qquad (11)$$

$$T = (t - 1050)/50 \qquad (12)$$

where t = regeneration temperature, °C

Equation 9 was found to be a good mathematical model of the dependence of the extent of CaO regeneration on regeneration temperature and solids residence time in the reactor for the investigated experimental range.

The decomposition reactions that the sorbent undergoes are the calcination reaction:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2 \qquad (14)$$

and the reductive decomposition reactions (Eq. 1 and 2). All of these decomposition reactions are endothermic and their thermal requirements are provided by the coal ($CH_m + nH_2O$) combustion reactions which are represented as follows in the model. For oxidizing conditions:

$$(CH_m + nH_2O)(s) + (\frac{m}{4} + 1)O_2 \rightarrow CO_2\ (\frac{m}{2} + n)H_2O \qquad (15)$$

for reducing conditions:

$$(CH_m + nH_2O)(s) + 1/2\ O_2 \rightarrow CO + \frac{m}{2} H_2 + nH_2O \qquad (16)$$

From the above decomposition and combustion reactions, it is apparent that the gas volume increases as a result of reactions in the reactor.

In the model, the energy balance is performed by assuming that (1) the feed streams are first cooled to 25°C, (2) the feed streams are then reacted, and (3) the product solid and gas streams are heated to the operating reactor temperature. The sensible heats of the streams are based on the rates and compositions of the streams.

The total heat requirement (Q) in the regenerator reactor is:

$$Q = Q_{lost} + Q_{des} + Q_{cal} + Q_{sorb} + Q_{gas} + Q_{ec} \qquad (17)$$

where

Q_{lost} = heat losses from the reactor
Q_{des} = heat of desulfation
Q_{cal} = heat of calcination
Q_{sorb} = sensible heat difference between regenerated and sulfated sorbent
Q_{gas} = sensible heat difference between effluent and input gas
Q_{ec} = sensible heat for the unburned elutriated coal

It is assumed that this internal heat requirement will be satisfied by the combustion of coal.

$$Q = Q_{ci} + Q_{cc}$$

where

Q_{ci} = heat liberated during the required incomplete combustion of coal (Eq. 16)

If $Q_{ci} < Q$,

Q_{cc} = additional heat requirements to be supplied by complete combustion of coal (Eq. 15)

If $Q_{ci} > Q$,

Q_{cc} = heat which must be removed from the process

The major assumptions and properties of the model are summarized below:

1. The solids and the off-gas exit at the reactor temperature.
2. The sorbent is fully calcined during regeneration.
3. The extent of regeneration is a function of solids residence time and temperature (Eq. 9).
4. The heat capacities of solid and gas constituents are temperature-dependent.
5. Oxygen concentration in the feed gas can be varied.
6. Total coal utilization is 80% (experimental average).

Using the stated assumptions, the above mass and energy relations are interlocked and solved for different conditions, as shown in the flow diagram for the model (Fig. 18).

Examples of plotted calculated output and comparisons with some experimental results are given in Figs. 19 through 23, to which the following operating conditions apply:

Temperature: 1094°C (2000°F)
Fluidizing-gas velocity: 1.07 m/sec (3.5 ft/sec)
Pressure: 153 kPa (22.5 psia)
Reactor ID: 10.8 cm (4.25 in.)

Nominal fluidized-bed height: 46 cm (19 in.)
Feed gas temp: 344°C (650°F)
Feed solids temp: 25°C (77°F)
Solids residence time: 2-200 min (mass feed rates: 90-0.9 kg/hr)
Sulfated Tymochtee dolomite: 9.5% sulfur and 9.5% CO_3^{2-}

Predicted Effects of Solids Residence Time on Volumetric Gas Change. The input functional dependence of extent of CaO regeneration (Eq. 9) is regiven in Fig. 19, along with the calculated increase in gas volume during regeneration, as a function of solids residence time (SRT). At SRTs of less than 10 min, large gas volumetric increases are predicted, caused by necessarily increased coal combustion due to (1) increased heat requirements (sensible heat differences of solids and gases, and heat of decomposition reactions) and (2) increased solids decomposition for the process. The increases in gas volume dilute the SO_2 in the effluent gas.

Coal Feed Rate and Oxygen Concentration. In Fig. 20, the predicted coal feed rate and the predicted required oxygen concentration are given as functions of SRT. The experimental conditions and results for the measured variables in experiments CS-11 and -12 are also plotted for comparison with the predictions. Agreement of predicted values with experimentally obtained values was good.

Off-Gas Composition. The predicted off-gas constituent concentrations as functions of solids residence time are given in Fig. 21. The concentrations of all pertinent constituents increase with decreasing SRT (increasing solids feed rate). At a SRT of 5 min, a SO_2 concentration of 9.4% in the dry off-gas is predicted for the experimental conditions described above.

Heat Requirements. The predicted individual heat requirements for the one-step regeneration process are plotted in Fig. 22 as functions of solids residence time. At low SRT, the sensible heat requirements of the solids and gas constitute most of the required heat.

Cost for Regeneration Fuel. The fuel cost for regeneration per electric power unit produced when burning 3% sulfur coal has been predicted as a function of SRT and is shown in Fig. 23. The experimental conditions for regeneration are given above. The costs plotted are relative costs obtained to estimate the effect of operating conditions such as SRT and feed solid and gas temperatures. In an industrial process, these costs would be lowered by recovering the sensible heat from the effluent regenerator streams. (A coal cost of $29/tonne was used in predicting the regeneration fuel costs.) It has been found that for the experimental conditions outlined above, the energy cost of regeneration is optimum at a SRT of ∿9 min. (For an industrial process, it is expected that the optimimum will occur at a lower solid residence time.) At lower solids residence times, the extent of regeneration decreases, and the sensible heat requirements for the solids and gas increase rapidly for these conditions (cold solids and gas feed).

Preliminary Sensitivity Analysis on Selected Process Design Conditions

Table 4 shows, for a solids residence time of 5 min, the predicted

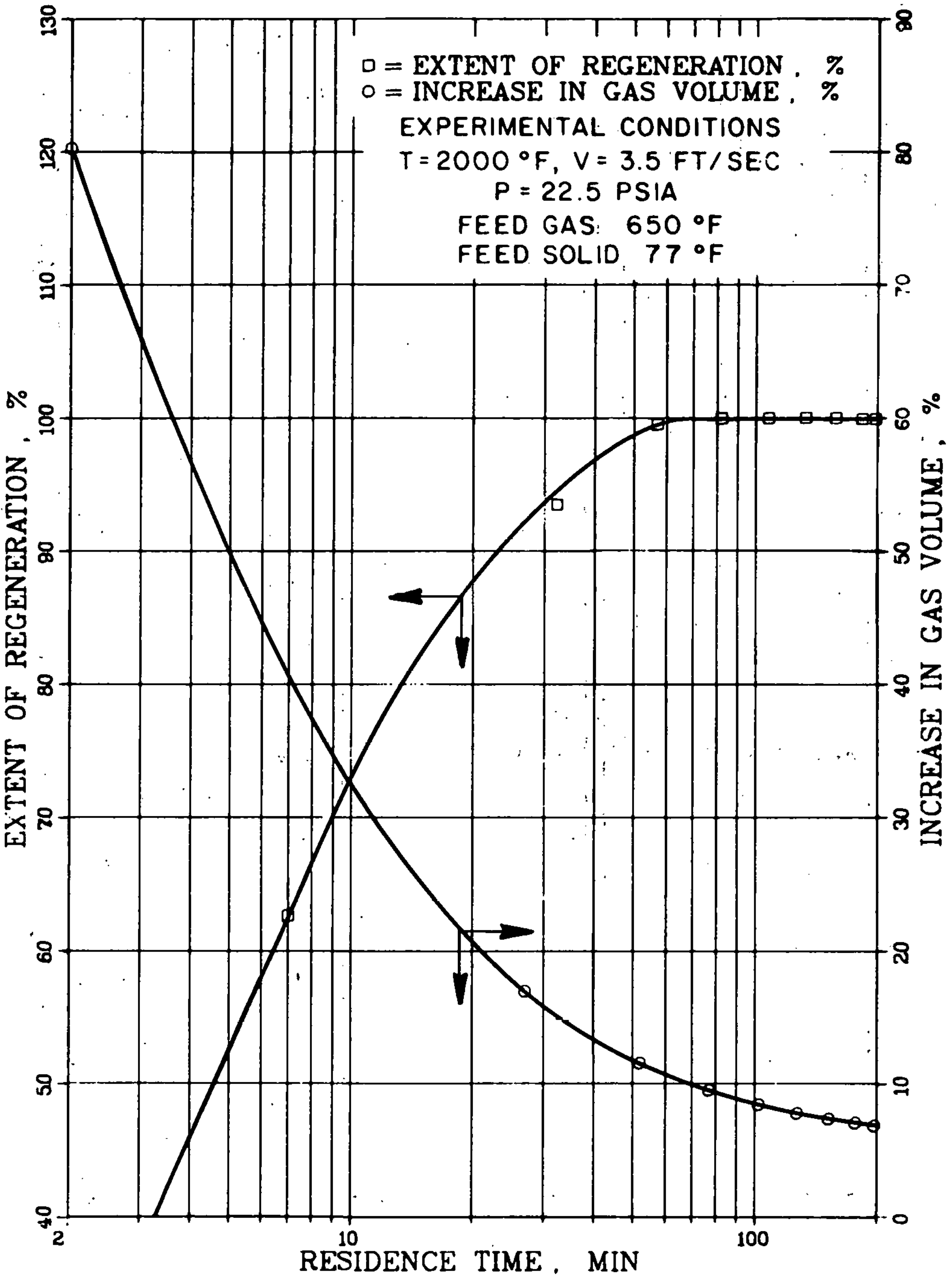

Fig. 19. Experimental solids regeneration and predicted increase in gas volume during regeneration as functions of solids residence time

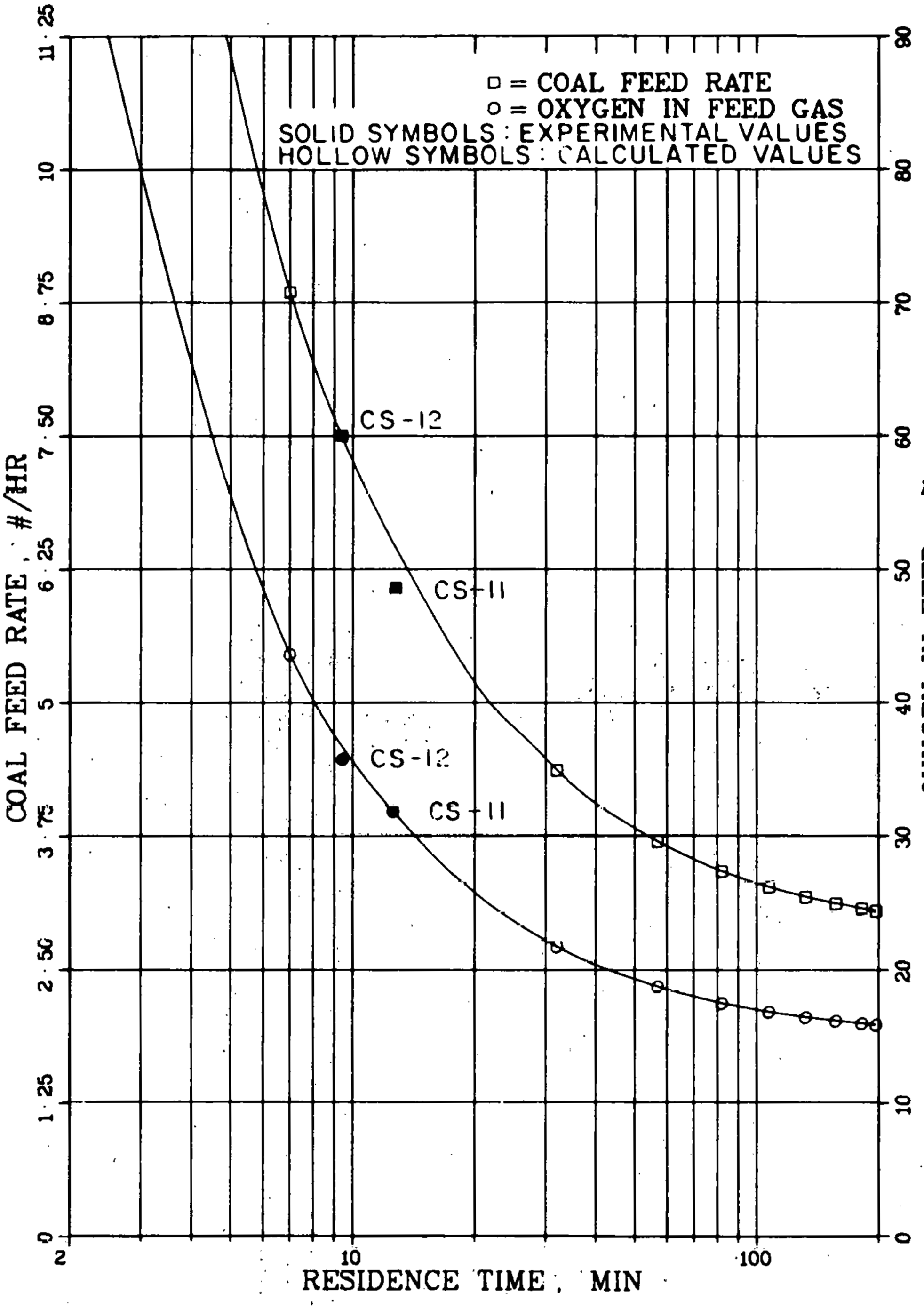

Fig. 20. Predicted and experimental required coal feed rate and oxygen concentration in the feed gas as functions of solids residence time

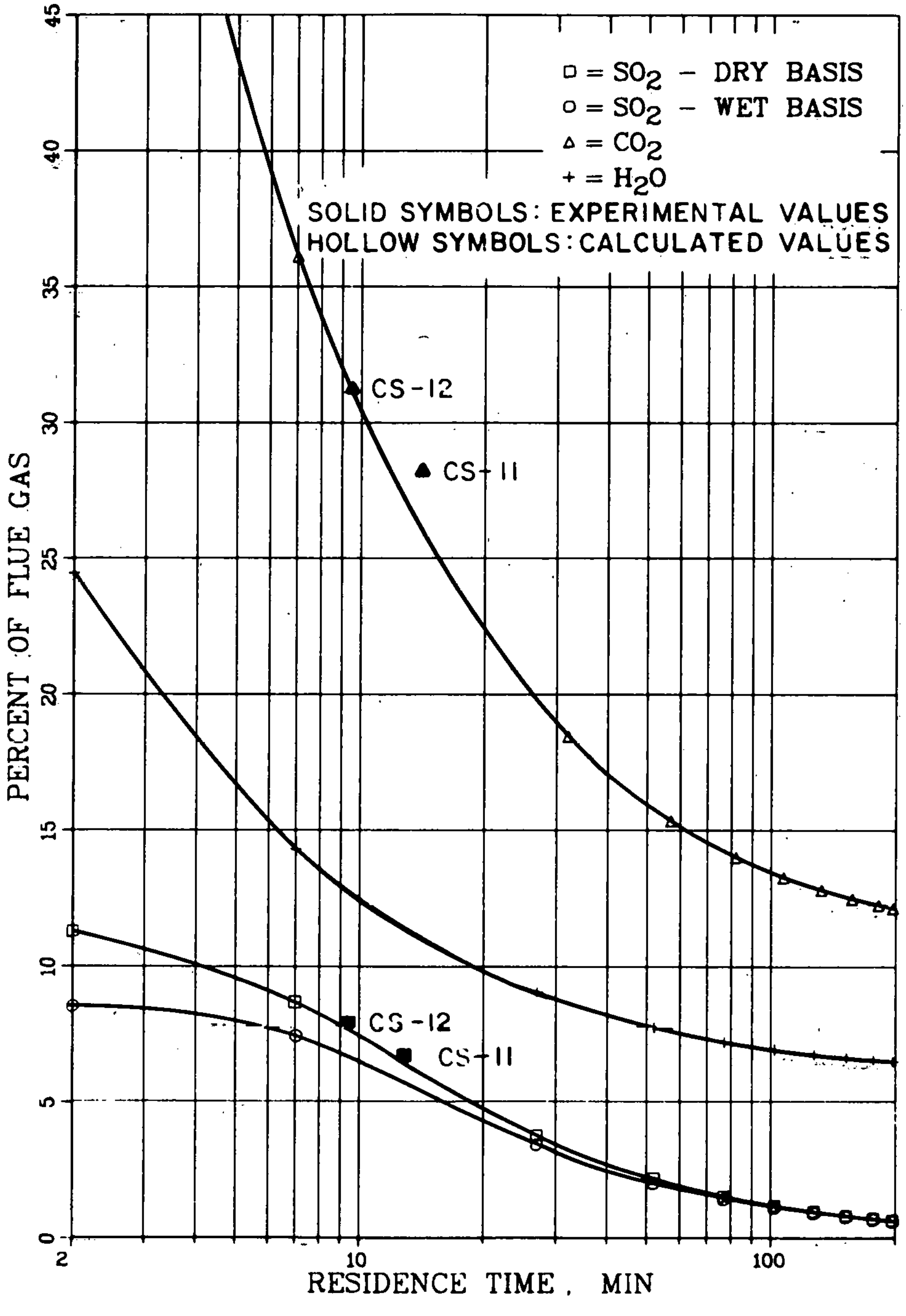

Fig. 21. Predicted off-gas constituent concentrations as functions of solids residence time

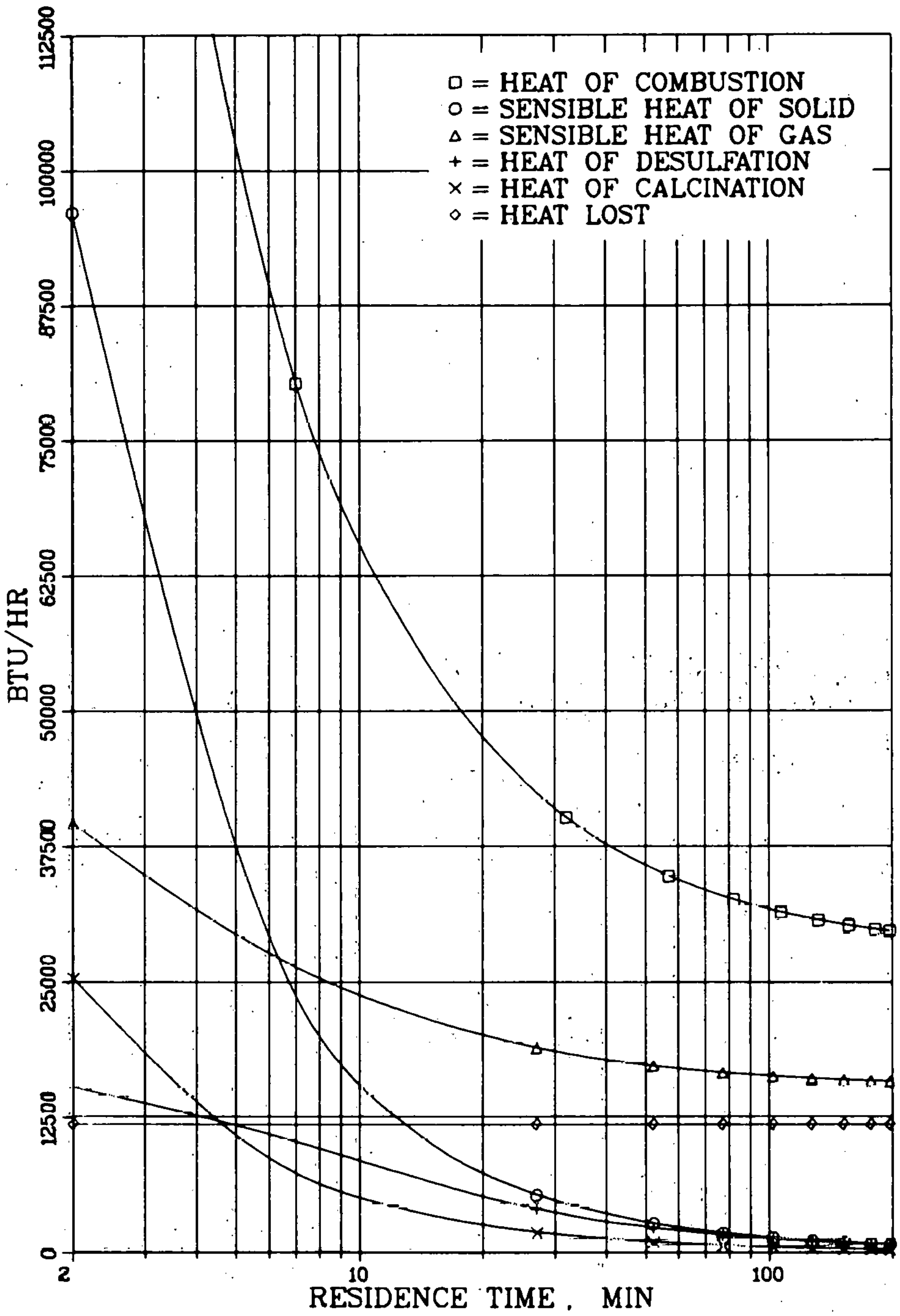

Fig. 22. Predicted individual heat requirements as a function of solids residence time

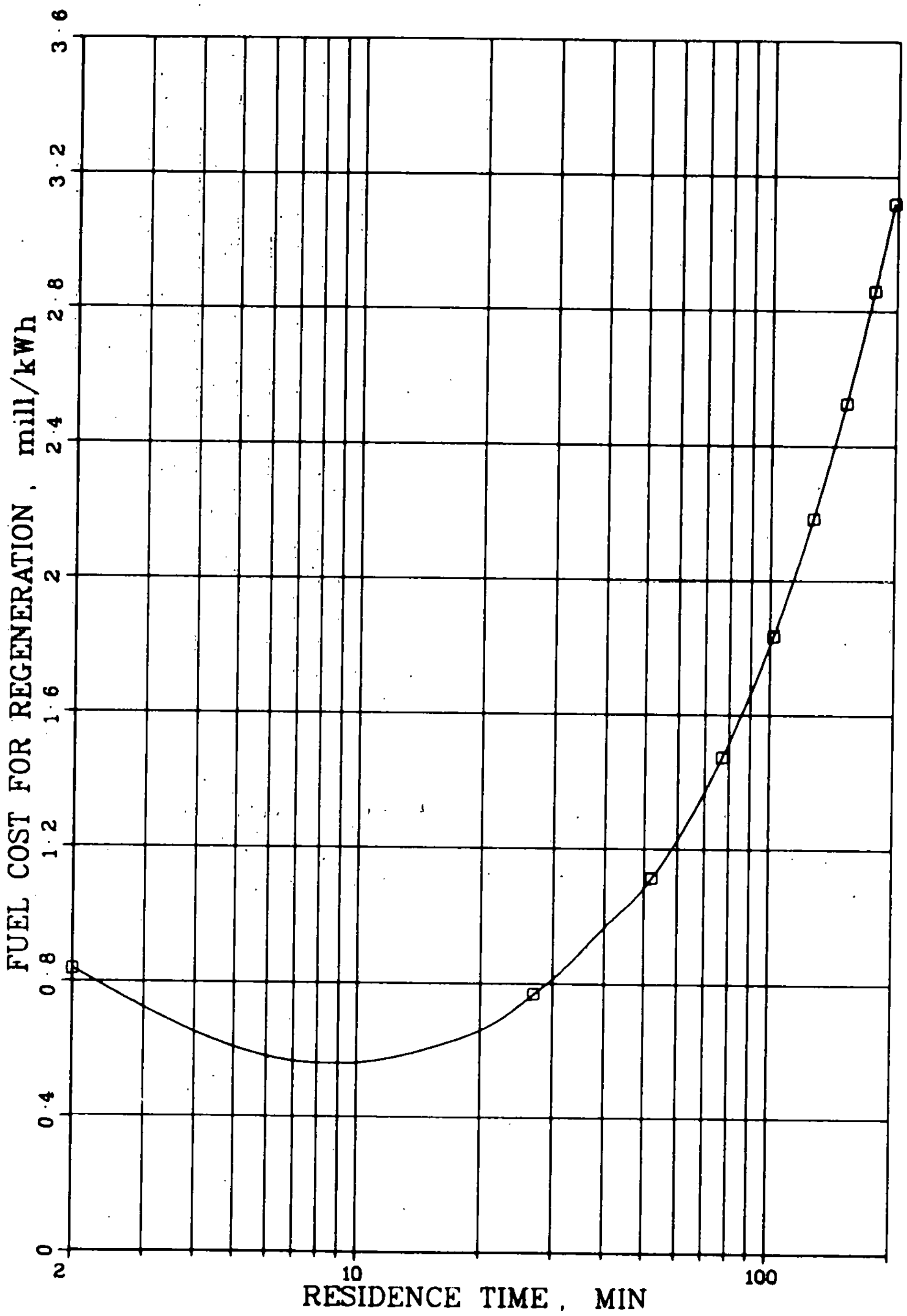

Fig. 23. Predicted fuel cost for regeneration per electric power unit produced when burning 3% sulfur coal as a function of solids residence time. (These costs are not representative of those in a commercial plant since conditions have not been optimized.)

Table 8. Predicted effects of design conditions on regeneration results.

Sulfated Sorbent: Tymochtee Dolomite (9.5 wt % S)
Regeneration Temperature: 1094°C
Solids Residence Time: 5 min
Fluidizing Velocity: 1.07 m/sec

	Design Conditions					Predicted Results					
	Pressure, kPa	Solids Feed Temp, °C	Gas Feed Temp, °C	Carbonate in Sulfated Sorbent, %	Reactor Dia, cm	SO_2 in Dry Off-Gas, %	Req. Feed O_2, %	Gas Volume Increase, %	Process Heat Requirement, Btu/hr	Fuel Cost for Regeneration[a] mills/kWh	Tonnes of Coal for Regeneration/Tonne of Coal for Combustion[b]
1	153	25	345	9.5	10.8	9.6	53.5	49.4	89 K	0.59	0.068
2	153	650	650	9.5	10.8	9.4	38.6	46.1	62 K	0.45	0.052
3	153	650	650	9.5	21.6	9.3	34.9	45.2	220 K	0.41	0.048
4	153	650	650	9.5	43.2	9.3	33.6	44.9	841 K	0.40	0.046
5	153	650	650	0	10.8	10.3	33.3	32.5	52 K	0.40	0.046
6	102	650	650	9.5	10.8	12.7	54.6	67.4	58 K	0.43	0.049
7	153	870	870	9.5	10.8	9.3	32.0	44.5	50 K	0.39	0.045
8	153	1094	870	9.5	10.8	9.2	26.0	43.2	39 K	0.33	0.038
9	153	870	1094	9.5	10.8	9.3	31.0	44.3	48 K	0.38	0.043
10	153	1094	1094	9.5	10.8	9.2	25.0	42.9	37 K	0.32	0.037

[a] These costs are not representative of those in a commercial plant since conditions have not been optimized and no credit for recoverable sensible heat is given. Coal cost, $29/tonne.

[b] A 3 wt % S coal was assumed to be burned in the combustion step.

effects of solids and gas feed temperatures, fluid bed temperature, fluidizing gas velocity, experimental pressure, carbonate concentration, and reactor diameter on: SO_2 concentration in the off-gas, oxygen requirement in the feed, increase in gas volume, process heat requirement, fuel consumption, and fuel cost for regeneration. Case 1 represents the input conditions for the experimental capabilities of the existing (process development-scale) experimental regeneration system. The predicted SO_2 concentrations as a function of solids residence time and temperature are given in Fig. 16 for the experimental conditions of Case 1.

In Cases 2, 3, and 4, the effects of increasing the reactor ID from 10.8 cm to 43.2 cm were predicted. For the two larger reactors, the heat losses are lower and thus the energy cost of regeneration is reduced. The SO_2 concentration in the dry off-gas is predicted to be unaffected by this fourfold increase in diameter.

The effect of carbonate content in the sulfated sorbent was predicted by comparing Cases 2 and 5. Decreasing the concentration of $CO_3{}^{2-}$ from 9.5% to 0 would result in increasing the SO_2 concentration in the dry off-gas from 9.4% to 10.3%.

The most effective parameter for influencing the SO_2 concentration in the dry off-gas was found to be experimental pressure. Decreasing the pressure from 153 kPa (22.5 psia) in Case 2 to 102 kPa (15 psia) in Case 6, the SO_2 concentration in the off-gas would increase from 9.4% to 12.7% because the total gas feed rate would decrease by ∿50%.

In Cases 2, 7, 8, 9, and 10, the effects of preheating the feed solids and gas to temperatures as high as 1094°C (2000°F) are predicted for a solids residence time of 5 min. The SO_2 concentration in the wet effluent gas (not shown) is predicted to increase from 8.1 in Case 1 (16% water) to 8.3% in Case 10 (9.1% water). However, the SO_2 concentration in the dry off-gas is predicted not to increase because the amount of water formed decreased. The required oxygen concentration in the feed gas decreased from 53.5% in Case 1 to 31% in Case 9. The possible effect of preheating the sulfated sorbent on the rate of regeneration was not considered. These predictions suggest that for a realistic plant situation in which air would be utilized rather than oxygen-enriched gas, a fluidizing gas velocity greater than 1.07 m/s will be required to satisfy the oxygen requirements of the system at the same solids residence time of 5 min.

The energy cost of regeneration (per unit of electric power generated with the combustion of 3% sulfur coal) decreased from 0.6 mill/kWh (Case 1) to 0.3 mill/kWh (Case 10). In terms of relative amounts of coal required for regeneration compared to that required for power generation, regeneration coal requirements decreased from 7% (Case 1) to 4% (Case 10). It was assumed that no energy was recovered from the hot (1095°C) solids and gas effluent streams. It is expected that with proper energy credits, the regeneration reactor will impose an energy burden of 2-3% on the power plant.

IV. CONCLUSIONS

From a technical standpoint, the fluidized-bed sorbent regeneration process using coal as the fuel has been found to be a promising process for reducing the potentially large waste disposal problem from fluidized-bed coal combustion processes. Ongoing economic evaluations at ANL will determine its economic feasibility.

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D. DeCoursin, Fluidyne Engineering Co.
T. E. Dowdy, Babcock and Wilcox Company
S. Ehrlich, Electric Power Research Institute
M. Evans, Aerotherm Division of ACUREX Corporation
M. H. Farmer, Exxon Research & Engineering Co., Linden, NJ
C. Fisher, Univ. Tennessee
T. Fitzgerald, Oregon State U.
J. F. Flagg, Universal Oil Products Co.
H. B. Forbes, Stone & Webster Engineering Corp.
V. Forlenca, Englehard Industries
R. L. Gamble, Foster Wheeler Energy Corporation
D. E. Garrett, Garrett Energy Research and Engineering, Inc.
L. Gasner, U. Maryland
J. Geffken, DOE-CCU (5)
R. Glenn, Combustion Processes, Inc.
O. J. Hahn, Univ. Kentucky
W. Hansen, Babcock & Wilcox Co., Barberton, O.
M. J. Hargrove, Combustion Engineering, Inc.
R. D. Harvey, Illinois State Geological Survey
R. Helfenstein, Illinois State Geological Survey
R. G. Hickman, Lawrence Livermore Lab.
D. Huber, Burns & Roe, Inc., Paramus, NJ
F. D. Hutchinson, Gibbs and Hill
D. L. Keairns, Westinghouse Research Laboratories
W. E. Kramer, Fluidized Combustion Co.
H. Lange, Babcock & Wilcox Co., Alliance, O.
C. B. Leffert, Wayne State University
A. M. Leon, Dorr-Oliver Inc.
R. M. Lundberg, Commonwealth Edison Co.
J. J. Markowsky, American Electric Power Service Corp., New York City
W. McCurdy, DOE-CCU
W. McGough, Jr., Tetra Tech, Inc.
J. Mesko, Pope, Evans and Robbins (2)
T. A. Milne, Midwest Research Institute
W. G. Moore, Dow Chemical, USA
S. Moskowitz, Curtiss-Wright Corporation
W. Norcross, Combustion Engineering, Inc.
T. A. Pearce, Dow Chemical
W. A. Peters, Massachusetts Institute of Technology
C. Petty, Michigan State U.
J. T. Reese, Tennessee Valley Authority
A. F. Sarofim, Massachusetts Institute of Technology
R. D. Smith, Combustion Power Company, Inc.
C. Space, Reynolds, Smith & Hills, Jacksonville, FL
W. K. Stair, Univ. Tennessee
F. Staub, General Electric Corp., Schenectady
W. Steen, U. S. Environmental Protection Agency (16)
M. Steinberg, Brookhaven National Laboratory
W. Strieder, Univ. Notre Dame
S. E. Tung, Massachusetts Institute of Technology
V. Underkoffler, Gilbert Associates, Inc.
F. A. Walton, Combustion Power Co.

A. E. Weller, Battelle Columbus Labs.
T. D. Wheelock, Iowa State University
J. S. Wilson, Morgantown Energy Research Center
K. Yeager, Electric Power Research Inst.
D. Zallen, Univ. Kentucky
R. E. Zoellner, Stearns-Rogers
J. Highley, U.K. National Coal Board, England
H. R. Hoy, BCURA Ltd., England
H. Schreckenberg, Bergbau-Forschung GmbH, Germany
G. Moss, Esso Research Centre, England
B. A. Wiechula, Imperial Oil Enterprises, Canada