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A DEVELOPMENT PROGRAM ON PRESSURIZED FLUIDIZED-BED COMBUSTION

Quarterly Report

July 1, 1975—September 30, 1975

by

G. J. Vogel, P. Cunningham, J. Fischer,
B. Hubble, S. Lee, J. Lenc, J. Montagna,
S. Siegel, R. Snyder, S. Saxena,
W. Swift, I. Wilson, and A. A. Jonke

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Coal Conversion and Utilization—
Direct Combustion of Coal
(UC-90e)

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

A DEVELOPMENT PROGRAM ON PRESSURIZED FLUIDIZED-BED COMBUSTION

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Chemical Engineering Division

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16. Abstracts

A development program on pressurized fluidized-bed combustion is being carried out in a bench-scale pilot plant capable of operating at 10-atm pressure. The concept involves burning fuels such as coal in a fluidized bed of particulate lime additive that reacts with the sulfur compounds formed during combustion to reduce air pollution. Nitrogen oxide emissions are also reduced at the combustion temperatures used, which are lower than those used in a conventional coal combustor. The $CaSO_4$ produced in the combustor is regenerated to CaO that is recycled to the combustor for removal of sulfur compounds.

This report presents information on the effects of coal and additive particle size on SO_2 and NO emissions, one-step regeneration of sulfated limestone, laboratory-scale experiments on the reaction of calcium sulfide with calcium sulfate, volatile constituents in the effluent gas from coal combustion, properties of a dolomite bed of a range of particle sizes and shapes at minimum fluidization, and the status of separation of the combustion system and regeneration system.

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Fluidized-Bed Processing
Sulfur Oxides
Dolomite
Fossil Fuel
Combustion
Coal
Calcium Sulfates
Additives
Sulfur
Calcium Oxides
Calcium Carbonate
Flue Gas
Aluminum Oxide
Roasting
Calcium Sulfide
Lignite
Sorbents
Ashes
X-ray Diffraction
Desulfurization
Particle Shape
Particle Size
Flue Dust
Fly Ash
Particle Size Distribution
Fragmentation
Agglomeration
Hydrogen
Methane

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Air Pollution Control
Stationary Sources
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Supported Additives
Additive Regeneration
Fluidization Velocity

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SUMMARY

Bench-Scale, Pressurized, Fluidized-Bed Combustion Experiments

The 6-in.-dia, pressurized, fluidized-bed combustor was returned to service while work to provide ancillary components for a separate regeneration system continued. Several unsuccessful attempts were made to complete combustion experiment LIG-2, in which Glenharold lignite coal was burned in an inert fluidized bed of alumina. The purpose of this experiment was to examine the sulfur retention capability of lignite ash, which has a high calcium content. Most of the operating problems were minor and were related to returning the combustor to operating status after it had been out of operation for a long period of time. The most serious problem involved the rupture of an internal cooling coil. Examination of the coil indicated that the coil had been burned through at a point ∿14 in. above the coal feed point. The 48-in.-high standpipe had also been burned off at about the same level. Corrosion did not appear to be a factor in either failure. Failure was probably caused by highly intense and localized hot spots resulting from poor fluidization, as evidenced by erratic ΔP measurements of bed density and total bed pressure drop and erratic temperature measurements and profiles. The coil and standpipe were replaced.

Further attempts at completing experiment LIG-2 were deferred and four combustion experiments (PSI-series) were completed to measure the effects of coal and additive particle size on combustor response variables such as sulfur retention and NO_x emissions. Arkwright coal with mass-mean particle size levels of ∿150 μm and ∿740 μm and Tymochtee dolomite with mass-mean particle size levels of ∿370 μm and ∿740 μm were used in the series of experiments (2^2 factorial design). The experiments were performed at 843°C (1550°F), 8 atm, and ∿17% excess combustion air. The calculated gas velocity, designed to be 1.07 m/sec (3.5 ft/sec), ranged from 0.73 to 0.94 m/sec. Possible explanations for the incongruously low measured gas velocities are (1) unusually poor combustion efficiencies or (2) unmeasured air leaks through the peripheral seals on the rotary valve coal feeder into the coal transport air line.

The level of SO_2 in the effluent gas ranged from a low of 160 ppm (∿93% sulfur retention) in experiment PSI-3 (fine coal, fine additive) to 240 ppm (∿89% sulfur retention) in experiment PSI-4 (fine coal, coarse additive). The results indicate a slight increase in sulfur retention with decreasing additive particle size. No significant effect of coal particle size on sulfur retention was observed.

No noticeable effect of coal or additive particle size on NO levels in the flue gas (120 to 150 ppm) was observed. Using a recently obtained chemiluminescence analyzer, NO_x levels of 160 to 210 ppm were recorded. NO_2 levels (NO_x level - NO level) were ∿40 to ∿60 ppm, which are considerably higher than the anticipated NO_2 levels of 5 to 10 ppm.

Following the completion of the PSI-series of experiments, an additional attempt to complete experiment LIG-2 was unsuccessfully ended when the coal feed line plugged. Subsequently, a crack was discovered at the hairpin section of one of the internal cooling coils. This damaged section will be examined to determine the cause of the failure.

One-Step Regeneration of Additive

Several preliminary reductive decomposition (one-step) regeneration tests have been performed in the 3-in.-dia unit, using partial combustion of coal to supply heat and reducing gases. The major constraint for the existing regenerator, which was not designed for coal feeding, has been found to be its small internal diameter. The volume of air required for transporting coal into the fluidized bed was greater than 50% of the total fluidizing gas in the regenerator. The transport air jetting into the bed probably caused poor fluidization of the particles. A thinner refractory lining has been cast in the existing regenerator, enlarging the ID to 4.25 in. (10.8 cm). This should improve fluidization quality.

Sulfated limestone obtained from Pope, Evans, and Robbins (Test 620) was regenerated during the partial combustion of either British coal (Welbeck) or Arkwright coal. During a relatively smooth operating segment of one test (1-hr duration) with Welbeck coal, a SO_2 concentration of 2.9% in the wet effluent gas was reached. Bed temperature excursions, followed by partial agglomeration of the sulfated limestone bed, terminated this experiment and some of the other coal-burning test experiments. Because none of these test experiments reached a steady state, no chemical analyses of the products were made.

Sulfation and Regeneration of Supported Additives

Calcium oxide impregnated in α-Al_2O_3 is being investigated as an alternative to dolomite and limestone as an additive for lowering the sulfur dioxide level in the off-gas from fluidized-bed coal combustors. In this program, the capability of the supported calcium oxide to react with sulfur dioxide and of the resulting calcium sulfate to be regenerated is being studied experimentally, using thermogravimetric analysis.

The α-alumina pellets containing 6.6% calcium oxide by weight were sulfated at 900°C, using concentrations of sulfur dioxide in the gas stream ranging from 0.05-3%. Calcium utilizations ranged from 74 to 90%, and the time for the reaction to go to completion ranged from 4 to 10 hr.

The oxygen concentration in the gas phase had only a small effect on the sulfation rate when oxygen was present in stoichiometric excess. However, when sulfur dioxide was in excess, the rate was first order in oxygen concentration.

The sulfation rate of the pellets increased with temperature up to 900°C, where it became independent of temperature. Above 900°C, the reaction is probably diffusion controlled.

Tymochtee dolomite and calcium oxide in α-alumina pellets were sulfated under similar experimental conditions to allow comparison. The calcium oxide in α-alumina pellets was 95% sulfated in 6 hr at 900°C, using 0.3% sulfur dioxide and excess oxygen, while the dolomite was only 60% sulfated in 19 hr. However, the dolomite contained four times as much calcium as the pellets did.

Sulfated pellets were regenerated using various reducing gases (CO, H_2, and CH_4). In each case, the reaction was 0.8 order in reducing gas concentration. The rate was the same for hydrogen and methane and the rate for carbon monoxide was one third the former rate. The addition of carbon dioxide (15% or more) to the reducing gas lowered the regeneration rate due to the reaction of carbon dioxide with hydrogen to form carbon monoxide. Comparison of other data showed that dolomite was regenerated at a slightly lower rate than was the supported additive; moreover, the product of the reaction when dolomite was regenerated was 50% CaO-50% CaS and not 100% CaO as with the supported additive.

Ten cyclic sulfation-regeneration reactions were performed on pellets. A substantial decrease in sulfation rate was found during the second cycle. The sulfation rate increased with each succeeding cycle up to cycle 7, where the rate became essentially constant. The rate of regeneration was the same in each cycle in which the same concentration of hydrogen was used.

Sulfur Emission Control Chemistry

Results are presented on solid-solid regeneration by reaction of CaS and $CaSO_4$. Yeilds of CaO as high as 68% are reported. The results also suggest that higher yields of CaO occur when the CaS content of the dolomite stones is in excess of the stoichiometric requirement for the reaction.

In other work, two experiments have been performed in which spent dolomite additive from a combustion experiment was reacted with CaS at 1025°C while the effluent gas stream was monitored: the resultant solid products also were analyzed. In one experiment (CAS-10) in which unaltered (only partially calcined) sulfated dolomite was used, the reaction did not proceed well. However, in the other experiment (CAS-12), a gas stream containing 10.5% SO_2 was observed during reaction of fully calcined dolomite particles with CaS. In addition, preliminary estimates of product composition from the CAS-12 experiment indicate that the reaction went to at least 50% completion.

Speculation as to the reaction mechanism is also presented. A possible explanation is that the CaS removes the oxygen generated by decomposition of $CaSO_4$, promoting the decomposition reaction.

Coal Combustion Reactions

The Determination of Inorganic Constituents in the Effluent Gas from Coal Combustion. Some chemical elements carried by combustion gas are known to cause severe metal corrosion. The purpose of this study is to determine quantitatively which elements are present in the hot combustion gas of coal, in either volatile or particulate form, and to differentiate between volatile and particulate species. The identification of the compound form and amount of particulate species and the determination of the amount and form of condensable species are of interest.

The detailed design and the engineering drawing of the laboratory-scale batch unit combustor have been completed. A work project for construction has been set up, and the fabrication specification of the combustor has been written. A design/preliminary safety review of this combustor is being arranged.

Installation of the induction heating unit is continuing. About 95% of the electrical work has been done.

Systematic Study of the Volatility of Trace Elements in Coal. Knowledge of the vaporization characteristics of trace elements in coal and the rate of their volatilization is important for combined cycle turbine operation. The objective of this study is to obtain data on the volatility of these elements under practical coal combustion and gasification conditions.

Work has been completed on the electricity and water supplies for the experimental equipment. Setting up of the experimental apparatus is under way.

Properties of a Dolomite Bed of a Range of Particle Sizes and Shapes at Minimum Fluidization

Earlier reported data from a series of seven fluidization experiments with partially sulfated dolomite have been reexamined, and an improved correlation has been presented in the form of Ergun's correlation. The correlation of Wen and Yu (suitably modified) has been tested and found to be less accurate than Ergun's correlation for purposes of predicting minimum fluidization velocities as a function of temperature and pressure.

The minimum fluidization air velocities for a fresh unreacted dolomite bed of a known particle-size distribution over a range of temperature and pressure conditions were determined. These were correlated on the basis of the Ergun relation. Several other relations developed for predicting minimum fluidization velocities were critically examined on the basis of current experimental data.

Separation of Combustion and Regeneration Systems

As originally installed, the pressurized, fluidized-bed combustor and the regenerator utilized several components in common. Due to the dual function of these components, the two units could not be operated simultaneously. Modifications, as well as installation of additional equipment, were undertaken to physically separate the two units and permit concurrent investigations of the combustion process and the regeneration process.

Alterations to the combustion system equipment were completed and the system was returned to service. Installation of the new regeneration system is near completion. Preliminary testing of the new system is in progress. The status of the items required to complete installation of the new system is presented.

INTRODUCTION

In this program, funded by the Energy Research and Development Administration and the Environmental Protection Agency, fluidized-bed combustion is being studied as a method of removing from the gas phase nearly all atmospheric pollutants (sulfur and nitrogen compounds) generated during the combustion of fossil fuels. The concept involves burning of fuels such as coal in a fluidized bed of particulate lime solids that react with the sulfur compound formed during coal combustion. In another step, the sulfated lime is regenerated for reuse in the combustor.

This quarterly report presents information on pressurized, fluidized-bed combustion experiments intended to measure (1) the effect of calcium in the coal mineral matter on sulfur retention by combusting a high-calcium lignite coal in an inert fluidized bed of alumina, and (2) the effects of coal and additive particle sizes on sulfur retention and NO_x emissions. Results of preliminary regeneration experiments consisting of *in situ* combustion of coal in the 3-in.-dia regenerator are described. Studies on the sulfation and regeneration of supported additives, the chemistry of sulfur emission control, coal combustion reactions, properties of a dolomite bed of a range of particle sizes and shapes at minimum fluidization, and separation of the combustion and regeneration systems are also discussed.

BENCH-SCALE, PRESSURIZED, FLUIDIZED-BED COMBUSTION EXPERIMENTS

The 6-in.-dia, pressurized, fluidized-bed combustor was returned to service while work to separate the combustion and regeneration systems (discussed in a following section of this report) continued. Reported here are (1) attempts to examine the sulfur retention capability of lignite ash that has a high calcium content by combusting Glenharold lignite coal in an inert fluidized bed of alumina and (2) the preliminary results of four combustion experiments (using Arkwright coal and Tymochtee dolomite) to measure the effects of coal and additive particle size on response variables such as SO_2 removal, NO_x emissions, and combustion efficiency (the latter not reported here).

Equipment

The major items of the ANL bench-scale equipment are coal and additive feeders, a preheater for the fluidizing gas, a 6-in.-dia fluidized-bed combustor, a 3-in.-dia regenerator, cyclones and filters, and gas sampling and analyzing equipment. The combustor and regenerator are designed for operation at pressures up to 10 atm. The temperatures of the combustor and regenerator are controlled by electrical heaters and cooling coils. The gas analysis system provides on-line measurement of the flue gas components SO_2, NO, NO_x, CH_4, CO_2 and O_2 on a continuous basis. The system is thoroughly instrumented and is equipped with an automatic data-logging system.

Coal and additive are conveyed pneumatically from the feeders to the bottom of the combustor. A nominally constant bed level of 36 in. is maintained in the combustor by use of an overflow pipe.

Combustion of Lignite in a Fluidized Bed of Alumina

Experiment LIG-2 was designed to duplicate all operating conditions but one of a previous combustion experiment, LIG-1. Combustion in LIG-1 had been carried out in a fluidized bed of Tymochtee dolomite with a 1.1 Ca/S mole feed ratio whereas LIG-2 was to be carried out in a fluidized bed of alumina.

Sulfur retention for LIG-1 had been 85%, which corresponded to an emission of ∿0.2 lb $SO_2/10^6$ Btu. It has been proposed, however, that sulfur is retained in the ash when lignite is burned, even at combustion temperatures as high as 1200°C (2200°F).[1] If the coal calcium is included in the Ca/S mole ratio for experiment LIG-1, the effective Ca/S mole ratio could potentially be 3.0. The results of LIG-2 are expected to indicate the relative effectiveness of the calcium in the additive and the calcium in the ash.

Several unsuccessful attempts were made to complete combustion experiment LIG-2. Most of the problems encountered were relatively minor and were related to returning the combustor to service after it had been out of operation for an extended period of time while regeneration experiments were performed. The most serious problem involved the rupture of an internal cooling coil. Examination of the coil indicated that the coil had been burned through at a point ∿14 in. above the coal feed point, which is 2 in. above the gas distributor. The 48-in.-high standpipe (an overflow pipe) had also been burned off at about the same level. Preliminary examinations of the burn-through areas gave no indications that corrosion was a factor in the tube failures. The probable cause of failure was localized hot spots caused by poor fluidization, as evidenced by erratic ΔP measurements of bed density and total pressure drop across the bed. Measured temperatures were also erratic, indicating poor fluidization. Several large agglomerates of alumina and ash were recovered from the combustor, a further indication of poor fluidization resulting in localized hot spots.

Attempts at completing experiment LIG-2 were temporarily deferred until after the completion of the particle size experiments (PSI-series), the preliminary results of which are presented below.

An additional attempt was subsequently made to complete experiment LIG-2. The attempt was unsuccessful because the coal feed line plugged. Following shutdown of the combustor, a crack was discovered in the hairpin section of one of the internal cooling coils. The affected coil has been removed from the combustor and the damaged section of the coil will be examined to determine the cause of failure.

Effects of Coal and Additive Particle Sizes

Four combustion experiments (PSI-series) were completed to measure the effects of coal and additive particle sizes on combustor response variables such as sulfur retention and NO_x emissions. The experiments were made in a 2^2 factorial design at two levels each of coal and additive mean particle sizes. Arkwright coal with mass-mean particle size levels of ∿150 μm (-50 mesh) and ∿640 μm (+50 mesh) and Tymochtee dolomite with mass-mean particle size levels of ∿370 μm (-30+50 mesh) and ∿740 μm (-14+30 mesh) were used in the series of experiments.

The as-received Arkwright coal was sieved at a 50-mesh breakpoint which resulted in approximately a 50-50 split by weight and a factor of ∿4 difference in the mass-mean diameters of the two fractions. The Tymochtee dolomite size ranges also resulted in a 50-50 split by weight of the as-received material and a factor of ∿2 difference in the mass-mean diameters of the two fractions. The -50 mesh dolomite was removed from the finer fraction of dolomite to reduce elutriation of bed material from the combustor. Sieve analyses of the coal and additive feed materials are given in Tables 1 and 2, respectively.

Table 1. Sieve Analyses of Arkwright Coal Size Fractions Used in PSI-Series of Combustion Experiments.

	Coarse Material		Fine Material	
	U.S. Sieve No.	% on Sieve	U.S. Sieve No.	% on Sieve
	+14	0.0	-30 +45	2.4
	-14 +20	15.2	-45 +50	3.8
	-20 +30	37.3	-50 +80	27.1
	-30 +45	37.2	-80 +170	34.0
	-45 +50	6.4	-170 +230	10.0
	-50 +80	3.8	-230 +325	10.0
	-80	0.0	-325	12.6
		99.9		99.9
Mass-Mean Diameter, $\bar{d}_m$		∿640 μm		150 μm
Surface-Mean Diameter, $\bar{d}_m$		∿560 μm		78 μm

The nominal operating conditions chosen for the series of experiments were a bed temperature of 843°C (1550°F), 8 atm pressure, ∿17% excess combustion air (3% O_2 in dry flue gas), 1.07 m/sec (3.5 ft/sec) fluidizing-gas velocity, and 0.9 m (3 ft) fluidized-bed height. It should be indicated here, however, that the fluidizing-gas velocity is not a directly controlled operating variable. Rather, the conditions

Table 2. Sieve Analyses of Tymochtee Dolomite Size Fractions Used in PSI-Series of Combustion Experiments.

Coarse Material		Fine Material	
U.S. Sieve No.	% on Sieve	U.S. Sieve No.	% on Sieve
+14	0.0	-20 +30	1.5
-14 +20	28.7	-30 +35	2.0
-20 +25	18.6	-35 +45	51.6
-25 +30	18.2	-45 +50	23.0
-30 +35	12.1	-50 +60	11.7
-35 +45	19.6	-60 +80	7.0
-45	2.8	-80	3.2
	100.0		100.0
Mass-Mean Diameter, $\bar{d}_m$, μm	$\sim$740		$\sim$370
Surface-Mean Diameter, $\bar{d}_p$, μm	$\sim$620		$\sim$320

of coal feed rate (in this case, 12.8 kg/hr) and oxygen level in the flue gas (3%) are specified as operator-controlled variables. The design velocity of 1.07 m/sec theoretically derives from the controlled variables (at 100% combustion efficiency). The value of 1.07 m/sec was selected for this series of experiments to prevent elutriation of large amounts of bed material, particularly in the experiments with the finer size fractions of dolomite. The actual operating conditions and flue gas analyses for the four combustion experiments are summarized in Table 3. The bed temperature and flue gas analysis data for the four experiments are plotted in Figs. 1 to 4.

The level of SO_2 in the flue gas ranged from a low of 160 ppm in experiment PSI-3 (fine coal, fine additive) to 240 ppm in experiment PSI-4 (fine coal, coarse additive). These correspond to sulfur retentions of $\sim$93 and $\sim$89%, respectively. The observed levels of SO_2 for the four experiments (Table 3) indicate a slight increase in sulfur retention when the additive particle mass-mean diameter is reduced from 740 μm to 370 μm. Sulfur retentions were 92 and 93% with the finer dolomite fraction (PSI-2 and -3) as compared with 90 and 89% with the coarser fraction (PSI-1R and -4).

In terms of the observed SO_2 levels for the PSI-series of combustion experiments, the effects of increasing the additive particle size at the low and high levels of coal particle size were +80 ppm and +30 ppm, respectively. This represents an average effect of increasing the SO_2 level in the off-gas by 55 ppm (an average percent increase of 33%). Similarly, the effects of increasing the coal particle size at the low and high levels of additive particle size were +20 and -30 ppm, respectively. This represents an average effect of decreasing the SO_2 level in the off-gas by only 5 ppm, an insignificant amount.

Table 3. Operating Conditions and Flue-Gas Analysis for PSI-Series of Combustion Experiments

Combustor: ANL, 6-in. dia
Bed Temp: 843°C (1550°F)
Pressure: 8 atm abs

Fluidized-Bed Height: 0.9 m (3 ft)
Excess Air: ~17%

	Arkwright Coal		Tymochtee Dolomite				Avg Flue-Gas Composition, Dry Basis				
Exp. No.	$\bar{d}_p$,[a] µm	Feed Rate, kg/hr	$\bar{d}_m$,[a] µm	Feed Rate, kg/hr	Ca/S Mole Ratio	Gas Velocity, m/sec	O_2, %	SO_2, ppm	NO, ppm	NO_x, ppm	CO, ppm
PSI-1R	640	13.9	740	3.3	1.3	0.94	2.8	210 (90%)[c]	120	160	*[b]
PSI-2	640	12.6	370	3.1	1.4	0.85	3.1	180 (92%)[c]	120	170	*[b]
PSI-3	150	12.3	370	2.8	1.3	0.73	3.1	160 (93%)[c]	130	180	62
PSI-4	150	13.2	740	3.2	1.4	0.82	3.0	240 (89%)[c]	150	210	50

[a] Mass mean particle diameter.

[b] Analyzer inoperative.

[c] Sulfur retention.

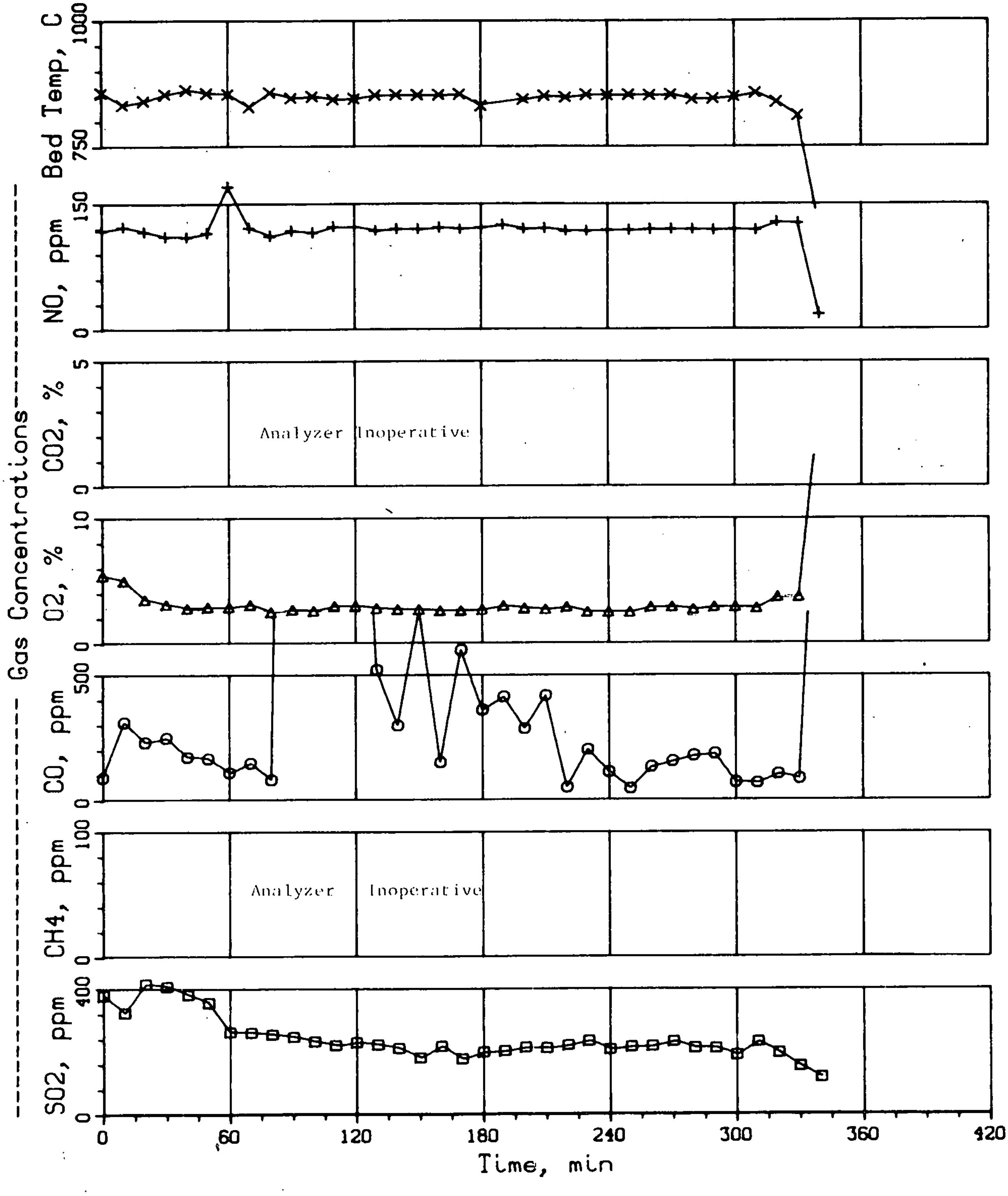

Fig. 1. Bed Temperature and Flue-Gas Composition, Experiment PSI-1R

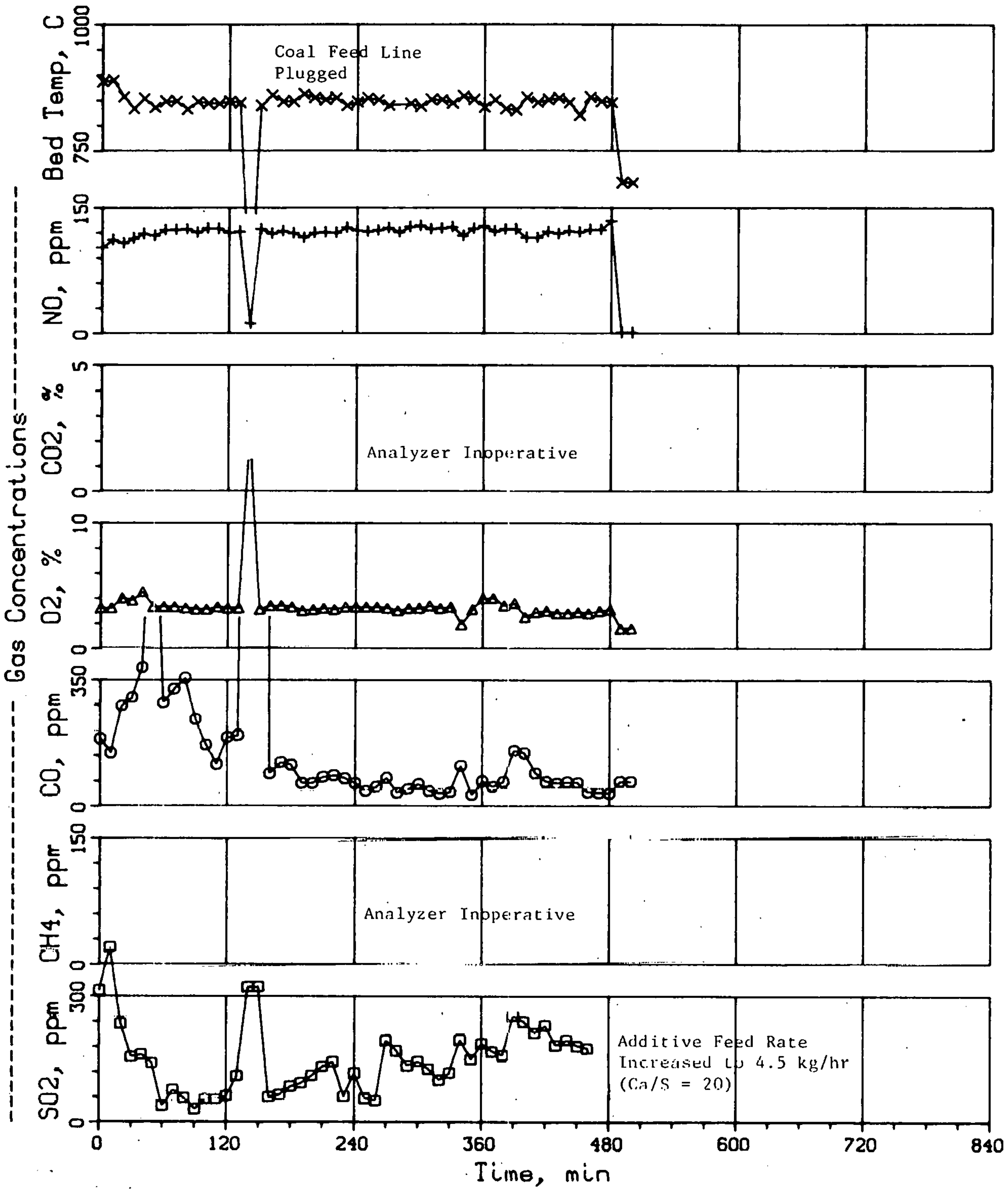

Fig. 2. Bed Temperature and Flue-Gas Composition, Experiment PSI-2

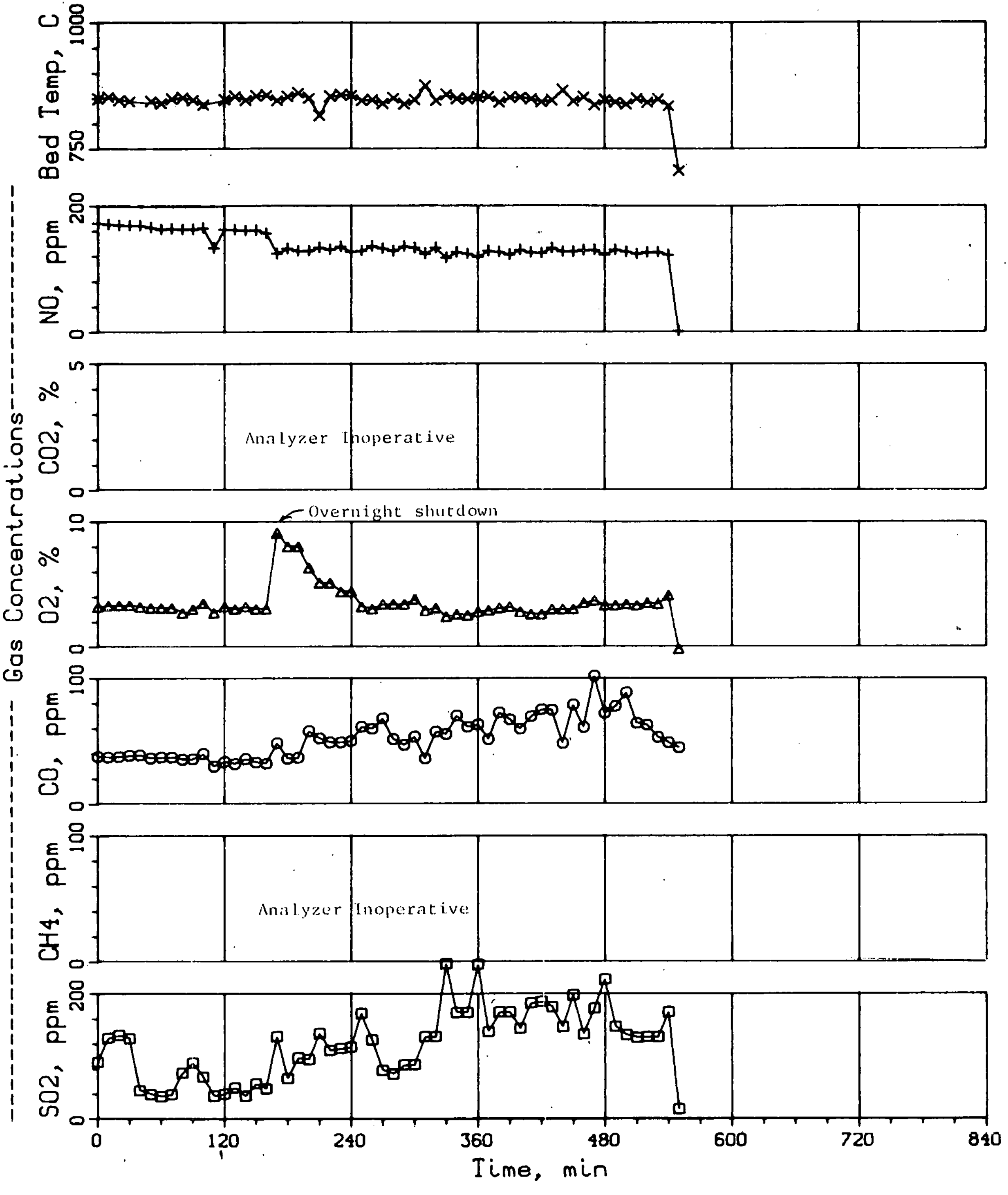

Fig. 3. Bed Temperature and Flue-Gas Composition, Experiment PSI-3

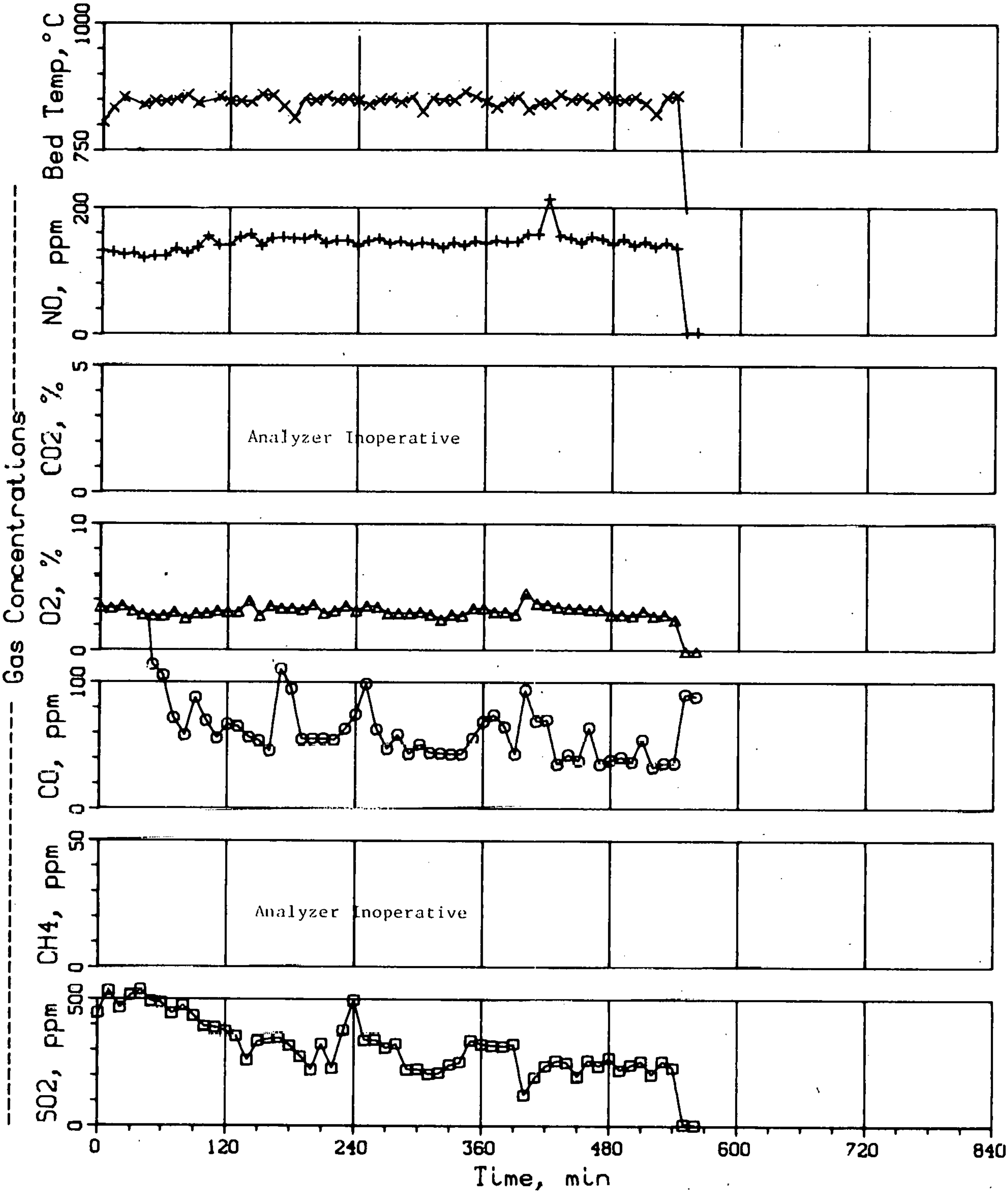

Fig. 4. Bed Temperature and Flue-Gas Composition, Experiment PSI-4

With the exception of the SO_2 level of 240 ppm for experiment PSI-4 (fine coal, coarse additive), the recorded SO_2 levels for the PSI experiments are considerably lower than the SO_2 levels that would be predicted using the correlation of SO_2 levels based on the VAR-series of combustion experiments.[2] The Arkwright coal used in the VAR-series experiments had a mass-mean diameter of 320 μm (surface-mean diameter of 120 μm) and the Tymochtee dolomite a mass-mean diameter of 750 μm (surface-mean diameter of 560 μm). Thus, in terms of particle size, experiment PSI-4 corresponds most closely with the VAR-series conditions (on the basis of surface-mean diameters). The remaining PSI-series experiments were performed using either finer additive and/or coarser coal as compared with the VAR-series experiments. This is in keeping with the effect indicated above of decreasing additive particle size reducing SO_2 levels in the off-gas. While not demonstrated by the PSI-series experiments, there is in the comparison with the VAR-series experiments some indication that increasing coal particle size may also reduce SO_2 levels in the flue gas. An effect of coal particle size on SO_2 levels may be indirectly related to an expected effect of coal particle size on combustion efficiency (*i.e.*, poorer combustion with larger coal particles release less SO_2 and thereby result in apparently better sulfur retention). Further comment on this will be reserved until sufficient analytical work has been completed to determine combustion efficiencies for the PSI-experiments.

In combustion experiments made previously at ANL at atmospheric pressure,[3] no significant effect of additive particle size on sulfur retention was observed. The earlier experiments were done with Illinois No. 6 coal and limestone No 1359 having average particle sizes of 25 and 100 μm. Since the observed effect of additive particle size during the PSI-series of combustion experiments was quite small (an average difference of only 55 ppm SO_2), it is not unreasonable to expect that the effect at even finer sizes of additive could become insignificant.

The levels of NO were quite low for all four combustion experiments, ranging from 120 to 150 ppm. Thus, as expected, particle size does not appear to affect NO emissions significantly.

By use of a recently installed, on-line chemiluminescence analyzer, it was also possible to obtain values for total NO_x emissions during the four combustion experiments. Values for NO_x (see Table 3) ranged from 160 to 210 ppm, indicating that NO_2 levels (NO_x level - NO level) were ∿40 to ∿60 ppm. These values of NO_2 levels are considerably higher than the anticipated levels of 5 to 10 ppm.[2]

One aspect of the data reported in Table 3 that is incongruous with the design experimental conditions (and with past experience with the combustor) is the low gas velocities reported for the four combustion experiments. As indicated above, the design operating conditions for this series of experiments (consistent with a coal feed rate of 12.9 kg/hr and 17% excess combustion air) was a gas velocity of 1.07 m/sec (3.5 ft/sec). Measured gas velocities ranged from 0.73 m/sec for experiment

PSI-3 to 0.94 m/sec for experiments PSI-1R. After adjustment for variations from the design coal feed rate of 12.9 kg/hr, the measured velocities ranged from ∿70 to ∿80%, respectively, of the expected velocities of 1.02 to 1.17 m/sec.

No explanation has been found for this discrepancy in the data, although at least two possibilities exist. One explanation would be unusually poor combustion efficiencies of 70 to 80% (as compared with 90 to 95% combustion efficiencies observed in the VAR-series experiments). Solid samples from the PSI-series are being analyzed for the purpose of making material balance and combustion efficiency calculations.

A second possible explanation pertains to the rotary valve coal feeder. The rotary valve has peripheral seals to which an external air pressure is applied that is approximately equivalent to the system pressure. During maintenance of the valve following completion of the series of experiments, it was found that the peripheral seals on the coal feeder were leaking badly. It is thus possible that a large supplemental air flow (unmetered) was introduced through the peripheral seals of the rotary valve into the flow of coal transport air. A rotameter has been installed to measure the air leakage rate.

ONE-STEP REGENERATION OF ADDITIVE

One of the research goals at ANL is to develop a regeneration process that will regenerate CaO from additive that has been sulfated during the combustion of coal. A scheme receiving attention is the one-step regeneration of sulfated additive, with *in situ* combustion of coal generating the necessary heat and reducing gases.

The present 3-in.-ID (7.6-cm) regenerator and ancillary equipment were not designed for the *in situ* combustion of coal. A new atmospheric pressure regenerator with a larger ID is being constructed that will be utilized after the initial phases of this one-step regeneration program are performed with the existing regenerator.

Preliminary test experiments using the *in situ* combustion of coal in the 3-in.-ID (7.6-cm) regenerator have been performed to evaluate some of the anticipated problems with this regeneration scheme. Sulfated Greer limestone from Pope, Evans, and Robbins (PER), Test 620, was regenerated. The major constraint for the regenerator was that its small internal diameter (7.6-cm) restricts the total amount of fluidizing gas that could be used. The pneumatic transport of coal for feeding into the regenerator required a relatively large amount of transport air. For example, during the test experiments, well over 50% of the fluidizing gas in the regenerator was coal transport air. This led to poor fluidization because the transport air jets upwards into the bed.

In all, seven test experiments were attempted to test the coal combustion regeneration scheme. In attempts to reduce the coal transport air required, smaller particle size coal (British coal, -20 mesh) was used. However, bridging in the feed hopper resulted in noncontinuous feeding.

During a smooth feeding segment of one of these tests at 1040°C (Coal Burn Test No. 3) with British coal (Welbeck coal) and with the PER sulfated additive fed at 6 lb/hr (∿2.7 kg/hr), a SO_2 flue gas (wet) concentration of 2.9% was obtained. The coal feed rate during this test was ∿4 lb/hr (∿1.8 kg/hr); a large portion (∿50%) of it did not burn and was recovered in the off-gas cyclone and filters. Temperature excursions followed by bed agglomeration caused termination of this and some of the other test experiments.

The agglomerated sulfated limestone bed material was analyzed by X-ray diffraction; merwinite, $Ca_3Mg(SiO_4)_2$, was found to be the major constituent. The melting point of this class of materials, which is near 1250°C, has not yet been measured. Similar material was found in agglomerated sulfated dolomite from the FAC-experiments.[4] Further experiments using a DTA (differential thermal analyzer) are planned to find the agglomerating reaction temperature at different environmental conditions.

Because the above test experiment (Coal Burn Test No. 3) and other attempted test experiments could not be completed, no chemical analyses of the products were made. The British coal was initially chosen for these tests because of its high ash fusion temperature at reducing conditions (initial deformation temp, >1100°C). Because of feeding problems with this -20 mesh coal, Arkwright coal (-14 mesh) was used in later tests to eliminate the bridging of coal in the hopper.

The 3-in.-ID (7.6-cm) regenerator is presently being reworked. To allow recasting of the refractory lining, the inner 8-in.-dia (20.3-cm) pipe has been replaced with a new one. A thinner refractory liner has been cast, and the rebuilt regenerator will have an internal diameter of 4.25 in. (10.8 cm). This will reduce the ratio of coal transport air to total fluidizing gas in future regeneration experiments. Also, new clamshell type heaters have been installed on the outer wall of the 8-in.-dia (20.3-cm) pipe. The larger regenerator diameter should improve fluidization in the regenerator. These modifications are not expected to be a total solution to bed temperature excursions and/or agglomeration of bed material.

SULFATION AND REGENERATION OF SUPPORTED ADDITIVES

A research program has been initiated to determine methods of supporting calcium oxide in a highly dispersed state in a matrix of a high-strength, inert material. Calcium oxide is probably more reactive in a dispersed state than is massive CaO; an inert support material would supply the strength needed to eliminate the decrepitation problem which probably occurs with dolomite and limestone. In this program, the capability of calcium oxide supported on α-Al_2O_3 to react with sulfur dioxide and of the resulting $CaSO_4$ to be regenerated is being studied. The equipment and procedures are described in a previous report.[4]

In this quarterly report, kinetic data are reported on the rate of sulfation of 6.6% CaO-αAl_2O_3 as a function of temperature and of SO_2 and O_2 concentrations in the gas phase. Also, a comparison was made of the rate of sulfation of the pellets with that of Tymochtee dolomite. Modeling of the kinetic data was initiated. The rate of regeneration of the sulfated pellets at 1100°C, using various reducing gases, was determined. Also, the effect of CO_2 in the reducing gas on the regeneration rate of the sulfated pellets was measured. Sulfated Tymochtee dolomite was regenerated to allow comparison with the regeneration rate of sulfated pellets. Finally, cyclic sulfation-regeneration experiments were performed.

Effect of SO_2 Concentration on Sulfation Rate at 900°C

Sulfation experiments over a SO_2 gas concentration range of 0.05 to 3% at 900°C were performed. Preparation of the gas mixtures for these reactions required the blending of O_2, SO_2, and N_2 to the various specified concentrations. Mass spectrometric analyses were performed on two blended gas samples to confirm the concentration of each constituent. For gases blended to (1) 0.3% SO_2, 5% O_2, and the balance N_2 and (2) 0.05% SO_2, 5% O_2, and the balance N_2, the mass spectrometric results were in good agreement; concentrations were (1) 0.3% SO_2, 5.3% O_2 and (2) 0.047% SO_2, 5.2% O_2, respectively.

The sulfation kinetic results are shown in Fig. 5 (an earlier version appeared as Fig. 20 of ANL/ES-CEN-1011), where the percent conversion of CaO in the α-alumina pellets to $CaSO_4$ is given as a function of time and SO_2 concentration in the gas stream. The results are based on the assumption that the CaO was completely sulfated. Samples have been submitted for wet chemical analysis to determine the extent of reaction in each experiment. The time required for the reaction to go to completion was 4 to 10 hr, depending on the SO_2 concentration in the gas stream. Additive residence times will probably be several hours in commercial fluidized beds, and therefore, the rate of sulfation appears to be sufficient.

The order of reaction as a function of SO_2 concentration in the gas mixture was found to be 0.7. This is in good agreement with the results of 0.76 reported by Yang *et al.*[5] They also reported that the rate was first order in SO_2 when H_2O was present. In some future experiments, water will be added to the sulfation gas to determine its effect on sulfation rate.

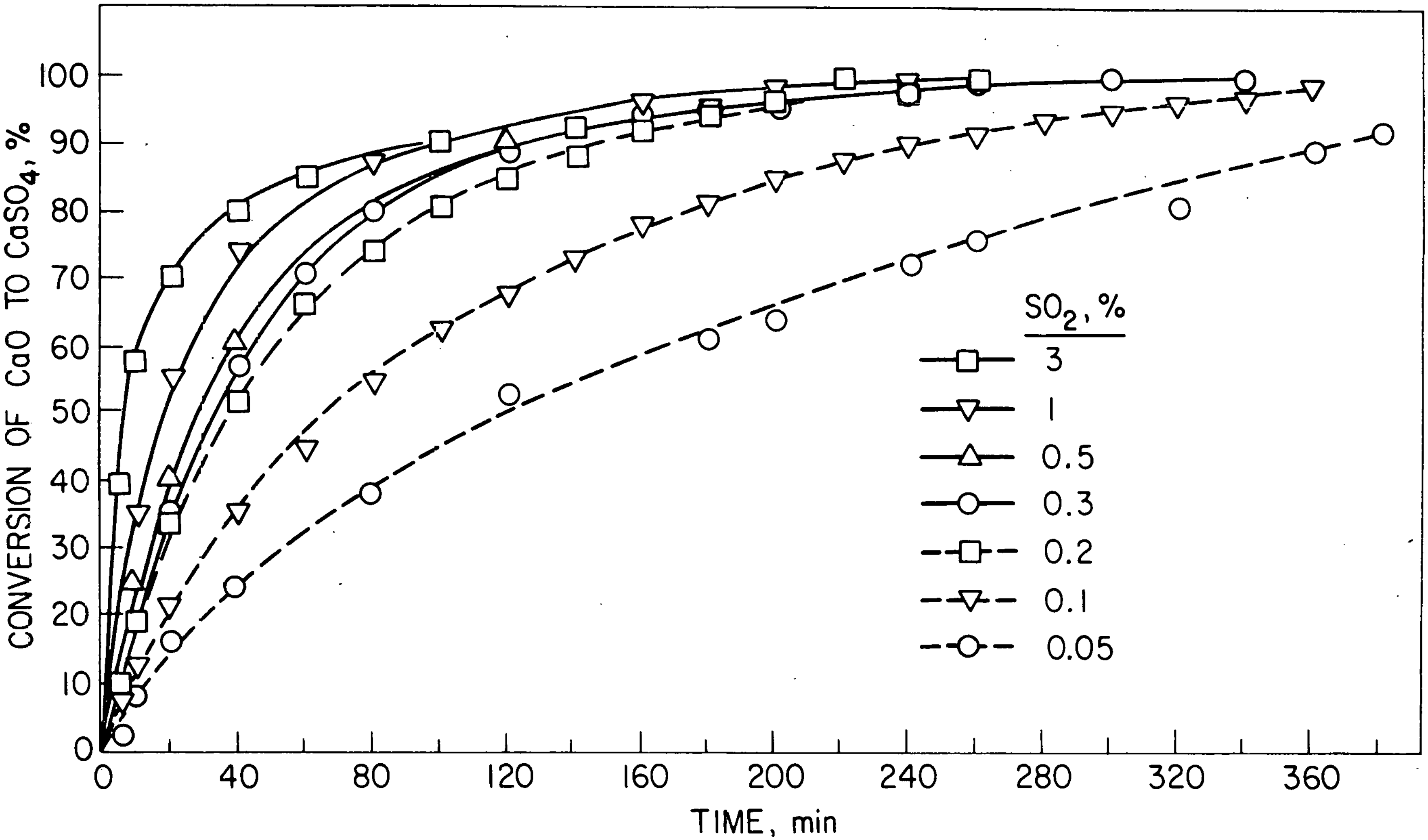

Fig. 5. Rate of Sulfation of 6.6% CaO in α-Al_2O_3 as a Function of the SO_2 Gas Concentration at 900°C. In all runs, the gas contained 5% O_2 and the balance was nitrogen.

Percent Sulfation of Supported Additive

In Table 4, the calculated percent conversion of CaO to $CaSO_4$ is given for the seven sulfation experiments at 900°C and one experiment at 1000°C. The calculations were based on the assumption that the pellets contained 6.64 wt % CaO (obtained from weight gain during impregnation step) and on the experimental weight gain found from weighing the sample before and after each reaction. Since the calcium concentration varies from sample to sample due to the nonhomogeneity of the pellets, wet chemical analysis will be required to help quantify the kinetic data.

Table 4. Calculated Conversion of CaO to $CaSO_4$ at 900°C and 1000°C

Temp, °C	SO_2 Gas Concentration, %	Duration	Sulfation Completeness, %
900	3	4 hr	90
900	1	5 hr	74
900	0.5	5 hr, 20 min	78
900	0.3	6 hr, 30 min	85
900	0.2	4 hr, 40 min	81
900	0.1	7 hr	85
900	0.05	10 hr, 10 min	74
1000	0.3	5 hr, 10 min	79

Effect of Oxygen Concentration in the Feed Gas on Sulfation Rate at 900°C

Experiments have been performed to determine the effect of the O_2 concentration on the sulfation rate of pellets. Results for runs at 900°C using 0.3% SO_2 mixed with 5%, 0.5% or 26 ppm O_2 (balance is nitrogen) are shown in Fig. 6. When oxygen is in excess, the rate is nearly independent of oxygen concentration and is approximately 0.1 order. However, when SO_2 is in excess, the rate is first order in oxygen concentration. This is consistent with the assumption that SO_2 reacts with O_2 to form SO_3 before reacting with CaO.

$$SO_2 + 1/2\ O_2 \rightarrow SO_3$$

$$SO_3 + CaO \rightarrow CaSO_4$$

Effect of Temperature on Sulfation Rate

As shown in Fig. 7, the rate of sulfation increases with temperature up to 900°C, where it becomes independent of temperature (within experimental error). The results were reproducible for various CaO/SO_2 ratios and there-

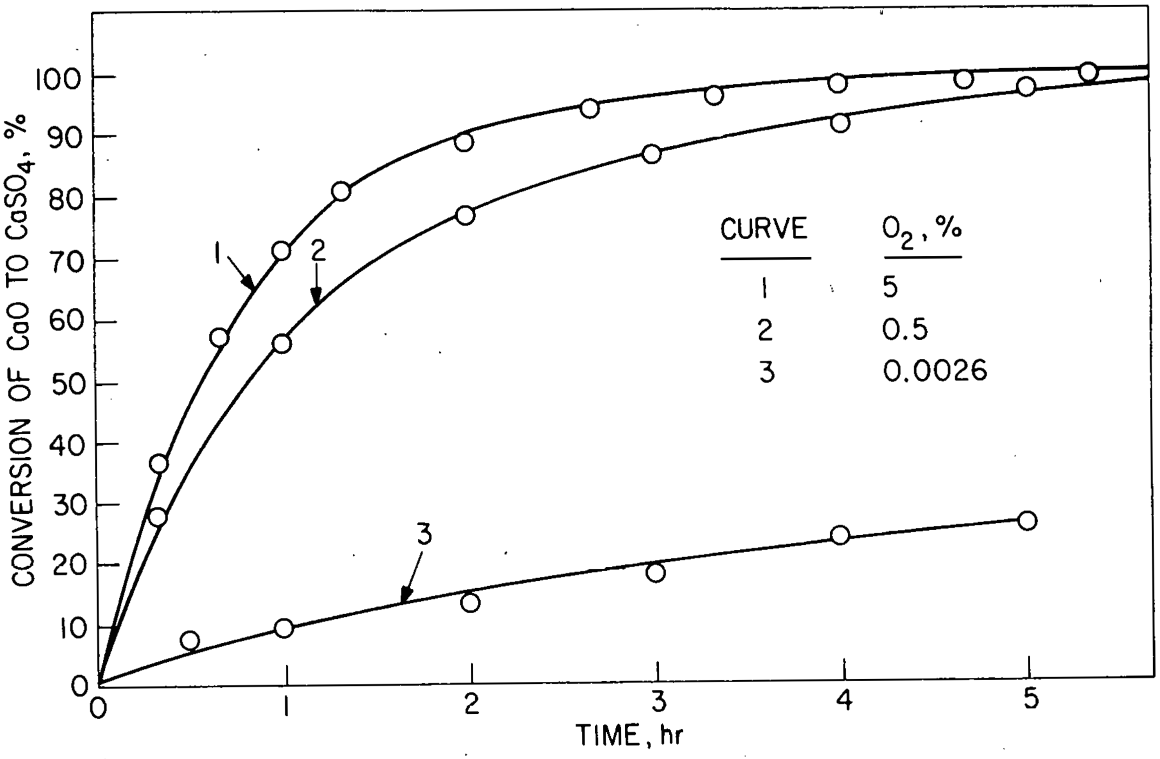

Fig. 6. Effect of Oxygen Concentration on the Rate of Sulfation of 6.6% CaO in α-Al_2O_3 at 900°C. Sulfating Gas Mixture; 0.3% SO_2 in N_2 plus Indicated Concentration of O_2.

fore the sulfation rates were not SO_2 limited. The independence of the rate at temperatures above 900°C probably indicates that the reaction is diffusion controlled at and above that temperature.

Comparison of Sulfation Rates of Tymochtee Dolomite and Supported Additive

Tymochtee dolomite was sulfated in the TGA unit at 900°C, using 0.3% SO_2-5% O_2 in N_2, for comparison with the supported additive (Fig. 8). The information obtained will help in determining the relative effectiveness of the supported additive in reducing SO_2 concentrations in the effluent gas from a fluidized-bed combustor. Sulfation of the supported additive was complete in 6 hr; sulfation of the Tymochtee dolomite was approximately 60% complete in 19 hr. In an earlier EA-series experiment in the combustor,[4] approximately 60% calcium utilization was obtained for Tymochtee dolomite in the fluidized bed, which is in good agreement with the calcium utilization obtained for dolomite in the TGA unit.

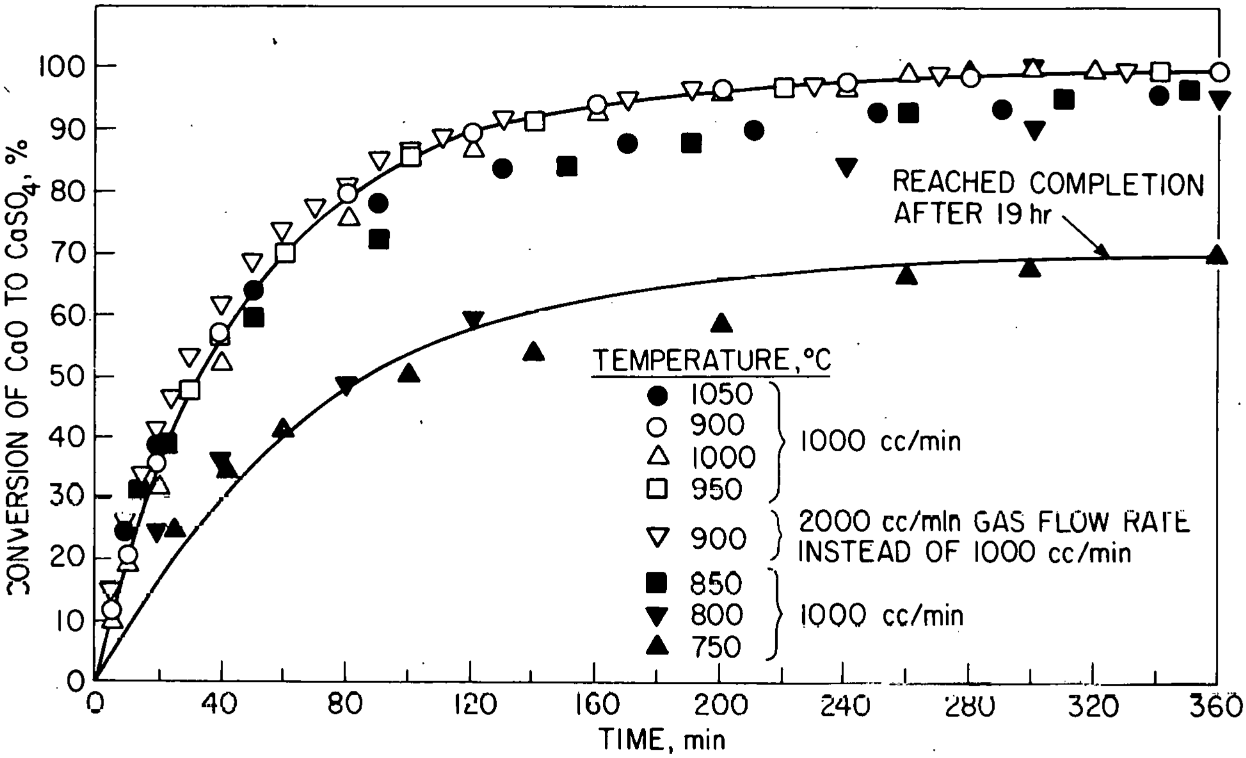

Fig. 7. Effect of Temperature on the Rate of Sulfation of 6.6% CaO in α-Al_2O_3 using 0.3% SO_2-5% O_2

It must be remembered that the dolomite contains approximately four times as much calcium as the pellets. Therefore, in 6 hr the dolomite utilized approximately 2.5 times the quantity of calcium utilized by the supported additive.

In an earlier VAR-series of combustion experiments, calcium utilization in dolomite in the fluidized bed ranged from 33 to 83% and was inversely proportional to the Ca/S ratio.[2] The maximum calcium utilization (83%) was obtained with low Ca/S ratios in the VAR-series. By comparison, the TGA runs were performed with excess SO_2 and therefore low Ca/S ratios. However, calcium utilization was only 60% in the TGA runs. Thus, TGA results do not agree with results of the VAR experiments. Possibly, long residence times could account for the high calcium utilization results obtained in the fluidized bed. Also, H_2O (which should increase the reaction rate) was absent from the TGA sulfation gas.

Regeneration of Sulfated Pellets using Various Reducing Gases

One-step regeneration studies are being performed on sulfated pellets using various gas compositions and temperatures. Regeneration experiments using CO, H_2, and CH_4 at 1100°C are complete.

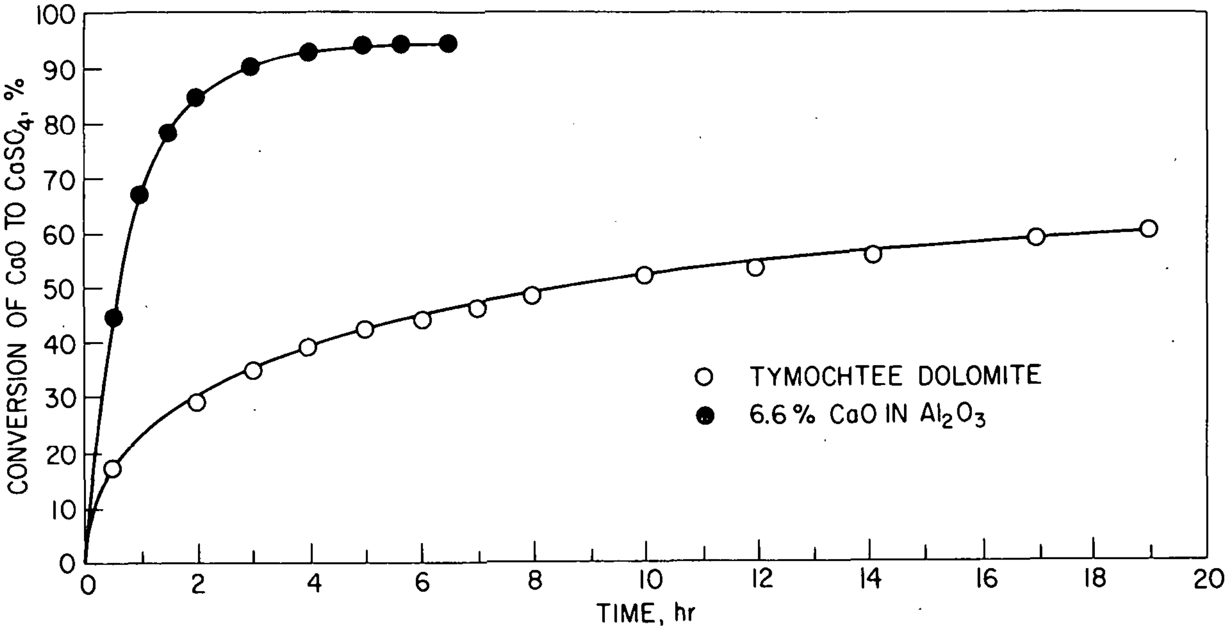

Fig. 8. Comparison of the Rates of Sulfation of Tymochtee Dolomite and 6.6% CaO in α-Al_2O_3. Sulfation Gas Mixture: 0.3% SO_2 and 5% O_2 in N_2. Sulfation Temperature: 900°C

The regeneration rates at 1100°C as a function of reducing gas concentration for CO, H_2, and CH_4 are given in Figs. 9, 10, and 11, respectively. For each reducing gas, the percent reduction of $CaSO_4$ is given as a function of time, for reducing gas concentrations ranging from 0.1% to 6%. In each case, the reaction is 0.8 order in reducing gas concentration, less that 4 minutes being required for complete regeneration when using a 6% reducing gas concentration. X-ray diffraction results on the regenerated pellets showed that the product was a mixture of $CaO{\cdot}Al_2O_3$ and $CaO{\cdot}2Al_2O_3$ and that no CaS or $CaSO_4$ was present. However, when methane was used as a reductant, SEM analysis showed trace amounts of sulfur were present using a scanning electron microscope.

Data plotted in Fig. 9-11 are based on the assumption of 100% regeneration of $CaSO_4$ to CaO. This seems reasonable on the basis of weight loss information. Table 5 presents the percent regeneration that occurred for each run, calculated from the experimental weight loss. In the regeneration runs, the experimental weight loss was obtained by weighing the sample before and after each reaction.

A comparison of the rate of regeneration of $CaSO_4$ in α-Al_2O_3 and in sulfated dolomite using CO, H_2, and CH_4 is given for a 1% reducing gas concentration in Fig. 12.

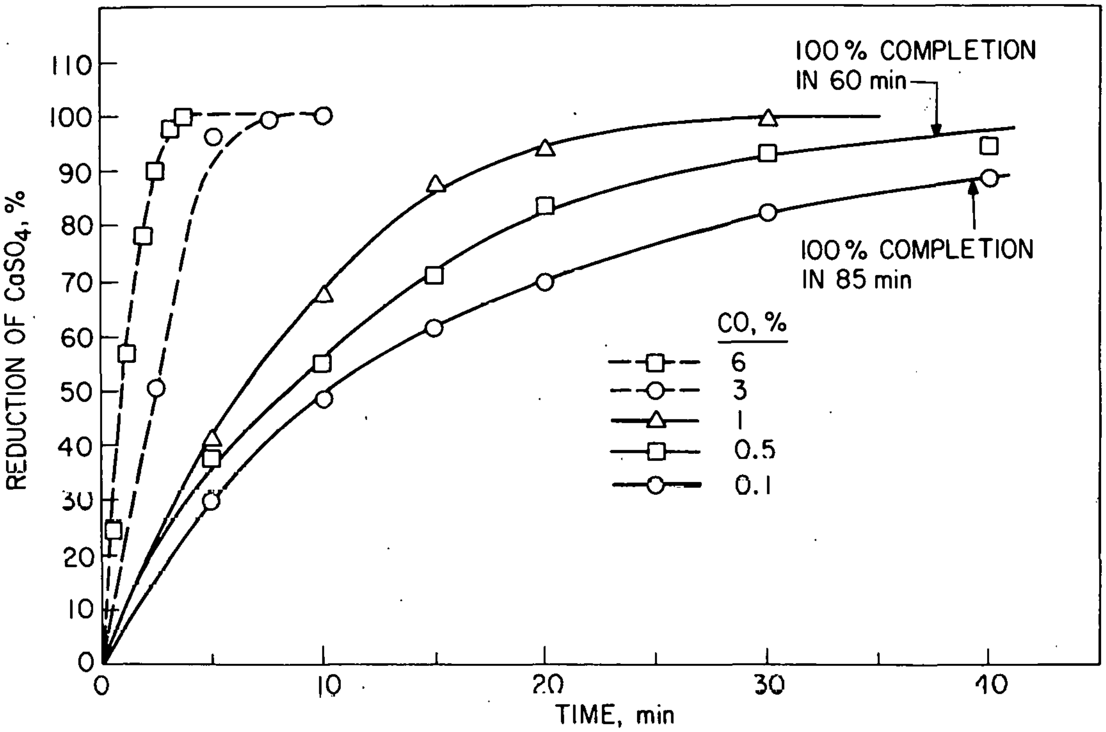

Fig. 9. Rate of Regeneration of $CaSO_4$ in α-Al_2O_3 using Indicated Concentrations of Carbon Monoxide (the balance--nitrogen) at 1100°C.

The rates of regeneration when CH_4 and H_2 were used are essentially the same, while the regeneration rate when CO was used is lower at each reducing gas concentration. Thermodynamically, the decomposition of CH_4 to C and H_2 is favored at 1100°C. Therefore, it is thought that hydrogen is the actual regeneration gas when CH_4 is used, and that the decomposition of CH_4 is not rate-limiting. Hence, the same rate of regeneration was obtained using CH_4 and H_2. Further evidence in support of this idea was found when pellets reduced with methane, hydrogen, or carbon monoxide were sectioned for SEM analysis. The pellets reduced with CH_4 were black on the interior while those regenerated with H_2 or CO were white. Analysis verified that carbon deposition occurred when CH_4 was used.

Analyses have shown that if 1.3 mg of C (from the reduction of CH_4 to C and H_2) was present in each 35 mg pellet, enough H_2 would also be produced to reduce all of the $CaSO_4$ to CaO. Table 6 gives the quantity of carbon found in the pellets after regeneration at various reducing gas concentrations. The amount of carbon deposition in the pellets is less than that needed to obtain enough hydrogen for complete regeneration of the $CaSO_4$. However, carbon deposition might also have occurred throughout the TGA unit, making available the required amount of hydrogen for regeneration.

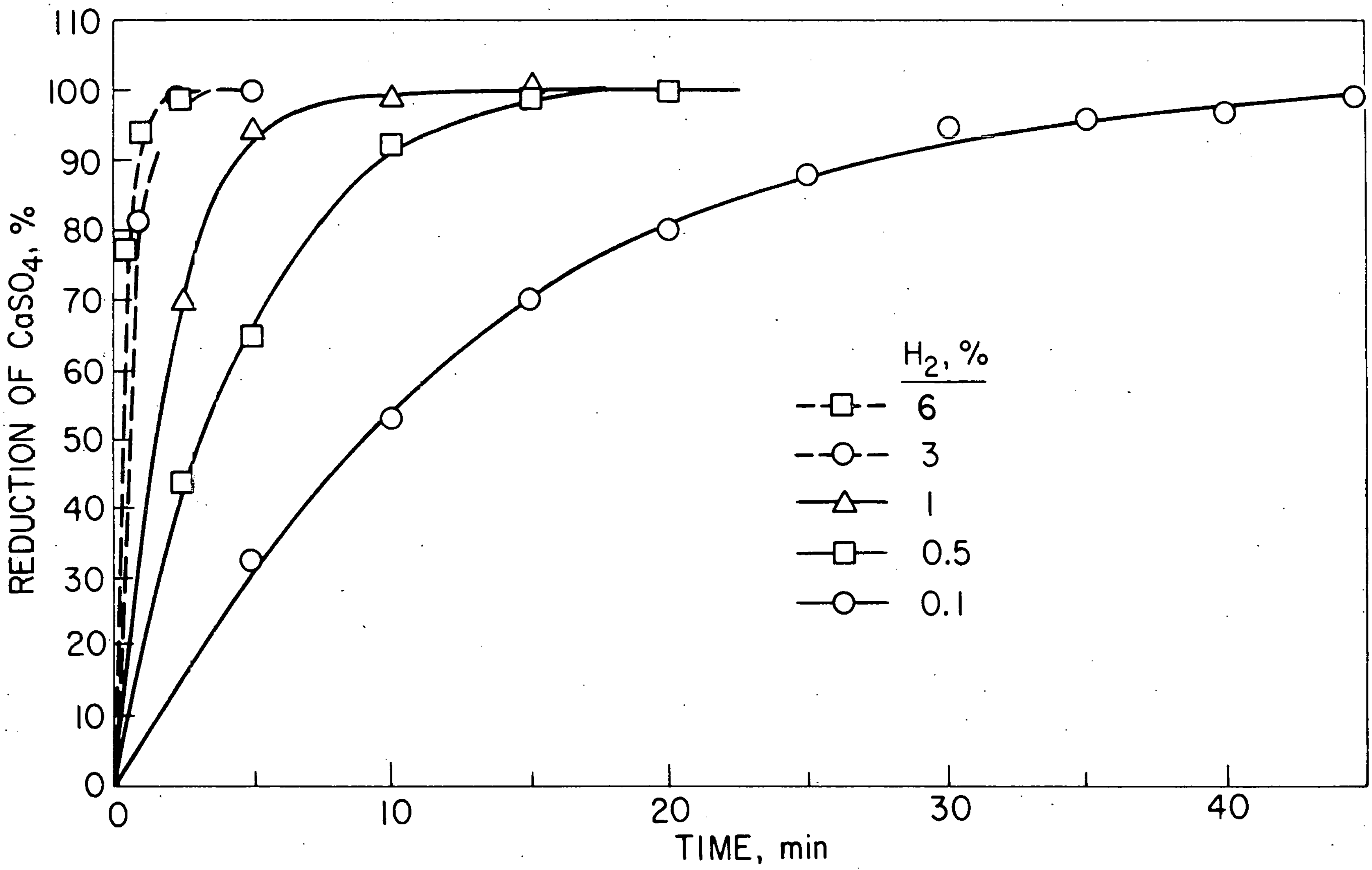

Fig. 10. Rate of Regeneration of $CaSO_4$ in α-Al_2O_3 using Indicated Concentrations of Hydrogen (the balance nitrogen) at 1100°C.

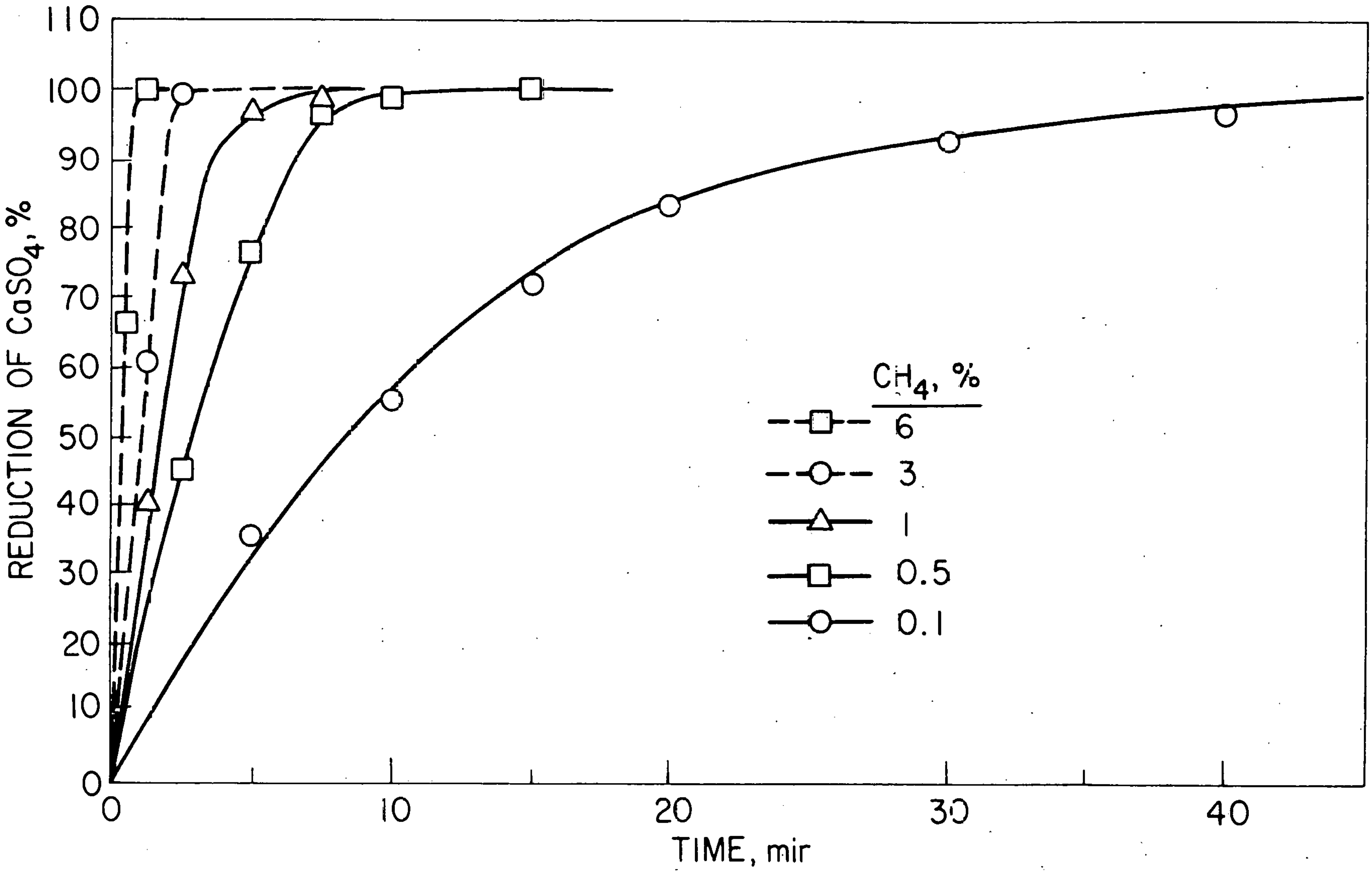

Fig. 11. Rate of Regeneration of $CaSO_4$ in α-Al_2O_3 using Indicated Concentrations of Methane (the balance--nitrogen) at 1100°C.

Table 5. Calculated Regeneration of $CaSO_4$ to CaO

Reducing Gas Conc, %	Calculated Completeness of Regeneration, % CO	H_2	CH_4
6	102	93	87
3	102	99	109
1	96	106	98
0.5	86	108	89
0.1	110	103	92

Effect of CO_2 in Reducing Gas on Regeneration Rate

The effect of CO_2 concentration in the reducing gas on the regeneration rate of sulfated sorbent supported on α-Al_2O_3 is being studied. Carbon dioxide should decrease the rate due to the thermodynamically favorable reaction of CO_2 with H_2 to form H_2O and CO.

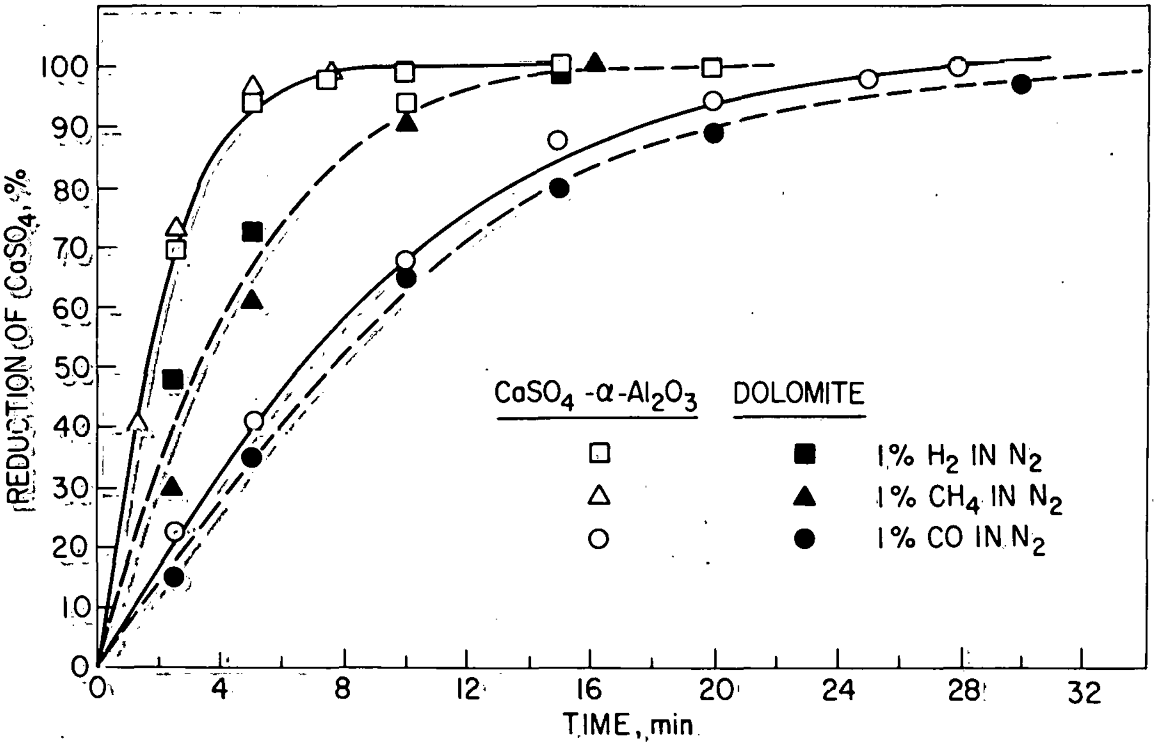

Fig. 12. Comparison of the Rates of Regeneration of $CaSO_4$-α-Al_2O_3 and Sulfated Dolomite, using 1% Methane, Hydrogen, or Carbon Monoxide at 1100°C

Table 6. Carbon Content of Pellets after Regeneration with Methane

Reducing Gas and its Concentration in Experiment	Pellets	
	Carbon, ppm	Carbon,[a] mg/35 mg pellets
6% CH_4	2300	0.41
1% CH_4	850	0.15
0.5% CH_4	400	0.07
3% H_2	200	0.04

[a] 1.3 mg of C from the reduction of CH_4 to H_2 + C would be needed in a 35-mg pellet to obtain enough H_2 to reduce all $CaSO_4$ in the pellet to CaO.

As reported above, when CO was used as the reducing gas, the rate of regeneration was approximately one-third that when hydrogen was used. In runs to examine the effect of CO_2 concentration, the rate seemed to decrease only when the CO_2 concentration became larger than 15% (Fig. 13).

Comparison of Regeneration Rates of Sulfated Pellets and Sulfated Tymochtee Dolomite

In an attempt to generate meaningful data applicable to pilot plant fluidized-bed regeneration experiments, Tymochtee dolomite that had been sulfated in the coal-fired, fluidized-bed combustor was reduced using CO, H_2, and CH_4 at 3% and 1% concentrations for comparison with regeneration of the supported additive pellets. Data are plotted in Fig. 14 for 3% reducing gas concentration. The dolomite contained 10.1% S and was expected to lose about three times more sulfur than the pellets during regenerations. Also the pellets were approximately three times larger than the dolomite particles.

The regeneration rates for dolomite were somewhat lower than those for the additive pellets; the decomposition rate of $CaSO_4$ in the dolomite decreased rapidly near the end of the reaction. This decrease in rate was not observed for the pellets. However, the residence times in a regenerator would not differ significantly for dolomite or pellets.

The major difference was the product found at the end of the reaction. As stated above, for the pellets, the products were $CaO \cdot Al_2O_3$ and $CaO \cdot 2Al_2O_3$; for dolomite, the products were CaO and CaS. (In neither case was $CaSO_4$ found.) Wet chemical analysis will be used to quantify the amount of CaS in the dolomite. X-ray diffraction data indicate that CaS might constitute as much as 30-50% of the product.

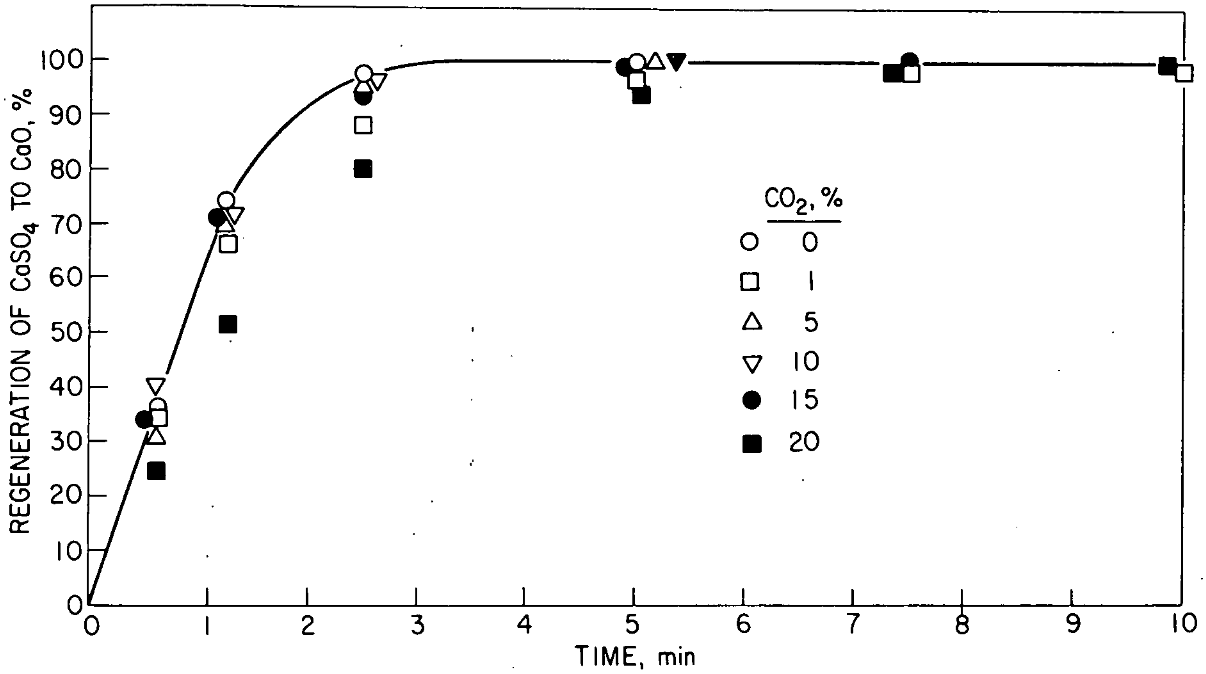

Fig. 13. Effect of CO_2 Concentration in the Reducing Gas on the Rate of Regeneration of Sulfated 6.6% CaO in α-Al_2O_3 at 1100°C. Regeneration Gas: 1% CO, 1% H_2, 1% CH_4 in N_2 + indicated CO_2

The SEM results showed that most of the sulfur in the dolomite was near the surface of the particles. This is not surprising since these particles were only 50% sulfated in the combustor before being reduced in the TGA. It should also be noted that both iron and chlorine were also found on the dolomite surface.

Cyclic Sulfation-Regeneration Studies

Ten cyclic sulfation-regeneration reactions were performed to determine if any loss in reactivity would occur as a function of the number of cycles. After each sulfation and regeneration step, one pellet was removed for analysis. The percent calcium utilization in sulfation and the percent conversion of $CaSO_4$ to CaO during regeneration of the sulfated pellets were calculated from the analyses and are given in Table 7. Over 93% calcium utilization was found in all cycles except the initial sulfation cycle.

In Figs. 15 and 16, the rates of sulfation for cycles 1 to 10 are given. The sulfation rate for cycle 2 was much lower than for cycle 1. In following cycles, the rate increased with each cycle up to cycle 7, where the rates became essentially constant. The pellets had been heat-treated at 800°C during preparation. However, during regeneration at

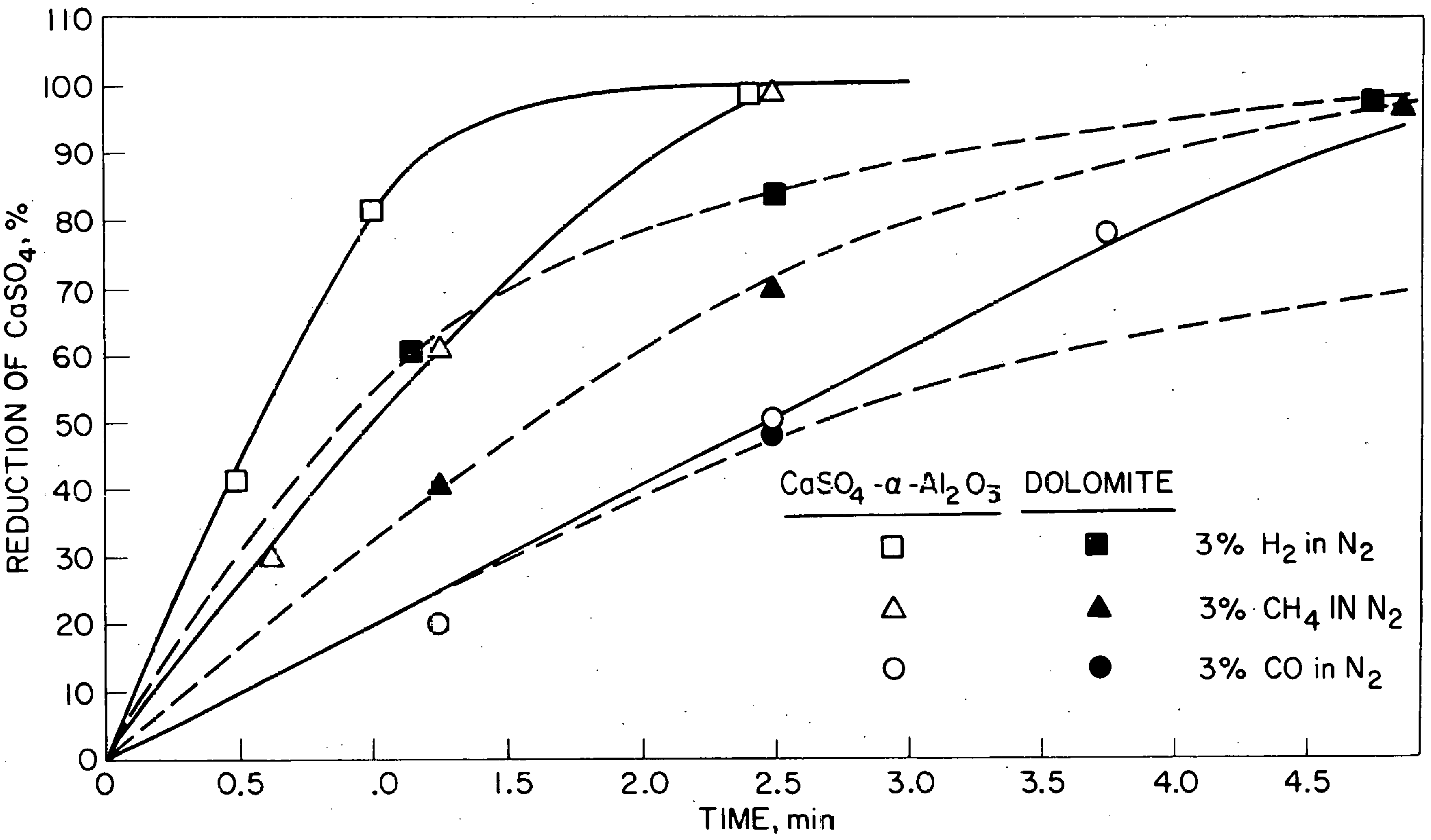

Fig. 14. Comparison of the Rate of Regeneration of $CaSO_4$-α-Al_2O_3 and Sulfated Dolomite using 3% CH_4, H_2, or CO at 1100°C

Table 7. Completeness of Sulfation and Regeneration in Cyclic Experiment

Sulfation		Regeneration	
Cycle	Completeness of Sulfation,[a] %	Cycle	Completeness of Regeneration,[a] %
1	85.3	1	95.2
2	98.8	2	96.4
3	97.0	3	97.4
4	96.1	4	97.6
5	95.3	5	96.9
6	93.3	6	94.3
7	93.5	7	95.0
8	94.4	8	97.1
9	97.3	9	95.4
10	93.2	10	96.3

[a] Calculations based on the assumption that the pellets originally contained 6.6% CaO in α-alumina. The data in Figs. 15 and 16, in contrast, are based on the assumption that 100% of the material reacted.

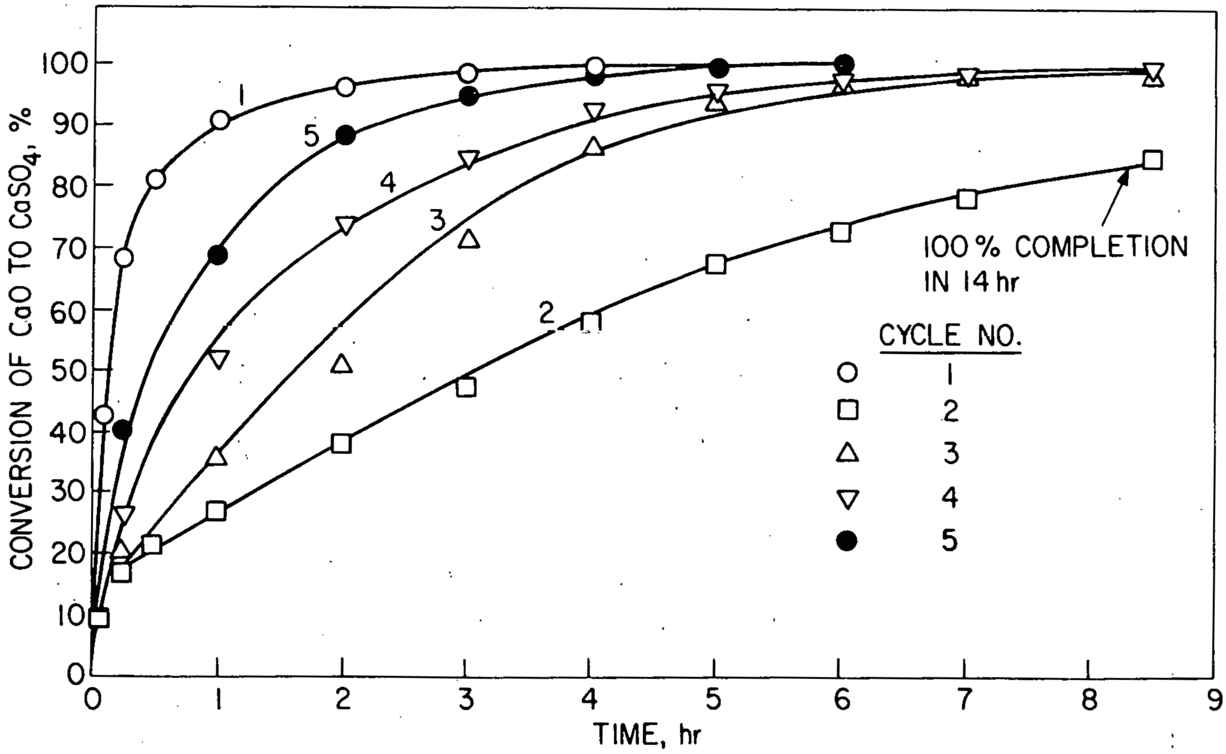

Fig. 15. Comparison of Sulfation Rates in Various Cycles at 900°C, Using 6.6% CaO in α-Al_2O_3. Sulfation Gas Mixture: 3% SO_2, 5% O_2, in N_2.

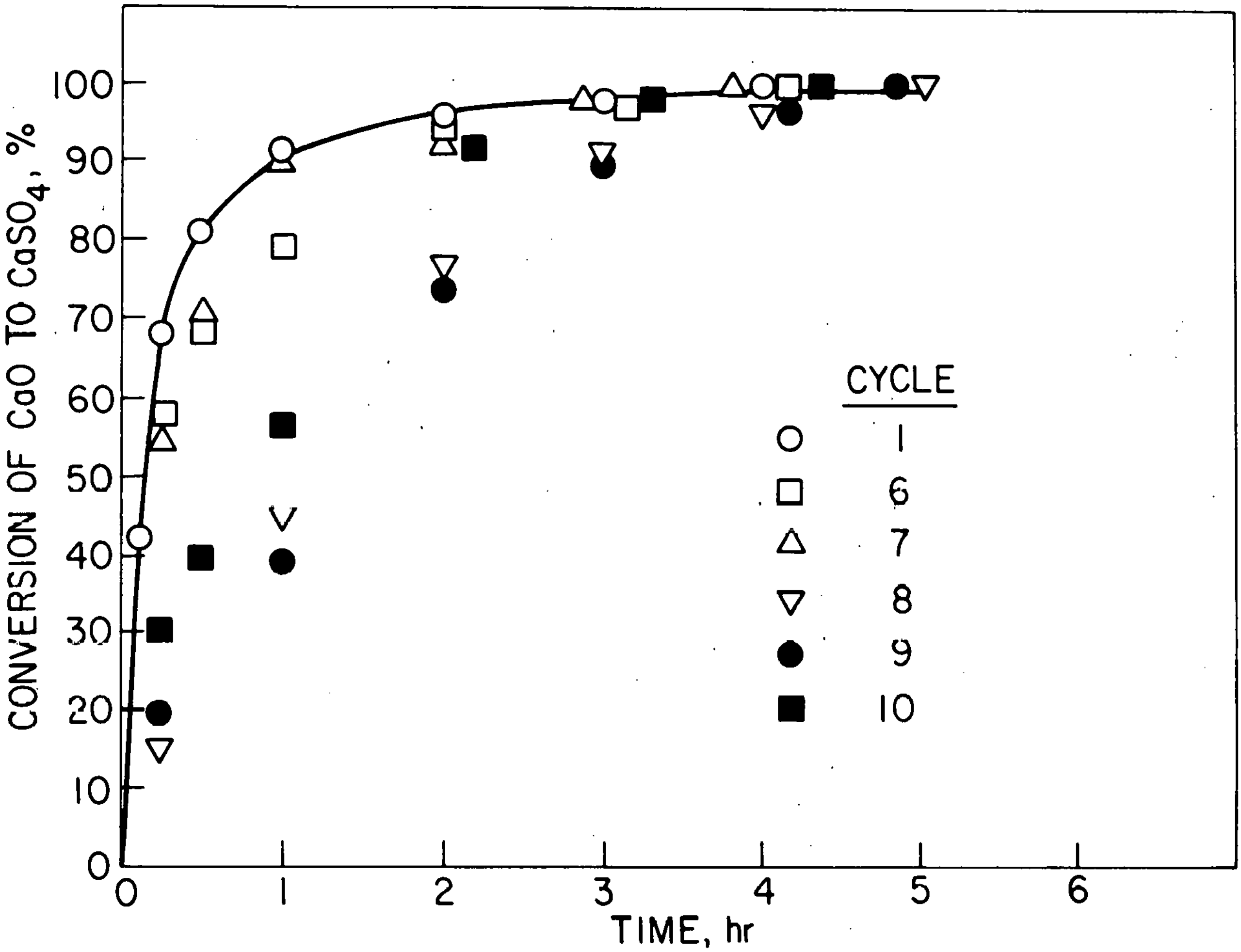

Fig. 16. Comparison of Sulfation Rate in Various Cycles for 6.6% CaO in α-Al_2O_3 at 900°C. Sulfation Gas Mixture: 3% SO_2 and 5% O_2 in N_2

1100°C, different calcium aluminates were formed; it is thought that this caused the different rates of sulfation. In the future, cyclic tests will be performed on pellets that have first been heat treated at 1100°C.

In Fig. 17, the rates of regeneration are given for cycles 1 to 10 (no data were obtained for cycle 9). Pellets in cycles 1 to 7 were reduced using 3% H_2; in cycles 8, 9, and 10 they were reduced using 1% H_2. The rates of regeneration were similar for cycles in which the same concentration of hydrogen was used.

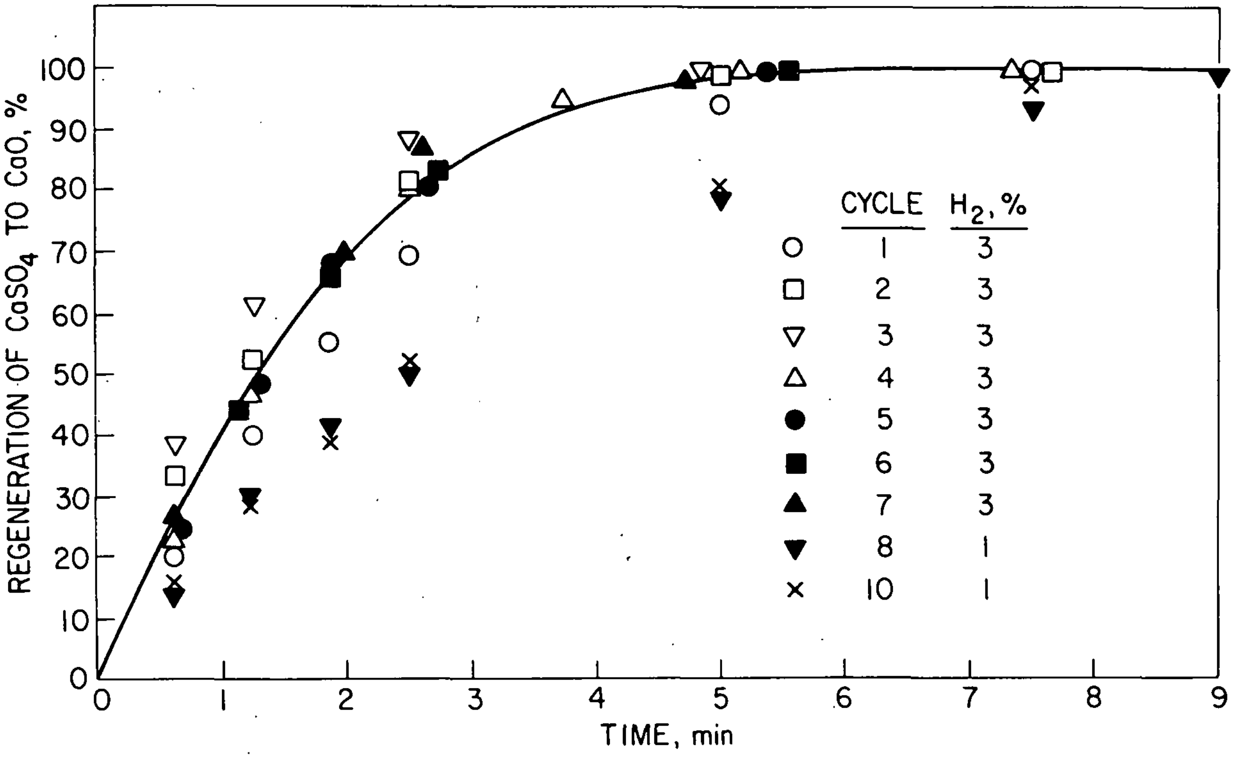

Fig. 17. Comparison of Regeneration Rates in Various Cycles for 6.6% $CaO-\alpha-Al_2O_3$ at 1100°C. Regeneration Gas Mixture: H_2 in N_2

SULFUR EMISSION CONTROL CHEMISTRY

Additional results are presented on the solid-solid reaction

$$3[CaSO_4 \cdot MgO] + [CaS \cdot MgO] \rightarrow 4[CaO \cdot MgO] + 4SO_2 \qquad (1)$$

Initial results on the feasibility of this regeneration method were given in a previous report.[4] The emphasis in the efforts being reported herein has been twofold: (a) to investigate the nature of the effects caused by varying the composition of the starting material for the solid-solid reaction, and (b) to initiate a study of the correlation between TGA results and the results obtained from application of the earlier reported X-ray method.[4]

The experimental procedure employed was as follows: A large stock supply of sulfated dolomite No. 1337 was prepared, and stones from this stock supply were used in every experiment. The sulfated dolomite stock supply was prepared by half-calcining the stone and subsequently sulfating in a 4% SO_2, 5% O_2 simulated flue gas mixture until the gaining of weight halted.

The starting materials for experiments to study the solid-solid reaction, Eq. (1), were always prepared under identical conditions, *i.e.*, aliquots of sulfated dolomite were reduced to the desired extent, using a gas mixture containing 3% H_2 and the balance helium at a reaction temperature of 880°C. Starting materials were prepared that had sulfide concentrations of 24 to 39% (by TGA analysis).

In addition, all sulfate-sulfide reaction experiments were performed under the same conditions, *i.e.*, under 1-atm partial pressure of helium at 950°C. Most sulfate-sulfide reaction experiments were run for 5 hr, but some were run overnight.

X-ray diffraction analyses were performed on samples of the starting material and on samples of the products of all sulfate-sulfide reaction experiments. In all cases, aliquots of 30 to 50 stones were analyzed to minimize sampling error problems.

The results of these experiments are summarized in Table 8. The first column identifies the experiment and the sample analyzed by X-ray, and the second column gives the sample history. The third through the seventh columns list TGA results. The third column gives the percentage of the available material in the stones that has been converted. The fourth, fifth, and sixth columns give the compositions of the samples as percentages of maximum weights possible of CaO, $CaSO_4$, and CaS, respectively. ("Maximum weights possible" refers to a pure species, *e.g.*, for the fourth column, 100% CaO, with no $CaSO_4$ or CaS). The seventh column lists calcium material balances as total percentage of calcium species existing in the stones. The eighth through the eleventh columns list X-ray diffraction results. Columns eight, nine, and ten give the compositions of the samples as percentages of the maximum weights possible of CaO, $CaSO_4$, and CaS, respectively. The eleventh column lists the X-ray calcium species material balances as total percentages calcium existing in the stones.

Varying the composition of the starting material for the solid-solid reaction had the following effects: In all cases, the increase in CaO concentration was substantial, that is, in the 30 to 60% range. However, it is apparent from columns 3 and 8 that a starting material containing greater than 25% sulfide (the stoichiometry of Eq. (1) indicates that 25% sulfide is required) is necessary to approach higher yields (*i.e.*, consumption of most of the $CaSO_4$ and CaS before the reaction stops). For example, in experiment II, in which the starting material contained 25% of the CaS form, the CaS was completely consumed and a substantial amount of $CaSO_4$ remained when reaction ceased. From these preliminary results, it is believed necessary that a starting material contain about 35% of the reduced form to force the solid-solid reaction toward completion at a reaction temperature of 950°C. Continued investigation is planned to determine if the reaction will go to completion and to gain an understanding of why overreduction is necessary.

Table 8. Summary of TGA and X-Ray Results for Solid-Solid Reaction Experiments at 950°C

		TGA Results					X-ray Diffraction Results			
Experiment Number - Sample Number	Sample History	Available material converted, %	Percent of maximum weight of CaO possible	Percent of maximum weight of $CaSO_4$ possible	Percent of maximum weight of CaS possible	Total Ca %	Percent of maximum weight of CaO possible	Percent of maximum weight of $CaSO_4$ possible	Percent of maximum weight of CaS possible	Total Ca %
I	Stock Material	92% sulfated	15	85	0	100	11	64	4	79
II-A	Partial Reduction	25% reduced	15	64	21	100	13	62	--[b]	75
II-B	Sulfate-sulfide reaction, 5 hr	--[a]	--[a]	--[a]	--[a]	--[a]	40	42	--[b]	83
II-C	Sulfate-sulfide reaction, overnight	--[a]	--[a]	--[a]	--[a]	--[a]	58	21	--[b]	79
III-A	Partial Reduction	32% reduced	15	58	27	100	12	66	10	88
III-B	Sulfate-sulfide reaction, 5 hr	--[a]	--[a]	--[a]	--[a]	--[a]	58	12	7	77
IV-A	Partial Reduction	36% reduced	15	54	31	100	15	58	20	93
IV-B	Sulfate-sulfide reaction, 5 hr	--[a]	--[a]	--[a]	--[a]	--[a]	43	19	--[b]	62
V-A	Partial Reduction	36% reduced	15	54	31	100	15	58	16	89
V-B	Sulfate-sulfide reaction, overnight	--[a]	--[a]	--[a]	--[a]	--[a]	68	7	4	79
VI-A	Partial Reduction	40% reduced	15	51	34	100	10	57	21	88
VI-B	Sulfate-sulfide reaction, 5 hr	--[a]	--[a]	--[a]	--[a]	--[a]	49	14	13	76

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[a] Due to the manner in which these experiments were performed, it was not possible to monitor sulfate-sulfide reaction progress from TGA weight changes.

[b] CaS lines in X-ray patterns were either not detectable or, when detectable, were not intense enough to measure.

The following observations refer to correlations between TGA and X-X-ray results. (Unfortunately, due to the manner in which these experiments were performed, quantitative comparison of TGA and X-ray results is possible only for reduction reaction. In the future, it is planned to design experiments to allow comparison of the two types of results for the solid-solid reaction.)

Comparison of TGA and X-ray results for the reduced stones (Table 8, columns 4 and 8 and columns 5 and 9) in each of the experiments suggests that the two methods are generally in agreement. The agreement for the amounts of CaO and $CaSO_4$ in the samples is extremely good. However, the agreement for the amount of CaS present is not as good as might be hoped; in each case, the X-ray result is lower than the TGA result. In addition, the X-ray method yields a poor material balance, as indicated by the values in the eleventh column in Table 8, which are always less than 100%. Any of a number of factors might lead to experimental errors that could cause the lack of agreement: (a) the use of peak heights instead of integrated intensities, (b) the presence of amorphous materials, and (c) complete masking of the usable CaS lines by the $CaSO_4$ lines, leading to substantial error in the CaS estimates. The use of a diffractometer to obtain line intensity measurements should greatly reduce the errors caused by factors (a) and (c).

The MgO has been used as a reference standard. However, it has been observed that a line shift is sometimes present at large scattering angles. This can occur when a solid solution of an unknown material exists in the MgO phase. The net result can be to modify the MgO line intensities to some extent. It has also been observed that the 004 and 040 line combination of $CaSO_4$ is, for some reason, generally weaker than expected. All of these factors have an effect on accuracy.

Two additional experiments were performed to study the feasibility of the reaction between calcium sulfate and calcium sulfide as a viable regeneration scheme. In these experiments, partially calcined sulfated dolomite particles (experiment CAS-10) and fully calcined sulfated dolomite particles (experiment CAS-12), both from the VAR-7 combustion experiment performed previously in the ANL 6-in.-dia, fluidized bed combustor, were reacted with a stoichiometric excess of CaS.

The experiments were performed by packing a mixture of ~90 g of sulfated dolomite (34.8% $CaSO_4$) and ~23 g of CaS into a quartz reactor tube and heating to 1025°C (1877°F). A stream of nitrogen gas provided a neutral atmosphere, as well as the purge medium. During the heatup period (~4 hr) and after temperature stabilization, the off-gas was monitored continuously for SO_2 content, using an infrared analyzer. Off-gas samples were also taken at various times for analysis with a mass spectrometer to check analyzer accuracy and to determine what other constituents were in the gas stream. X-ray diffraction analysis was used to determine the composition of the product solids. Table 9 lists the reactants, reaction times, major products, amounts of SO_2 produced, and estimates of the completeness of reaction.

Table 9. Reaction of Calcium Sulfate with Calcium Sulfide in Experiments CAS-10 and CAS-12

Exp. No.	Reactants	Reaction Time	Major Products	Max Conc of SO_2 in the Off-gas, %	Reaction Completeness, %, Based on		
					Wt Loss due to SO_2 Prod.	Total SO_2 (Gas analysis)	CaO Prod. (Solid analysis)
CAS-10	partially calcined sulfated dolomite (93.8 g); CaS (23.2 g)	∿7 hr[a]	CO_2,SO_2	1.1	<2	<5	<5
CAS-12	fully calcined[b] sulfated dolomite (89.2 g); CaS(23.2 g)	∿43 hr[c]	SO_2,CaO	10.5	90	∿88	∿50[d]

[a] Terminated after this time because SO_2 concentration remained at 0.1% for ∿5 hr after the peak level of 1.1% was reached.

[b] Heated in air to 850°C (1550°F) for approx. 16 hr.

[c] Reaction during ∿7-hr periods -- heating was not continuous.

[d] Subject to change after X-ray diffraction patterns obtained by the use of more appropriate standards are completed.

Experiment CAS-10 was designed to determine if calcium sulfide would react with partially calcined, sulfated dolomite to produce a high concentration of SO_2 in the off-gas stream. Little reaction occurred. A possible explanation is that the CaS is oxidized by CO_2 (released from the calcining dolomite), forming more $CaSO_4$ and thus inhibiting the solid-solid reaction.[6]

The reaction of CaS with fully calcined sulfated dolomite (experiment CAS-12) had more favorable results. Figure 18 illustrates the concentration of SO_2 produced as a function of time and temperature during CAS-12. As indicated in Fig. 18, the concentration of SO_2 in the reactor off-gas varied from a high of 10.5% at 12 cc/min nitrogen flow to a low of 3.3% at 1000 cc/min nitrogen flow, the highest flow rate tested. Extrapolation of these data indicates that the SO_2 equilibrium concentration with nitrogen present but no flow (at 1 atm) would be ∿11%. This is near the theoretical value of 9% at 1877°F (1025°C) as determined from the Zawadzki[7] data plotted in Fig. 19.

Figure 18 also shows that the maximum observed rate of reaction (33 cc SO_2/min) occurred at the maximum nitrogen purge flow rate used during the experiment, 1000 cc/min. This high a reaction rate may not be an advantage, however, in a conventional process (such as the Claus process) to convert the SO_2 to elemental sulfur because such a process requires a high concentration of SO_2 (such as those observed in this work at the lowest nitrogen flow rates) for economically attractive operation.

X-ray analyses of the CAS-12 product were also done to help determine where CaO formed in the additive particles. The diffraction patterns indicated that most of the CaO produced was associated with the large dolomite stones, rather than being deposited as a residue with the powdered CaS reactant. Analysis of the fines indicated that only a minor portion was CaO, and a very small portion was $CaSO_4$. Wet chemical analyses are planned to determine more precisely the reaction material balance.

Speculation regarding the mechanism that controls reaction (2), below, centered around a solid-gas-solid theory presented by Curran *et al.*[8] They postulated that this reaction

$$3/4\ CaSO_4 + 1/4\ CaS \rightarrow CaO + SO_2 \qquad (2)$$

represents the sum of three reactions:

$$CaSO_4 \rightarrow CaO + SO_3$$

(Decomposition of $CaSO_4$)

$$SO_3 \rightarrow SO_2 + 1/2\ O_2$$

(Decomposition of unstable SO_3)

and

$$1/4\ CaS + 1/2\ O_2 = 1/4\ CaSO_4$$

(Combination of available O_2 with unconverted CaS).

If this is the mechanism, the presence of CaS in at least a stoichiometric ratio to the $CaSO_4$ serves as a facile route for the removal of oxygen from the system, which tends to promote reaction. It has been found in preliminary studies that to force the solid-solid reaction toward completion at 950°C, a starting material containing about 35% CaS may be necessary. The data obtained from the two experiments reported here are not in disagreement with this postulation.

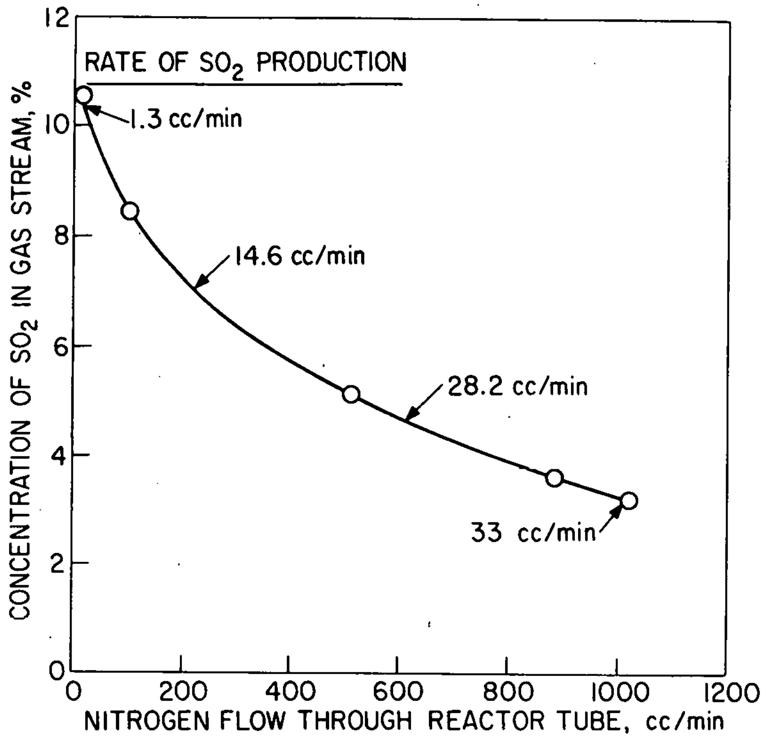

Fig. 18. Relationship of SO_2 Production and Purge Flow Rate in Solid-Solid Reaction. Temperature: 1025°C; Purge gas: nitrogen; Reactants: 4:3 mole ratio, CaS:$CaSO_4$ ($CaSO_4$ present as sulfated dolomite)

Plans have been made for additional investigation of the mechanism and feasibility of this approach as a regeneration scheme. An engineering-scale regeneration process would require that CaS be formed *in situ* (by the reduction of sulfated additive) rather than CaS being added. As a result, future laboratory experiments will be designed to reduce an appropriate fraction of the $CaSO_4$ in the sulfated additive to CaS prior to solid-solid reaction. Also, since limited data have been gathered to date on temperature effects above 1025°C, runs will be made at higher temperatures to obtain more temperature-reaction rate information.

COAL COMBUSTION REACTIONS

The Determination of Inorganic Constituents in the Effluent Gas from Coal Combustion

Some chemical elements carried by combustion gas are known to cause severe metal corrosion. The objective of this study is to determine quantitatively which elements are present in the hot combustion gas of

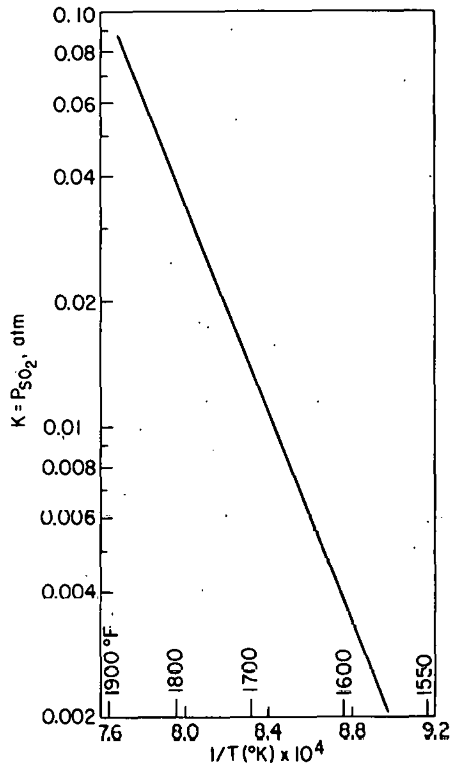

Fig. 19. Equilibrium for the Equation 3/4 $CaSO_4$ + 1/4 CaS = CaO + SO_2 (after Zawadzki)[7]

coal, in either volatile or particulate form, and to differentiate between volatile and particulate species. It is desirable to identify the compound form and amount of particulate species and to determine the amount and form on condensable species.

Detailed design and engineering drawings of the laboratory-scale batch unit combustor have been completed. The conceptual design of the combustor was presented in a previous report.[4] The drawings are being checked and reviewed. A work project for fabrication has been established. The fabrication specification for the combustor has been written, and a final design/preliminary safety review of the combustor is being arranged.

The multiprobe thermocouples required for temperature measurements of the entire system were received. All other components and materials needed for construction of this combustor have already been ordered.

Installation of the induction heating unit is continuing. The work includes the installation of a Tocco 30-kW generator and the installation of working and control stations. About 95% of the electrical work has been finished. Installation of the water piping required for the cooling system of the unit will be the final part of this job.

Systematic Study of the Volatility of Trace Elements in Coal

Knowledge of the vaporization characteristics of trace elements in coal and of the rate of their volatilization is important for combined cycle turbine operation. The purpose of this study is to obtain data on the volatility of these elements under practical coal combustion and gasification conditions. This study is also intended to obtain data supporting the study covered above.

The experimental setup for this study was presented previously.[4] Work on the electricity and water supplies required for the experimental work has been completed. All materials and components ordered have been received, and setting up of the experimental apparatus is under way.

PROPERTIES OF A DOLOMITE BED OF A RANGE OF PARTICLE SIZES AND SHAPES AT MINIMUM FLUIDIZATION

Examination of Earlier Experimental Results

In a previous report,[4] the results of a series of seven fluidization experiments performed in the ANL 6-in.-dia, fluidized-bed reactor on partially sulfated dolomite particles of a wide range of sizes (about 1410-88 μm) and shapes were described. The experimental pressure drop (ΔP) data as a function of fluidizing velocity (u) were interpreted to determine: the minimum fluidizing velocity (u_{mf}) as a function of bed temperature (T) and reactor pressure (P), the height of the bed at minimum fluidization ($\bar{L}_{mf}$), the mean bed void fraction or voidage at minimum fluidization ($\bar{\varepsilon}_{mf}$), and the mean shape factor or sphericity of the solid particles consituting the bed ($\bar{\phi}_s$). In that earlier work, the minimum fluidization velocity was found to be almost independent of bed temperature between 21 and 432°C (70-810°F), but it was found to decrease with increasing reactor pressure (26-121 psia) at a given temperature. The minimum fluidization velocities were correlated on the basis of the Ergun relation.[10] The correlations of Wen and Yu,[11] Andersson,[12] and Zenz and Othmer[13] were also examined with appropriate modifications for their applicability to a bed consisting of a wide range of particle sizes and shapes.

The results of the seven fluidization experiments are summarized in Table 10; column 6 lists the previously reported[4] values of the minimum fluidization velocities, u_{mf}. This table lists the values of the particle Reynolds number at minimum fluidization, $Re_{p,mf}$, computed from the following relation:

$$Re_{p,mf} = \frac{\bar{d}_p \, \rho_g \, u_{mf}}{\mu} \qquad (1)$$

Here, $\bar{d}_p$ is the average particle diameter, which has a value of 717 μm for the dolomite sample used in these experiments; ρ_g and μ are the density and viscosity of the fluidizing gas, respectively.

The Ergun correlation has the following form:

$$150 \, \frac{(1-\bar{\varepsilon}_{mf})}{\bar{\phi}_s^{2} \, \bar{\varepsilon}_{mf}^{3}} \, Re_{p,mf} + 1.75 \, \frac{Re_{p,mf}}{\bar{\phi}_s \, \bar{\phi}_{mf}^{3}} - Ga = 0 \qquad (2)$$

where

$$Ga = \frac{\bar{d}_p^{3} \, \rho_g \, (\rho_s - \rho_g) g}{\mu^2} \qquad (3)$$

Table 10. Calculation of Mean Sphericity of the Solid Particles, $\bar{\phi}_s$, and Correlation of Minimum Fluidization Velocity Data

Equipment: ANL 6-in.-dia combustor
Bed charge: 14.005 kg of partially sulfated dolomite
Fluidizing gas: air

Experiment No.	Temp, °C	Pressure, atm	$Re_{p,mf}$	$\bar{\phi}_s$	u_{mf}, cm/sec	
					Expt.	Calc.^{a} Eq. 2
2	20	2.04	36	0.388	36.0	38.1(5.7)^a
3	20	8.23	92	0.338	23.0	25.2(9.6)^a
4	20	4.90	70	0.360	27.7	30.0(8.2)^a
5	265±5	1.77	12	0.452	36.0	33.5(6.9)^a
6	240±15	8.16	33	0.355	23.5	26.4(12.3)^a
7	380±30	8.16	23	0.403	23.3	25.4(8.8)^a
8	425±15	4.97	14	0.359	25.9	25.8(0.4)^a
Mean				0.379		

[a] Percentage difference of calculated and experimental values of u_{mf}.

Here, $\bar{\epsilon}_{mf}$ is the mean bed void fraction at minimum fluidization; its value was experimentally determined to be 0.65.[4] Also, $\bar{\phi}_s$ is the mean shape factor or sphericity of the solid particles, Ga is the Galileo number, ρ_s is the density of the solid particles, and g is the acceleration due to gravity. From the pressure drop measurements at minimum fluidization for the experimental conditions of experiments 5 and 8, for which $Re_{p,mf}$ is less than 20 and the second term of equation 2 may be regarded as negligibly small, $\bar{\phi}_s$ was earlier determined to be 0.364.[4]

Here, $\bar{\phi}_s$ has been computed from the entire equation 2 for all seven experimental runs. These results are given in the fifth column of Table 10. We take the mean value of 0.379 to be a representative value for the sphericity of the range of solid particles constituting the bed. We checked this by computing the u_{mf} values from equation 2 for all experiments, using a value of 0.379 for $\bar{\phi}_s$, and (as seen from column 7, Table 10) these values are in good agreement with the directly measured values given in column 6 of Table 10. In the seventh column, in parentheses, are listed the percentage disagreements between the experimental and calculated u_{mf} values. This good agreement substantiates the concept of mean sphericity for the solid particles of a size range constituting the fluidized bed and its adequacy for correlating the minimum fluidization velocity data through the Ergun correlation. It may further be emphasized that the currently determined $\bar{\phi}_s$ value differs by less than 4% from the earlier value so that all conclusions based on the earlier $\bar{\phi}_s$ value remain valid.

The following modified correlation of Wen and Yu[11] was examined previously by computing the two sides of the relation and noting their departure from equality.

$$\varepsilon_{mf}^{-4.7}\ \bar{\phi}_s^{-2}\ Ga = 18\ Re_{p,mf} + 2.70\ \bar{\phi}_s^{-0.687}(Re_{p,mf})^{1.687} \qquad (4)$$

In Table 11, a more straightforward comparison is presented. After equation 4 was employed to calculate $Re_{p,mf}$ using the values of the parameters reported in Table 11, $Re_{p,mf}$ was used to calculate the values of u_{mf} with equation 2. In contrast to the earlier calculations, the results of Table 11 shed light on the adequacy of equation 4 to predict u_{mf}. It is clear that the relation of equation 2 is preferable to that of equation 4 since the accuracy of our experimental u_{mf} values is assessed to be approximately ±5%.

Table 11. Comparison of the Experimental Values of u_{mf} with the Values Calculated from Equation 4

($\bar{d}_p$ = 720 μm, $\bar{\phi}_s$ = 0.364, $\bar{\varepsilon}_{mf}$= 0.650)

Experiment No.	u_{mf}, cm/sec		Dev., %	Ga
	Expt.	Calc., Eq. 4		
2	36.0	38.2	6.0	75895
3	23.0	26.7	16.5	300959
4	27.7	32.0	15.6	188374
5	36.0	45.1	25.3	16506
6	23.5	28.1	19.5	70795
7	23.3	27.1	16.3	41961
8	25.9	22.8	11.9	22317

Properties of Unreacted-Dolomite Bed at Minimum Fluidization

A series of eight fluidization experiments were performed earlier on a sample of fresh dolomite.[4] These results are reported here with a view to investigating the validity of the conclusions presented earlier[4] and in Tables 10 and 11.

The reactor was charged with 14.786 kg of fresh dolomite having the particle size distribution given in column 3, Table 12. After completion of the eight runs, only 11.355 kg of the material was found in the reactor and 2.955 kg in the cyclones. Thus, about 3% of the material was not accounted for; a part of it had been entrained in the gas stream. On the other hand, about 23.2% of the bed, comprising the fines, was rapidly blown off. The final bed was found to have the

Table 12. Particle-Size Distribution of Fresh Dolomite Bed Material Before and After the Series C Runs

U.S. Sieve No.	Size Range, mm	Weight Fraction in the Range	
		Before	After
+14	>1.41	0.0000	0.0000
-14 +16	1.41 - 1.19	0.0241	0.0224
-16 +18	1.19 - 1.00	0.1478	0.1756
-18 +20	1.00 - 0.84	0.1688	0.2410
-20 +30	0.84 - 0.59	0.4067	0.4449
-30 +35	0.59 - 0.50	0.0881	0.0527
-35 +45	0.50 - 0.35	0.1478	0.0634
-45 +80	0.35 - 0.177	0.0105	0.0000
-80 +170	0.177- 0.088	0.0000	0.0000
-170	<0.088	0.0073	0.0000
Average Particle Diameter, μm		650	765

particle size distribution given in the fourth column of Table 12; the weight of the remaining bed corresponded to a pressure drop of 0.955 psi. The experiments confirmed this value. Consequently, this pressure drop value was employed in the correlations in determining u_{mf} from pressure drop data and an average particle diameter value ($\bar{d}_p$) of 765 μm. The experimentally determined u_{mf} values from the measurements of pressure drop as a function of the fluidizing velocity (u) are given in the fourth column of Table 13 for the operating conditions of temperature and pressure in columns 2 and 3, respectively. The first four runs (C-1 through C-4), performed at room temperature, are considered more reliable than the ones performed at higher temperatures and are therefore the only ones employed in determining the average sphericity of the solid bed particles.

The Ergun correlation at minimum fluidization is:[14]

$$\frac{\Delta P_{mf} g_c}{L_{mf}} = 150 \frac{(1-\bar{\varepsilon}_{mf})^2 \mu u_{mf}}{\bar{\varepsilon}_{mf}^3 (\bar{\phi}_s \bar{d}_p)^2} + 1.75 \frac{(1-\bar{\varepsilon}_{mf}) \rho_g u_m^2}{\bar{\varepsilon}_{mf}^3 (\bar{\phi}_s \bar{d}_p)} \qquad (5)$$

Further,

$$\Delta P_{mf} g_c = (\rho_s - \rho_g)(1-\bar{\varepsilon}_{mf}) L_{mf} g \qquad (6)$$

Here ΔP_{mf} is the pressure drop across a bed of height L_{mf}, g_c is the conversion factor and is equal to 980 g cm/(g wt)(sec^2), μ is the gas viscosity, ρ_g is the gas density, ρ_s is the solid particle density, and g is the acceleration due to gravity. The relation given in equation 6, in conjunction with the experimentally measured ΔP_{mf} values, lead to

Table 13. Values of u_{mf}, L_{mf}, $\bar{\varepsilon}_{mf}$, $Re_{p,mf}$, and $\bar{\phi}_s$ at Various Temperatures and Pressures

Experiment No.	Temp, °F	Pressure, psia	u_{mf}, ft/sec	L_{mf}, ft	$\bar{\varepsilon}_{mf}$,	$Re_{p,mf}$	$\bar{\phi}_s$
C-1	65	27	1.38	2.03	0.55	39	0.570
C-2	65	60	1.13	2.02	0.56	72	0.568
C-3	65	93	0.94	2.00	0.58	91	0.503
C-4	65	120	0.82	1.94	0.59	102	0.452
C-5	690±25	19	1.24	2.02	0.59	6.2	--
C-6	555±15	57	1.19	1.78	0.54	22	--
C-7	465±5	87	1.04	1.72	0.55	34	--
C-8	395±15	121	0.94	1.63	0.56	50	--
Mean					0.57		0.52

$\bar{\varepsilon}_{mf}$ values for eight experiments that are listed in column 6 of Table 13. A mean value of 0.57 for $\bar{\varepsilon}_{mf}$ was employed in all calculations reported here.

Thus with a known $\bar{\varepsilon}_{mf}$, equation 5 was used to compute $\bar{\phi}_s$ for experiments C-1 through C-4. The results are given in the eighth column of Table 13. A mean value of 0.52 for $\bar{\phi}_s$ was used throughout this work. Computed values of Reynolds number, $Re_{p,mf}$, from the following relation are given in column 7 of Table 13:

$$Re_{p,mf} = \frac{\bar{d}_p \rho_g \, u_{mf}}{\mu} \qquad (1)$$

SEPARATION OF COMBUSTION AND REGENERATION SYSTEMS

As originally installed, the 6-in.-dia, pressurized, fluidized-bed combustor and the 3-in.-dia, pressurized, fluidized-bed regenerator utilized several components in common. Due to the dual function of these components, the two units could not be operated simultaneously. The equipment common to both units included the inlet and outlet surge tanks, the gas preheater, the additive solids-feeder, the off-gas system (cyclones, filters, pressure-control valve, etc.), and the off-gas analysis system.

Modifications of both systems were undertaken to physically separate the two units and to provide each unit with its own ancillary equipment. The objective of the modifications is to permit concurrent investigations of the combustion process and the regeneration process, thereby increasing the capability for research relating to both processes.

The current status of the more significant items involved in the modifications is presented below:

1. Alterations to the combustion system equipment were completed and installation of the new regeneration system is nearly complete.

2. A new rotary-vane solids-feeder was delivered, leaving the off-gas conditioning system and the gas preheater as the only two major components for the new regeneration system still to be received. Delivery of these two items is expected in the near future; other available equipment has been substituted and installed pending delivery to permit testing of the new regeneration system.

3. Installation of the necessary pneumatic and electrical process and instrument services for the new regeneration system has been essentially completed. Only a minor amount of work remains to complete the final hookup of these services.

4. Provisions were made for feeding both coal and sulfated additive into the new regeneration system. (The coal, combusted under reducing conditions, will supply both the reducing gases and the heat required for one-step reductive decomposition of the sulfated additive.) Installation of the necessary feeding equipment for the coal and additive (scales, solids-feeders, feed-hoppers, etc.) was completed, and testing of the equipment is in progress.

5. Installation of the necessary sheet-metal ducts for venting the regeneration enclosure and associated equipment into the existing laboratory main ventilation system was begun and is expected to be completed in a few weeks.

6. Installation and calibration of the analytical instruments to be used for determining O_2, SO_2, CO, CO_2, H_2, H_2S, total hydrocarbons, NO-NO_x, and H_2O concentrations in the regenerator off gas have been completed except for minor revisions and operational testing.

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