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REGENERATION OF SULFATED LIMESTONE FROM FBCs

Annual Report
October 1978—September 1979

by

Irving Johnson, D. S. Moulton, F. F. Nunes,
W. M. Swift, F. G. Teats, and A. A. Jonke

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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Sulfur Oxides
Sulfur

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SO_2 - Sorbents
Sorbent Regeneration
Sulfur Production

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ABSTRACT

These studies are concerned with the development of processes for the regeneration of sulfated limestone from fluidized-bed combustors. The results of cyclic combustion/regeneration experiments on three limestones are reported. The reactivity of a low-reactivity limestone, Germany Valley, did not change significantly during cyclic combustion/regeneration. Studies of a high-reactivity limestone, Greer, at lower regeneration temperatures (1050°C) indicated an apparently better performance than at 1100°C. The sorbent utilization of type 2203 limestone in a three-cycle experiment was similar to that of Greer. The results of studies of a process for the recovery of elemental sulfur from SO_2 involving reaction with fly ash or coal ash-coal combinations are reported. The residual carbon in the fly ash was found to be an effective reductant for the SO_2 and high-purity sulfur was obtained. Regeneration of spent limestone sorbent in externally fired rotary kilns was accomplished, but only under conditions that resulted in rapid attack of the kiln materials by SO_2.

SUMMARY

Task A. Fluidized-Bed Reductive Decomposition Studies

Cyclic Studies. Cyclic combustion/regeneration experiments on three limestones have been completed. The tests were performed on the possibility that certain unreactive stones might increase in reactivity for sulfur retention during the first few utilization cycles, thus resulting in a significant reduction in sorbent requirements in comparison to a once-through process. Three-cycle combustion/regeneration experiments have been completed utilizing Germany Valley limestone and 2203 limestone at high-pressure combustor conditions and utilizing Germany Valley limestone at low-pressure combustion conditions. In addition, cyclic tests were completed with highly reactive Greer limestone (conducted at a lower regeneration temperature and longer regeneration residence times than in previous studies).

Results of the cyclic combustion/regeneration experiments with Germany Valley limestone (at low-pressure combustor conditions) indicate the absence of a significant increase in limestone reactivity that had been postulated

to occur due to heat and calcination effects in the first regeneration cycle. This agreed with poor results obtained utilizing Germany Valley limestone at the more reactive high-pressure combustor conditions. Regeneration of Germany Valley limestone could probably yield an off-gas with 7-8% SO_2 concentration. However, the solids circulation rate would be two to three times that for the more reactive Greer limestone. Thus, regeneration of Germany Valley would be considerably less attractive on an economic basis alone.

Results of cyclic combustion/regeneration experiments with Greer limestone are reported. A lower regeneration temperature (1050°C instead of 1100°C used in the previous ten-cycle series of experiments with Greer) and longer regeneration solids residence times (about 11 min and about 28 min vs. about 7 min in previous runs) were used in an effort to determine what changes (if any) in the reactivity of Greer limestone would result from changes in these variables. The previous ten-cycle study with Greer limestone indicated that the reactivity of the sorbent for sulfur retention was gradually lost with increasing utilization cycle (regenerability of the sorbent was unaffected in the ten combustion/regeneration cycles).

The present combustion-regeneration experiment with Greer limestone indicated that at the regeneration temperature of 1050°C and the lower regeneration solids residence time, i.e., about 11 min, no overall change in reactivity of the Greer limestone occurred in the first three cycles (sorbent utilization for a cycle remaining nearly constant at about 21% in these three cycles). This indicates an apparent improvement in the performance of Greer limestone over three cycles as compared with the earlier study which employed a regeneration temperature of 1100°C (the previous cyclic study showed a decrease in the cyclic sorbent utilization from 30% to 14% in the first three cycles). At the longer regenerator solids residence time (about 28 min), a marked decrease in the sorbent utilization per cycle over the three cycles was observed which closely followed the pattern displayed in the first three cycles of the previous ten-cycle series of experiments with Greer limestone. The effect of the lower regeneration temperature (1050°C vs. 1100°C in the previous study) appeared to be beneficial with respect to reactivity of the sorbent in three cycles except at the longer regeneration solids residence time (about 28 min). The lack of sintering of the sorbent particles at 1050°C and its recurrence when the sorbent particles were exposed for a longer time could explain the observed differences in cyclic reactivity of the Greer limestones. A more extensive cyclic study with Greer limestone at the lower regeneration temperature (1050°C) and short regenerator solids residence time (7-11 min) would be required to study further changes in the sorbent reactivity beyond three cycles. The regenerability of the sorbent exceeded or closely paralleled the predicted values at the regenerator solids residence times and temperatures used in this study.

Results of the cyclic studies with 2203 limestone showed that the sorbent reactivity changed little in three cycles. The sorbent utilization (per cycle) was comparable in magnitude to results observed with highly reactive Greer limestone, indicating that the reactivity of the two stones is similar. Since

there was no apparent loss of reactivity in three cycles, a more extensive investigation with 2203 limestone (similar in scope to the previous ten-cycle study with Greer limestone) is suggested to further determine the applicability of this stone. The regenerability of the stone ranged from 67-86% (based on solids analyses) which exceeded or closely paralleled the predicted values.

Task B. Alternative Regeneration Process Development

Reduction of SO_2 to Elemental Sulfur Using Ash and Ash-Coal Mixtures. When spent lime from a fluidized bed combustor is regenerated, the off-gas contains sulfur dioxide in a sufficient concentration that it can be used in a chemical process to make elemental sulfur, a nonpollutant. Several processes for converting sulfur dioxide to elemental sulfur are applicable to a fluidized-bed combustor system. The chemical literature pertaining to these processes is reviewed.

An experimental program was carried out to find a means of producing sulfur from sulfur dioxide, using coal and/or other materials readily available at a fluidized-bed combustor. To be useful, the method should result in a highly reliable sulfur dioxide reduction reactor (i.e., not easily plugged), and it should produce elemental sulfur which is not contaminated with coal volatiles.

Ash available at a fluidized-bed combustor may have several properties useful to the process. The ash from the atmospheric ANL fluidized-bed combustor contains carbon which can be used as the reductant, but ash from more advanced combustors probably will not contain sufficient carbon. However, most ash should possess catalytic activity for some of the reactions involved, and ash may be useful in preventing reactor plugging.

In a series of experiments, both ash and ash-coal mixtures were used as the reductant in a fixed-bed reactor for producing elemental sulfur. No reactor plugging was found when using ash-coal mixtures containing up to 17% coal; however, the sulfur product was contaminated with coal volatiles when ash-coal mixtures containing more than about 3% coal were used.

A different configuration utilizing two separate beds allowed the use of a larger overall percent of coal without contaminating the sulfur. The coal and ash were placed in the reactor separately, so that the sulfur dioxide flowed through the coal bed first, then through the ash bed. The bed contained 24% coal overall, and a high-quality sulfur product was obtained.

There was a large pressure drop in the gas stream when it passed through a packed bed of ash because of the ash being a fine particulate material. Pelletization of ash and ash-coal mixtures was attempted with a laboratory pelletizer and with a press, but the pellet quality was so poor that pelletization is not an attractive means of preventing a large pressure drop. Use of a fluidized bed reactor for sulfur dioxide reduction may be a better alternative, but has not been tried. Based on the experimental results obtained to date, producing elemental sulfur in a series of fluidized beds is proposed.

Rotary Kiln Regeneration. Previous emission control studies have demonstrated that spent limestone SO_2-sorbents can be regenerated with reducing agents at high temperatures in a fluidized-bed reactor. Experimental work to evaluate internally fired rotary kilns for use as regeneration reactors has been completed.

In an analysis of the data, predictions of empirical rate equations were found to have limited agreement with the kiln experimental results. The studies indicated that the rate of reaction in the kiln was limited by diffusion. It could not be determined, however, which diffusion mechanism was controlling.

The experiments demonstrated that regeneration can be accomplished in externally fired rotary kilns, but only under severe conditions. At 1060°C, about 85% of the calcium sulfate was converted to calcium oxide. Also, concentrated SO_2 in the off-gas can be obtained--at 1060°C, SO_2 concentrations in excess of 20% were measured. However, the materials of construction used in rotary kilns are not sufficiently durable to withstand these conditions.

TASK A. FLUIDIZED-BED REDUCTIVE DECOMPOSITION STUDIES

1. Cyclic Studies*

(F. F. Nunes, F. G. Teats, S. D. Smith, A. R. Pumphrey, J. R. Falkenburg, and W. M. Swift)

Many limestones are less reactive than the two sorbents (Tymochtee dolomite and Greer limestone) previously tested under cyclic combustion/regeneration conditions at ANL.[1] Many of these less reactive stones would be required in relatively large amounts for once-through operation, making their use undesirable. Depending upon limestone availability, regeneration may be more attractive for less reactive stones than for the more reactive stones. In the previous studies with highly reactive stones (Tymochtee dolomite and Greer limestone), a substantial percentage reduction in limestone requirements was seen to be possible by regeneration and recycle of the sorbents. However, for reactive stones, the savings from decreased limestone usage (as compared with limestone usage in a once-through process) would not equal the cost of the regeneration process.

On the possibility, however, that certain unreactive stones might actually increase in reactivity for sulfur retention during the first few utilization cycles (so that there would be a significant reduction in limestone requirements in comparison to a once-through process), tests were conducted to evaluate two additional limestones under cyclic combustion/regeneration conditions. These tests were reduced in scope considerably from the ten-cycle series of experiments utilizing highly reactive stones. In general, each stone was tested over three combustion/regeneration cycles at either high-pressure (825 kPa) or low-pressure (308 kPa) combustion conditions.

a. Equipment

The PDU-scale (process development unit) pressurized fluidized-bed coal combustion facility consists of a 15.2-cm-dia fluidized-bed combustor that can be operated at pressures up to 1014 kPa, a compressor to provide fluidizing-combustion air, a preheater for the fluidizing-combustion air, peripheral-sealed rotary feeders for metering solids into an air stream fed into the combustor, two cyclone separators and a filter in series for particulate removal from the flue gas, associated heating and cooling circuits and controls, and temperature- and pressure-sensing and display devices. A simplified schematic flowsheet of the combustion equipment (previously published) is presented in Fig. 1. Details on the PDU-scale combustor were presented previously.[1]

The flue gas (off-gas) is sampled continuously and is analyzed for the constituents of primary importance. Nitrogen oxide and total NO_x are analyzed using a chemiluminescence analyzer; sulfur dioxide, methane, carbon monoxide, and carbon dioxide determinations are made using infrared analyzers;

*The information in this section is also presented in the preceding report in this series, ANL/CEN/FE-79-9.

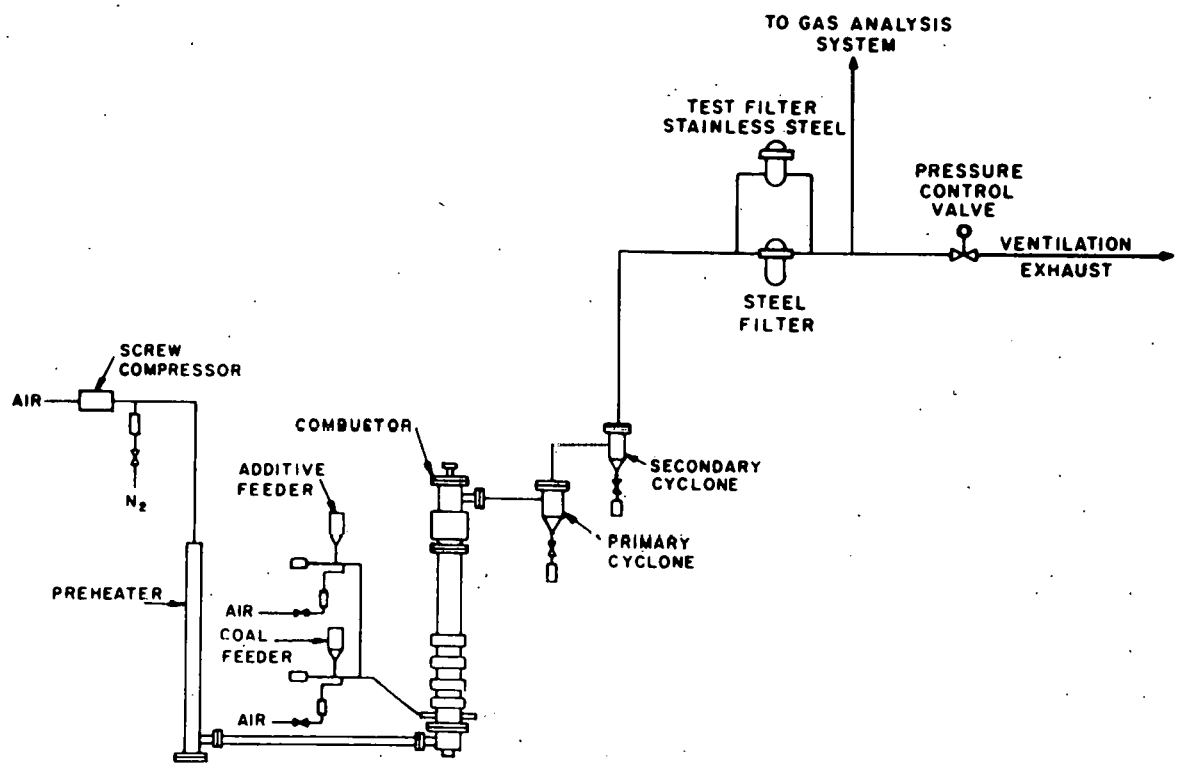

Fig. 1. Simplified Equipment Flowsheet of PDU Fluidized-Bed Combustor and Associated Equipment. The "additive feeder" is actually a "sorbent feeder."

oxygen is monitored using a paramagnetic analyzer; and total hydrocarbons are analyzed by flame ionization. Prior to and during each experiment, each analytical instrument is calibrated, using standard gas mixtures of flue-gas constituents in nitrogen.

Figure 2 is a schematic diagram (previously published) of the regeneration system used in this work. The reactor ID is 10.8 cm (4.25 in.), and the height of the fluidized bed (about 46 cm) is regulated by an overflow pipe external to the bed. The pressurized fluidized-bed reactor is lined with 4.8-cm-thick castable refractory. The coal and the sulfated sorbent are metered separately to a common pneumatic transport line which discharges solids into the fluidized bed above the gas distributor.

Other components of the experimental system are (1) an electrically heated line for preheating to about 400°C some of the fluidizing gas and air (used in start-up only) and (2) a particulate-removal system for the off-gas.

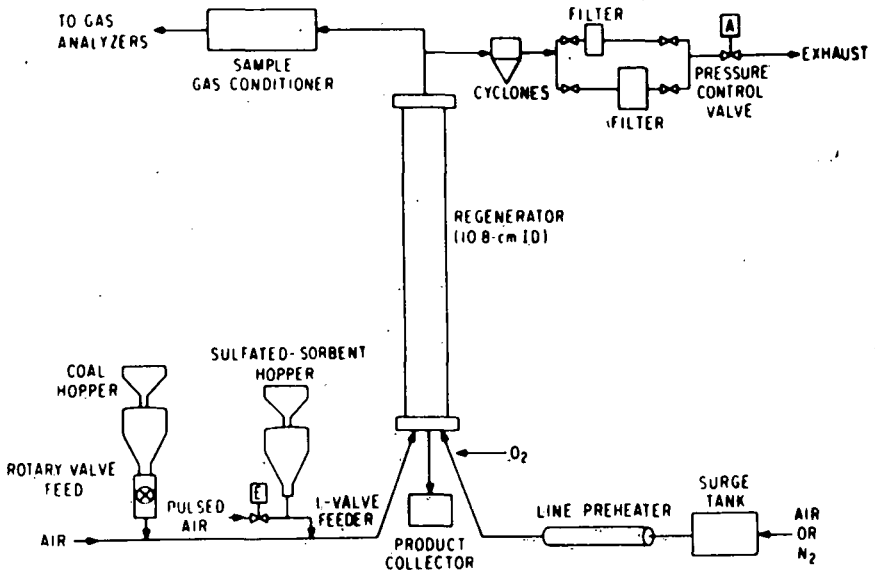

Fig. 2. Experimental Sorbent Regeneration System

b. Procedure

Since the capacity of the PDU-scale regenerator is greater than that of the combustor by about a factor of ten, sorbent cannot be continuously recycled between the reactors. Thus, cyclic sulfation and regeneration experiments were performed batchwise. In the combustion step of the first cycle, virgin limestone (or dolomite) was sulfated for the first time. Following the initial sulfation, the batch of limestone was alternately regenerated and sulfated, without fresh sorbent makeup, for the desired number of complete cycles. Each cycle consisted of a combustion step and a regeneration step.

c. Experimental Program

A listing of the cyclic studies performed and the corresponding nominal experimental conditions is shown in Table 1.

Germany Valley (ANL-9701 limestone) is a high-purity limestone (97.8 wt % $CaCO_3$) which exhibits a relatively low reactivity for sulfation. In TGA sulfation experiments, only 18.7% calcium utilization was achieved when a sample of the limestone was precalcined in 20% CO_2 - 80% N_2 at 900 C and then reacted at 900 C for 3 h in a simulated flue gas containing 0.3% SO_2-5% O_2-balance N_2. From these results, projections for atmospheric fluidized-bed combustion indicated that 1.0 to 1.3 kg of limestone/kg of coal (an excessive quantity) would be required to meet the EPA requirements for this coal. In the cyclic study with Germany Valley limestone, experiments were performed at both high and low combustor pressures.

Table 1. Nominal Experimental Conditions of Cyclic Experiments

	Combustion Step		Regeneration Step	
	Excess Combustion Air: ∿17% Coal: Sewickley SO_2 in off-gas: ∿700 ppm		Pressure: 136 kPa Coal: Sewickley Reducing Gas Conc.: 0.5-1.0%	
Sorbent Material	Combustor Pressure, kPa	Combustor Temperature, °C	Regenerator Temperature, °C	Regenerator Solids Res. Time, min
Germany Valley Limestone	825	900	1100	∿11
Germany Valley Limestone	308	900	1100	∿11
2203 Limestone	825	900	1100	∿11
ANL 8001 (Greer) Limestone	308	850	1050	∿11
ANL (Greer) Limestone	308	850	1050	∿28

Greer limestone (ANL-8001, 80.4% $CaCO_3$) and 2203 limestone (ANL-9601, 96.5% $CaCO_3$) display markedly higher reactivities for sulfation than does Germany Valley. The cyclic study with 2203 limestone was performed at high combustor pressure. The cyclic studies with Greer limestone were conducted at lower regeneration temperature and longer solids residence times than were employed in the previous cyclic study with Greer.[1]

d. Cyclic Studies with Germany Valley Limestone

The nominal experimental conditions that applied to all combustion experiments with Germany Valley limestone (Table 2) were as follows: a bed temperature of 900°C, 3% O_2 in the dry combustion flue gas, Sewickley coal, and an SO_2 concentration of about 700 ppm in the dry flue gas (equivalent to 83% sulfur retention). In each combustion cycle, the limestone feed rate was adjusted to obtain this value of the SO_2 concentration in the flue gas

(about 700 ppm). Thus, the amounts of limestone required to achieve 83% sulfur retention during the combustion cycles reflected changes in reactivity of the limestone over the three cycles.

(1) Combustion Cycle Results

Experiments HP-1, -2, and -3 were performed at high combustor pressure (825 kPa); experiments LP-1, -2, and -3 were conducted at low combustor pressures (308 or 412 kPa). In the high-pressure experiments (HP-1, -2, and -3), the mass ratio of sorbent to coal decreased from about 1.23 in the first combustion cycle to about 1.06 in the third combustion cycle. The low-pressure experiments showed a similar decrease (from 1.24 to 0.98). For either high- or low-pressure operation, limestone consumption on a once-through basis would be unreasonably high. With recycle, however, limestone consumption could be reduced to as little as 20% of that for a once-through system (a reasonable estimate based on previous analysis of cyclic tests). Thus, actual limestone consumption could be reduced to about 0.25 kg of limestone (0.2 times 1.24) per kg of coal.

The first low-pressure cycle (LP-1) with Germany Valley limestone showed that high temperature and high sulfur retention could not be achieved simultaneously (as indicated by the poor sulfur retention and low temperature). At the high sorbent feed rate of uncalcined stone, the thermal burden on the combustor was too great. Any increase in the sorbent feed rate to try to improve sulfur retention decreased the temperature further (this was not observed in the first-cycle experiment with Germany Valley limestone performed at 825-kPa pressure because of the higher volumetric heat-release rate at the higher pressure). Therefore, it could not be determined during the first combustion cycle how pressure affects the performance of Germany Valley limestone.

The sorbent for LP-2 and -3, had been completely calcined as a result of intervening high-temperature regeneration experiments. As a result, the limestone had sufficient reactivity to enable the SO_2 emission limit to be met.

Evaluation of the test data for indicated changes in limestone reactivity over three combustion cycles gives mixed results. Experiments HP-1 through -3 reveal that CaO/S mole ratios in both the second and third combustion cycles were higher than in the first, indicating that the reactivity of the sorbent decreases after the first combustion cycle. On the other hand, it is observed that sorbent utilization in a cycle (last column in Table 2) increased from 8.1% in HP-1 to 9.4% in HP-2 and then decreased in the third combustion cycle. It had been considered possible that an unreactive stone would have this type of response. However, the incremental increase in sorbent utilization to 9.4% for the second combustion cycle is questionable since it is based on an estimate of sorbent utilization in the limestone feed for that combustion experiment.

Table 2. Experimental Conditions and Test Results of Cyclic Combustion Experiments with Germany Valley Limestone

Coal: Sewickley
Sorbent Particle Size: 0.3-2.0 mm (-10 +50 mesh)
Excess Combustion Air: about 17%

Combustion Cycle	Temp., °C	System Pressure, kPa	Fluidizing Gas Velocity, m/s	Feed Rates		Sorbent to Coal Mass Ratio	CaO/S Mole Ratio[a]	SO_2 in Flue Gas, ppm	Sulfur Retention, %[b]/%[c]	Sorbent Utilization		
				Coal, kg/h	Sorbent, kg/h					Feed, %	Product,[d] %	Δ,[e] %
HP-1	900	825	0.77	15.1	18.5	1.23	8.9	700	85.1/72.1	0	8.1	8.1
HP-2	900	825	0.78	12.7	14.1	1.11	10.2	618	87.8/95.9	0.6[f]	10.0	9.4
HP-3	900	825	0.77	12.6	13.4	1.06	9.4	681	86.5/65.8	1.2	8.2	7.0
LP-1	840	308	1.03	7.6	9.4	1.24	8.8	1434	68.6/51.2	0.1	5.9	5.8
LP-2	900	410	1.01	8.8	10.9	1.24	11.7	615	88.6/90.0	0.6	8.3	7.7
LP-3	900	310	1.22	8.3	8.1	0.98	8.6	737	86.9/66.6	0.5	8.2	7.7

[a]Ratio of unsulfated calcium in sorbent feed to sulfur in coal feed.

[b]Based on flue gas analysis: calculated as [(sulfur in coal - sulfur in flue gas)/sulfur in coal] x 100.

[c]Calculated as (sorbent utilization in product - sorbent utilization in feed) x CaO/S ratio. Does not reflect the sulfur retained as unburned sulfur or the possibility that entrained sorbent is more highly utilized than is sorbent product.

[d]Steady-state sample of product overflow from combustor.

[e]Δ equals sorbent utilization of product minus sorbent utilization of feed.

[f]Estimated from analysis of steady-state overflow from first-cycle regeneration experiment.

In experiments LP-1 to -3, evaluation of the test data for changes in limestone reactivity in the three combustion cycles is complicated by the data obtained for the thermally hindered first-cycle run. Ignoring that data, we see that the CaO/S mole ratio decreased from 11.7 in the second cycle to 8.6 in the third cycle, an apparent increase in the reactivity of the sorbent. However, the sorbent utilization over a cycle (or its reactivity) did not increase from cycle 2 to cycle 3 but remained unchanged.

On the basis of the above, it is uncertain whether the reactivity of Germany Valley limestone changes in three utilization cycles at either high or low pressure. It is clear, however, that limestone reactivity did not increase significantly during the first few utilization cycles, which had been postulated to be possible due to heat and calcination effects in the first regeneration cycle.

Attrition losses were extremely low for each of the three combustion experiments performed in either the high- or low-pressure mode. In HP-1, attrition was about 4.5% of the sorbent feed. In HP-2 and -3, attrition of the sorbent feed was only 0.5%. LP-1 and 2 exhibited attrition rates of only 0.7% of the sorbent feed; LP-3 showed only a slight increase to 1.7%.

As is indicated above, the high CaO/S ratio required with Germany Valley limestone to meet the EPA SO_2 emission standard is unreasonably high for once-through operation. The test results indicate that with recycle, the limestone consumption could realistically be reduced to as little as 0.25 kg of limestone/kg of coal. However, the low utilization of the sorbent per cycle (7.0 to 9.4% in HP-1 thru -3; 7.7% in LP-2 and -3) would have adverse economic implications for the regeneration process in terms of regenerator reactor size, SO_2 levels achievable from the regenerator, and the quantity of sorbent that would have to be recycled.

(2) Regeneration Cycle Results

Table 3 describes the experimental conditions and test results of cyclic regeneration experiments with Germany Valley limestone. Data on both cyclic studies are included, i.e., RHP-1 through 3 and RLP-1 through 3, signifying material combusted at 825- and 308-kPa system pressures, respectively.

Regeneration of the sulfated Germany Valley limestone was done in the fluid-bed regenerator (Fig. 2). Sewickley coal was used as both the fuel and the reductant. The sulfur concentration in the sulfated sorbent in both studies was markedly lower than the sulfur content of Tymochtee dolomite or Greer limestone used in the previous ten-cycle studies (this being due to the lower reactivity of Germany Valley limestone). The sulfur concentration in the regenerated product was extremely low so that values for percent regeneration of $CaSO_4$ to CaO were excellent. In RHP-1 through -3, 91 to 93% regeneration was achieved (based on solids analyses); 88% regeneration was obtained for runs RLP-2 and -3. The low result for RLP-1 has less significance since the sulfur concentration of the sulfated sorbent feed was less than what

Table 3. Experimental Conditions and Test Results of Cyclic Regeneration Experiments with Germany Valley Limestone

Coal: Sewickley
Nominal System Pressure: 136 kPa
Sorbent Particle Size: 0.3-2.0 mm (-10 +50 mesh)

Regeneration Cycle	Temp., °C	Sulfur Conc. in Sulfated Sorbent, %	Sulfur Conc. in Regen. Product. %	O_2 Conc. in Feed Gas, %	Fluidizing-Gas Velocity, m/s	Solids Resid. Time, min	Reducing Gas Conc. in Dry Off-Gas, %	Ca as $CaSO_4$, % Feed/Prod.	CaO Regen., %[a]	SO_2 in Off-Gas %[b]/%[a]
RHP-1[c]	1090	2.01	0.29	34.5	1.55	14.4	0.2	6.4/0.6	91	0.5/2.1
RHP-2	1090	4.94	0.58[d]	31.8	1.23	13.4	0.6	12.5/1.2	91	2.2/4.6
RHP-3	1070	3.57	0.28	36.5	1.08	10.3	0.7	8.7/0.6	93	3.8/5.4
RLP-1[e]	1095	0.53	0.29[d]	31.5	1.20	10.9	1.2	1.1/0.6	48	1.8/1.8
RLP-2	1063	4.27	0.58[d]	34.4	1.02	9.3	0.5	9.8/1.2	88	3.0/6.8
RLP-3	1069	3.64	0.51	32.4	1.11	12.7	0.4	8.7/1.0	88	3.8/4.1

[a]Based on chemical analysis of limestone samples.
[b]Readings taken from infrared SO_2 analyzer.
[c]RHP-1 through -3 performed at 825-kPa system pressure during combustion step.
[d]Analysis derived from feed sample of subsequent combustion experiment.
[e]RLP-1 and -3 performed at 308 kPa; LP-2 at 412 kPa during combustion step.

would be desirable to produce an adequate SO_2 concentration in the off-gas (only 1.8% SO_2 was detected in the off-gas during RLP-1). Also, the low regeneration figure is subject to error since the sulfur concentration in the regenerated product (for RLP-1) was derived from analysis of the feed sample of the subsequent combustion experiment.

The final column in Table 3 indicates values of the SO_2 concentration in the off-gas taken directly from an infrared SO_2 analyzer, as well as values based on chemical analyses of limestone samples. For example, in RLP-2, the SO_2 concentration value taken directly from the SO_2 analyzer was 3.0%. This is in contrast to the predicted SO_2 concentration of 6.8% calculated from the 88% regeneration figure obtained by chemical analysis. It can be seen that, in general, the actual SO_2 concentration values are significantly below the calculated values. If the solids analyses were accurate, the SO_2 analyzer was reading low.

The reducing gas concentration used in all runs was low, 0.2-1.2% in the off-gas in comparison to previous cyclic experiments (3% reducing gas in the off-gas). The purpose was to alleviate agglomeration problems encountered at the higher reducing gas concentration. As stated above, excellent CaO regenerations were obtained for RHP-1 through 3 and RLP-2 and 3 despite the lower reducing gas concentrations used.

It has been estimated, using the ANL regenerator design code, that the SO_2 concentration in a "full-size" regenerator off-gas would be 8.3% and 9.9% for stones containing 2% and 5% sulfur, respectively. The average sulfur content for RHP-1 through 3 is 3.5% and would be even less in a continuously operated combustor-regenerator (assuming that pressurized fluidized-bed combustion is desired). Thus, a 7-8% SO_2 off-gas concentration could probably be realized using Germany Valley limestone. However, the solids circulation rate would be two to three times that for Greer limestone, making regeneration of Germany Valley considerably less attractive on an economic basis.

e. Cyclic Studies with Greer Limestone

Results of cyclic combustion/regeneration experiments with Greer limestone are reported here. A lower regeneration temperature (1050°C instead of 1100°C in the previous ten-cycle series of experiments with Greer) and longer regenerator solids residence times (11 min and 28 min vs. 7 min in previous runs) were used in an effort to determine any changes in the reactivity of Greer limestone with changes in these variables. In the earlier ten-cycle study with Greer limestone (1100°C regenerator temperature, 7-min regenerator solids residence time) there was a gradual loss of reactivity of the sorbent for sulfur retention with increasing utilization cycle. Regenerability of the sorbents was unaffected in the ten combustion/regeneration cycles.

(1) Combustion Cycle Results

Results of the present cyclic studies are shown in Table 4. Conditions for the combustion experiments were kept as close as possible to those in the previous ten-cycle study. They were (nominally) a bed temperature

of 850°C, a system pressure of 308 kPa, a fluidizing-gas velocity of 1.0 m/s, 3% O_2 in the flue gas, and the use of Sewickley coal.

As in the cyclic studies with Germany Valley limestone, in each three-cycle study, the limestone feed rate was adjusted to obtain an SO_2 concentration of about 700 ppm (corresponding to 83% sulfur retention, the EPA requirement for Sewickley coal). Thus, changes in the amount of limestone required to achieve 83% sulfur retention would reflect changes in the reactivity of the limestone over the three cycles.

During the combustion step of each cycle, LR-1 through 3 and HR-1 through 3 were performed at the same conditions but during the regeneration step different solids residence times were used (11 min for LR-1 through -3 and 28 min for HR-1 through -3). Thus LR-1 and HR-1 are the same experiment.

In experiments LR-1 through LR-3, the sorbent utilization in a cycle, (i.e., the final column of Table 4) decreased to 19.2% in LR-2 (from 22.7% in LR-1) but increased to 22.0% in LR-3. These observations indicate that there was no overall change in reactivity of the Greer limestone during cycles LR-1 to -3.

The unchanged reactivity is also seen by comparing the CaO/S mole ratios for cycles LR-1 to -3. In LR-2, the CaO/S mole ratio increased to 5.7 (from 4.7 in LR-1), indicating a slight loss of reactivity in the second cycle. The CaO/S mole ratio did not increase further in LR-3, but remained at 5.7, indicating no further change in reactivity. Thus, no significant change in reactivity during cycles LR-1 to -3 is noted by observation of the CaO/S mole ratio.

The results indicate a better performance of Greer limestone in three cycles than in the previous study in which the cyclic sorbent utilization decreased from 30% to 14% in the first three cycles. In addition, attrition losses were low (ranging from 6.0% in LR-1 to 4.3% in LR-3) in comparison to past data (i.e., ranging from 20.0% in the first cycle to 9.2% in the third cycle).

In HR-1 through HR-3, however, a marked decrease in sorbent utilization (over a cycle) was observed. Through the three cycles, the sorbent utilization steadily decreased from 22.7% in HR-1 to 13.7% in HR-3. The CaO/S ratio also steadily increased from 4.7 in HR-1 to 6.2 in HR-3. This decrease in reactivity of the sorbent closely followed the pattern displayed in the first three cycles of the previous ten-cycle series of experiments with Greer limestone.

With the solids residence time (11 min) during the regeneration step of runs LR-1 to -3 relatively close to that in the previous study (7 min), the improved reactivity of the sorbent through the three cycles was apparently an effect of the lower regeneration temperature (1050°C vs. 1100°C in the previous study). At the higher temperature, sintering of the particles in the fluidized-bed regenerator may have contributed to a loss of sorbent reactivity.

Table 4. Experimental Conditions and Test Results of Cyclic Combustion Experiments with Greer Limestone

Coal: Sewickley
Nominal Temperature: 850°C
Nominal Pressure: 308 kPa
O_2 in Flue Gas: 3%
Nominal Fluidizing Gas Velocity: 1.0 m/s
Sorbent Particle Size: -6 +30 mesh
Excess Combustion Air: about 17%

Combustion Cycle	Regenerator Solids Residence Time, min	Feed Rates		Sorbent to Coal Mass Ratio	CaO/S Mole Ratio[a]	SO_2 in Flue Gas, ppm	Sulfur Reten., %[b]/%[c]	Sorbent Utilization		
		Coal, kg/h	Sorbent, kg/h					Feed, %	Product,[d] %	Δ,[e] %
LR-1	11	7.63	7.56	0.99	4.7	710	88.1/94.8	0	22.7	22.7
LR-2	11	7.71	7.80	1.01	5.7	651	89.5/102.4	6.5	25.7	19.2
LR-3	11	7.82	7.71	0.99	5.7	670	89.3/92.2	6.5	28.5	22.0
HR-1	28	7.63	7.56	0.99	4.7	710	88.1/94.8	0	22.7	22.7
HR-2	28	8.16	7.71	0.94	5.6	650	90.1/88.0	1.8	19.1	17.3
HR-3	28	7.86	8.16	1.04	6.2[f]	633	89.9/89.2[f]	1.6[f]	15.3[f]	13.7[f]

[a]Ratio of unsulfated calcium in sorbent feed to sulfur in coal feed.
[b]Based on flue gas analysis: calculated as [(sulfur in coal - sulfur in flue gas)/sulfur in coal] x 100.
[c]Calculated as (sulfur in product sorbent - sulfur in feed sorbent)/sulfur in coal.
[d]Steady-state sample of product overflow from combustor.
[e]Δ equals sorbent utilization of product minus sorbent utilization of feed.
[f]Partly derived from second cycle regeneration overflow analysis (steady-state sample).

In HR-1 to -3, the longer exposure of the particles in the fluidized-bed regenerator (solids residence about 28 min. vs. about 11 min in LR-1 to 3) may also have caused the sorbent particles to sinter, leading to the loss of reactivity discussed above. A more extensive cyclic study of Greer limestone at the lower regenerator temperature (1050°C) and short regenerator solids residence time (7-11 min) is advisable for study of changes in the reactivity of the sorbent beyond three cycles.

(2) Regeneration Cycle Results

As for the regeneration of Germany Valley limestone, Sewickley coal was used as the fuel and reductant in the fluidized-bed regenerator. Regenerator conditions and performance for the present cyclic study with Greer limestone are indicated in Table 5.

As stated, the regeneration temperature (1050°C) was lower than in the previous study (1100°C), and the solids residence times were higher (11 min and 28 min vs. 7 min in the previous study). The reducing gas concentrations were lower, however (1.0% vs. 3.0% used in the past study). The regenerability of the sorbent during cycles RLR-1 to -3 ranged from 64 to 81% (based on chemical analysis of limestone samples). This is higher than would be expected at the solids residence time and temperature used in this study (about 50% regeneration would be predicted). Regeneration of the sorbent during cycles RHR-1 to -3 ranged from 90 to 93%, which is consistent with the expected value of about 90% at 28-min solids residence time and a temperature of 1050°C.

In experiments RLR-1 to -3, the adjusted SO_2 concentrations (based on solids analyses) in the off-gas were low (ranging from 4.2 to 5.8%) in comparison with previous data. This was due to greater dilution of the off-gas, in the present experiments, caused by the higher gas to solids feed ratios (i.e., longer solids residence times at a fixed reactor cross section and bed depth). As in the Germany Valley experiments, the SO_2 concentrations determined with the infrared analyzer were below the values based on chemical analyses (in RLR-1 to -3). This discrepancy was not observed in experiments RHR-1 to -3, but nevertheless the close correlation of CaO regenerability (based on solids analyses) with previous data leads one to be suspicious of the instrumental SO_2 readings.

Attrition and elutriation losses were high during runs RLR-1 to -3, ranging from 4.7% to 29.4% of the sorbent feed. This high figure was obtained in RLR-3 when, it is believed, a high gas velocity blew much of the sorbent feed into the cyclone. Attrition and elutriation losses were lower for runs RHR-1 to -3, ranging from 2.9% to 8.3% of the sorbent feed [but still high in comparison with previous data which showed attrition and elutriation losses no greater than 3% (in any one cycle) in ten regeneration cycles].

f. Cyclic Studies with 2203 Limestone

(1) Combustion Cycle Results

Results of the three-cycle study with 2203 limestone are shown in Table 6. The nominal experimental conditions were the following: a bed

Table 5. Experimental Conditions and Test Results of Cyclic Regeneration Experiments with Greer Limestone

Coal: Sewickley — Nominal System Pressure: 136 kPa
Nominal Temperature: 1050°C — Sorbent Particle Size: 0.6-3.4 mm (-6 +30 mesh)

Regen. Cycle	Solids Resid. Time, min	Sulfur Conc. in Sulfated Sorbent, %	Sulfur Conc. in Regen. Product, %	O_2 Conc. in Feed Gas, %	Fluidizing-Gas Velocity, m/s	Reducing Gas Conc. in Dry Off-Gas, %	Ca as $CaSO_4$, Feed/Prod.	CaO Regen., %[a]	SO_2 in Off-Gas, %[b]/%[a]
RLR-1	10.7	5.23	2.07	30.8	1.28	1.0	16.9/6.0	64	4.0/4.2
RLR-2	10.2	6.63	2.36	28.1	1.28	1.0	23.0/7.6	67	3.2/5.8
RLR-3	11.7	6.24	1.30	33.7	1.51	0.9	23.6/4.5	81	4.1/5.2
RHR-1	28.3	5.23	0.45	22.8	1.25	0.9	16.9/1.2	93	1.6/2.7
RHR-2	28.0	6.08	0.53	28.7	1.38	1.4	19.9/1.6	92	3.2/2.8
RHR-3	32.0	4.70	0.53	22.1	1.24	0.9	15.3/1.5	90	2.4/2.3

[a]Based on chemical analysis of limestone samples.
[b]Readings from infrared SO_2 analyzer.

temperature of 900°C, a system pressure of 825 kPa, a fluidizing-gas velocity of 0.75 m/s, 3% O_2 in the flue gas, and the use of Sewickley coal.

As in previous experiments, the limestone feed rate was adjusted (for each of the combustion cycles) to obtain an SO_2 concentration of about 700 ppm (corresponding to 83% sulfur retention, the EPA requirement for Sewickley coal). Thus, changes in the reactivity of 2203 limestone over the three cycles would be reflected by changes in the amount of limestone required to achieve 83% sulfur retention.

Through three cycles, the sorbent utilization (over a cycle) increased from 20.7% in the first cycle to 23.2% in the third. The CaO/S ratio increased in the second cycle to 4.70 (from 3.36 in the first cycle) but decreased in the third cycle to 3.61. The CaO/S mole ratio and sorbent utilization observed revealed little change in the sorbent reactivity over three cycles.

It was surprising that sorbent utilization (over a cycle) for 2203 limestone was comparable to that for highly reactive Greer limestone (indicating that the reactivity of the two stones is similar) since 2203 limestone is a purer stone than Greer (96.5% $CaCO_3$ vs. 80.4% $CaCO_3$ for Greer). Since poor results were obtained with the very pure Germany Valley limestone (98.7 wt % $CaCO_3$), one would expect that 2203 limestone would be less reactive than Greer limestone. However, the reactivity of 2203 limestone appeared to be quite similar to that of highly reactive Greer.

In addition, elutriation during three cycles for 2203 limestone was quite low (6.6, 2.5, and 3.3% in cycles one, two, and three, respectively). Since no apparent loss of reactivity occurred in three cycles, a more extensive investigation with 2203 limestone (similar in scope to the earlier ten-cycle study with Greer limestone) is suggested to further determine the utility of this stone.

(2) Regeneration Cycle Results

As in the regeneration of the other limestones, Sewickley coal was used as the fuel and reductant in the fluidized-bed regenerator. Regenerator performance for the three-cycle study with 2203 limestone is indicated in Table 7.

Although the nominal temperature planned for each regeneration step was 1100°C, temperatures were actually somewhat lower (from a low of 1073°C in cycle 2 to a high of 1093°C in cycle 3). Lack of sufficient material to run the cyclic combustion-regeneration experiments (particularly after the first regeneration cycle in which elutriation of the feed material was 48.5%) precluded obtaining temperatures in the regeneration step close to the nominal value. Greer data at 1050°C and 1100°C (from different studies) were extrapolated to the temperatures and solids residence times utilized in this study (it being assumed that Greer and 2203 limestone behave similarly) and were compared with the percent CaO regenerations achieved. The latter were as good or better than expected.

Table 6. Experimental Conditions and Test Results of Cyclic Combustion Experiments with 2203 Limestone

Coal: Sewickley
Nominal Temperature: 900°C
Nominal Pressure: 825 kPa
O_2 in Flue Gas: 3%

Nominal Fluidizing Gas Velocity: 0.75 m/s
Sorbent Particle Size: 0.3-2.0 mm (-10 +50 mesh)
Excess Combustion Air: about 17%

Combustion Cycle	Feed Rates: Coal, kg/h	Feed Rates: Sorbent, kg/h	Sorbent to Coal Mass Ratio	CaO/S Mole Ratio[a]	SO_2 in Flue Gas, ppm	Sulfur Retention, %[b]/%[c]	Sorbent Utilization: Feed, %	Sorbent Utilization: Product,[d] %	Sorbent Utilization: Δ,[e] %
1	12.3	7.21	0.59	3.36	553	88.9/69.5	0	20.7	20.7
2	13.3	8.84	0.66	4.70	626	88.3/98.7	3.8	24.8	21.0
3	13.5	8.16	0.60	3.61	628	88.3/84.0	7.0	30.2	23.2

[a]Ratio of unsulfated calcium in sorbent feed to sulfur in coal feed.

[b]Based on flue gas analysis: calculated as [(sulfur in coal - sulfur in flue gas)/sulfur in coal] x 100.

[c]Calculated as (sorbent utilization in product - sorbent utilization in feed) x CaO/S ratio. Does not reflect sulfur retained as unburned sulfur or the possibility that entrained sorbent is more highly utilized than is sorbent product.

[d]Steady-state sample of product overflow from combustor.

[e]Δ equals sorbent utilization of product minus sorbent utilization of feed.

Table 7. Experimental Conditions and Test Results of Cyclic Regeneration Experiments with 2203 Limestone

Coal: Sewickley
Nominal System Pressure: 136 kPa
Sorbent Particle Size: 0.3-2.0 mm (-10 +50 mesh)

Regenerator Cycle	Temperature, °C	Sulfur Conc. in Sulfated Sorbent, %	Sulfur Conc. in Regen. Product, %	O_2 Conc. in Feed Gas, %	Fluidizing-Gas Velocity, m/s	Solids Resid. Time, min	Reducing Gas Conc. in Dry-Off-Gas, %	Ca as $CaSO_4$, % Feed/Prod.	CaO Regen., %[a]	SO_2 in Off-Gas, %[b]/%[a]
1	1088	6.32	1.53[c]	43.1	1.03	10.4	1.2	22.1/3.8	82.7	3.5/7.8
2	1073	6.53	2.43[c]	34.9	1.04	11.3	0.5	20.8/6.9	66.7	6.0/6.1
3	1093	7.60	1.10	36.4	1.35	10.4	0.6	26.0/3.7	85.7	6.1/7.7

[a]Based on chemical analysis of limestone samples.

[b]Readings from infrared SO_2 analyzer.

[c]Analysis derived from feed sample of subsequent combustion experiment.

Once again, reducing gas concentrations were kept low in these studies (0.5-1.2%). The problem of inaccurate readings of the infrared SO_2 analyzer was still evident in these studies, as shown in the last column in Table 7 (i.e., the actual SO_2 concentration readings were somewhat lower than values based on chemical analysis of limestone samples). As previously stated, attrition and elutriation losses were high (48.5% of sorbent feed in the first cycle, 8.4% in the second cycle, no data are available for the third cycle).

TASK B. ALTERNATIVE REGENERATION PROCESS DEVELOPMENT

1. Sulfur Recovery Process Studies
(D. S. Moulton and W. M. Swift)

a. Introduction

The spent lime sorbent from a fluidized-bed combustor can be regenerated and reused. In the regeneration process, the sulfur is removed as a concentrated stream of gaseous sulfur dioxide which must be converted to a form posing no environmental hazard. Elemental sulfur at room temperature is a solid, nearly inert, and easily stored and transported. Because of these properties, studies were made of processes which could utilize the sulfur dioxide in the regenerator off-gas to make elemental sulfur.

Many processes for producing sulfur from SO_2 have been described, but most of them are not readily applicable to the fluidized-bed combustor system. In fluidized-bed combustion, lime is used as the sulfur-concentrating agent, whereas in a number of processes, other sulfur-concentrating agents are used which could not withstand combustion. Also, some processes use reductants other than coal, such as natural gas, for converting the SO_2 to elemental sulfur. However, since coal is available for use in the combustor, it is the preferred reductant.

If a bituminous or lower rank coal is used directly as the reductant, there will be two major problems:

1. The swelling and caking properties of many coals result in the reactor becoming plugged.

2. Volatile materials which are driven out of the coal when it is heated, later condense with the sulfur to produce an impure product.

These problems can be avoided by gasifying the coal and using the coal gasifier effluent as the reductant for converting SO_2 to elemental sulfur. Fig. 3 shows the general processing scheme applicable to the fluidized-bed combustor system. There is much information in the literature on processes which would fit into this processing scheme.

In addition to the literature review, some thermodynamic calculations were made and experimental work was done. The thermodynamics of the processing steps indicated in Fig. 3 were investigated to see if there are conditions allowing simplification of the overall process.

The experimental work was done to investigate the conversion of SO_2 to elemental sulfur, using both coal and ash as the chemical reducing agent. The experimental objectives were:

(1) To find a processing method which would yield a high-quality sulfur product by the use of only materials available at the combustor or sorbent regenerator;

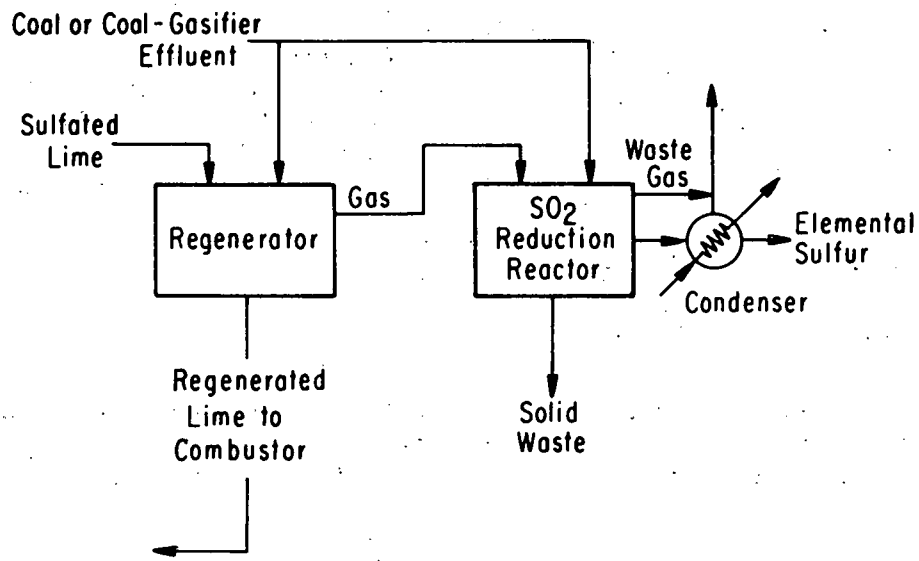

Fig. 3. Schematic of a General Form of Processing to Regenerate Sorbent and Produce Sulfur

(2) To demonstrate in laboratory-scale operation of the process that there are no problems precluding further scaleup, such as a large pressure drop in the SO_2 stream;

(3) To make preliminary measurements of the process kinetics; and

(4) To make recommendations for experimental work in support of further process development.

b. Literature Survey

(1) SO_2 Reduction Using Anthracite Coal

Reduction with anthracite coal has recently been developed as part of the Bergbau-Forschung/Foster-Wheeler process. A stream containing SO_2 and steam enters the bottom of a coal bed at 600-650°C[2] and cools as it flows upward. About 90% of the SO_2 is reduced to elemental sulfur, which is carried out in the effluent gas stream along with minor amounts of H_2S, COS, and CS_2. Some of the SO_2 is not reacted.[2,3]

Operating parameters control the product composition. As shown in Fig. 4, overall conversion of SO_2 increases with increasing steam content;[4] however, more hydrogen sulfide is formed. Under conditions which yield maximum sulfur production, the kinetics are poor. With increasing temperature, the kinetics improve markedly, but hydrogen sulfide then becomes the principal product. For conditions used in sulfur production,[5] the gas residence time is 3-8 s, and the coal residence time is 12 to 20 h.

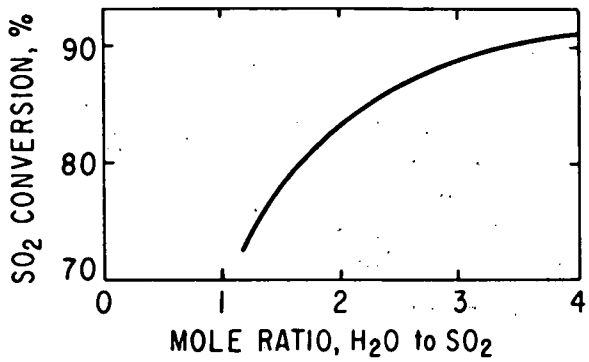

Fig. 4.

Relationship between (1) Sulfur Dioxide Conversion to Sulfur and (2) the Water to Sulfur Dioxide Ratio. All other parameters are constant. After Steiner[4]

Foster-Wheeler claims that the carbon reduction reactions are synergistic--that is, the reaction rate of the coal with both SO_2 and steam is greater than the sum of the individual rates for reactions 1 and 2.

$$C + SO_2 = CO_2 + 1/2\ S_2 \quad (1)$$

$$C + H_2O = CO + H_2 \quad (2)$$

Products of reaction 2 may be intermediates for increased SO_2 reduction, as in 3 and 4:

$$2CO + SO_2 = 1/2\ S_2 + 2CO_2 \quad (3)$$

$$2H_2 + SO_2 = 1/2\ S_2 + 2H_2O \quad (4)$$

Also, both steam and carbon dioxide are used in treating coal to form activated carbon, which has a greatly increased internal surface area and consequently much higher reactivity. Either the formation of reactive intermediates or the formation of activated carbon could explain the synergistic effect.

Foster-Wheeler uses a 2 to 1 steam to SO_2 ratio, but this high a ratio may be largely due to water originating in their upstream adsorption process[5] rather than a choice based on kinetic considerations.

Anthracite coal is used for the reduction, avoiding the problems found with lower rank coals; in addition, the anthracite coal or coal ash may possess a catalytic effect. Coals lower in rank than anthracite can be used if they are devolatilized first.[5,6]

(2) Coal Gasification

The reducing gas available from a coal gasifier presents an alternative to the use of either anthracite or coke. Several coal gasification processes are either commercially available or under intensive development. Generally, steam is fed to a gasifier along with air or oxygen, and reaction

heat is supplied by partial combustion. The effluent gas contains hydrogen carbon monoxide, methane, and minor amounts of oil and tars,[7,8] which can be removed between the gasifier and the SO_2 reduction reactor. Under suitable conditions, as discussed above, SO_2 can react with coal to produce hydrogen sulfide, and so H_2S is also a potential reductant. Hydrogen sulfide and other reducing gases from coal gasification were used in the Boliden process once commercialized in Sweden.[9] The reducing gas is supplied with the SO_2 to a catalytic reactor containing active, high-surface-area catalysts.

In addition to reactions 3 and 4, the following reactions are of interest:

$$CH_4 + 2SO_2 = 2H_2O + CO_2 + S_2 \quad (5)$$

$$2H_2S + SO_2 = 2H_2O + 3/2S_2 \quad (6)$$

Other reactions occur, forming small amounts of undesirable products:

$$H_2 + 1/2S_2 = H_2S \quad (7)$$

$$H_2O + 1/4S_2 = H_2 + 1/2\ SO_2 \quad (8)$$

$$CO + 1/2S_2 = COS \quad (9)$$

$$CO_2 + 2H_2S = CS_2 + 2H_2O \quad (10)$$

$$2CO + S_2 = CS_2 + CO_2 \quad (11)$$

$$CO_2 + H_2S = COS + H_2O \quad (12)$$

$$2CO_2 + 3S = SO_2 + 2COS \quad (13)$$

$$H_2S + (x-1)S = H_2S_x \quad (14)$$

d. Characteristics of SO_2 Reduction Catalysts

High-iron bauxites are the traditional catalysts for Claus processes (Reaction 6). They are also effective for other SO_2 reduction reactions. A number of other metals are active but have not had much commercial use. Under reaction conditions, the iron or other metal becomes sulfided, and the metal sulfide is the main catalytic agent.

Chowdhury and Datta[10] obtained evidence that the alumina also contributes to the catalytic activity. Alumina is well known as an attrition-resistant high-surface-area catalyst support. Haas et al.[11] showed that the activity could not be due to its surface area alone and found that there was a sharply defined iron to alumina ratio for maximum activity, (Fig. 5). The optimum composition was especially effective for dilute reactant streams. This implies that alumina is a calalyst for SO_2 reduction.

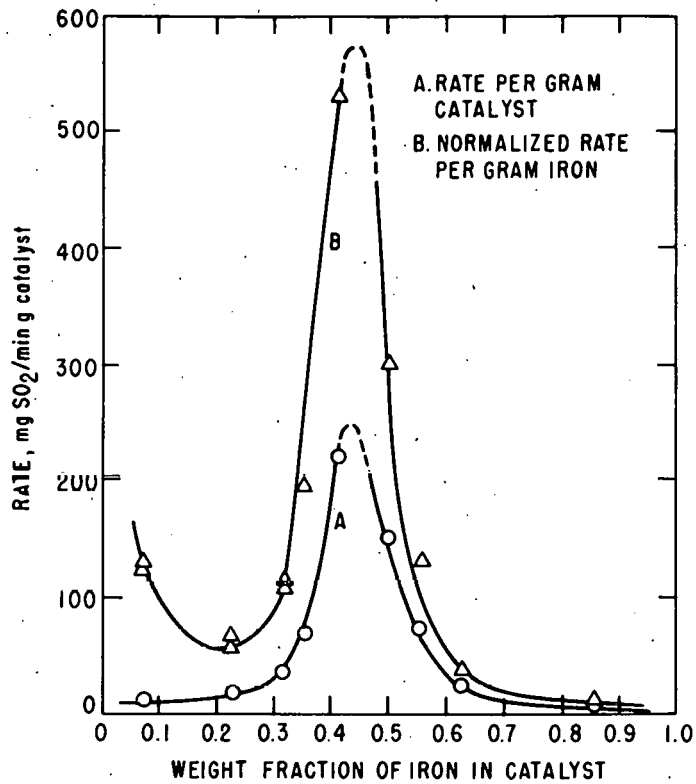

Fig. 5. Carbon Monoxide Reduction of SO_2. Dependence of SO_2 removal rate at 500°C on iron-alumina catalyst composition. From Haas et al.[11]

George[12] showed that the Claus reaction is catalyzed by bases in the activity order, Li > Na > K. It has been well established by Peri[13,14] that the dehydrated gamma alumina surface has exposed oxide ions which are strong base sites. These interact with the SO_2, which is a Lewis acid. Chang[15] in an IR study of adsorbed SO_2 found strong evidence that on alumina, the SO_2 is adsorbed on oxide ions, forming SO_3^{2-} species.

In summary, to possess maximum activity, a SO_2 reduction catalyst should contain a metal sulfide, commonly iron sulfide, and material which is chemically a strong base, and these should be present in an optimum ratio.

(4) Reduction with Constituents of a Coal Gasifier Effluent

Reduction with Hydrogen. Lepsoe,[16] in 1938, presented a comprehensive thermodynamic treatment for reactions 3 through 11 with equilibrium constants for stoichiometric conditions. Doumani et al.[17] also published thermodynamic data on hydrogen reduction of SO_2 and described a process. A more recent analysis by Murdock and Atwood[18] included sulfur species not treated in earlier work. Their results, with Lepsoe's are shown in Fig. 6.

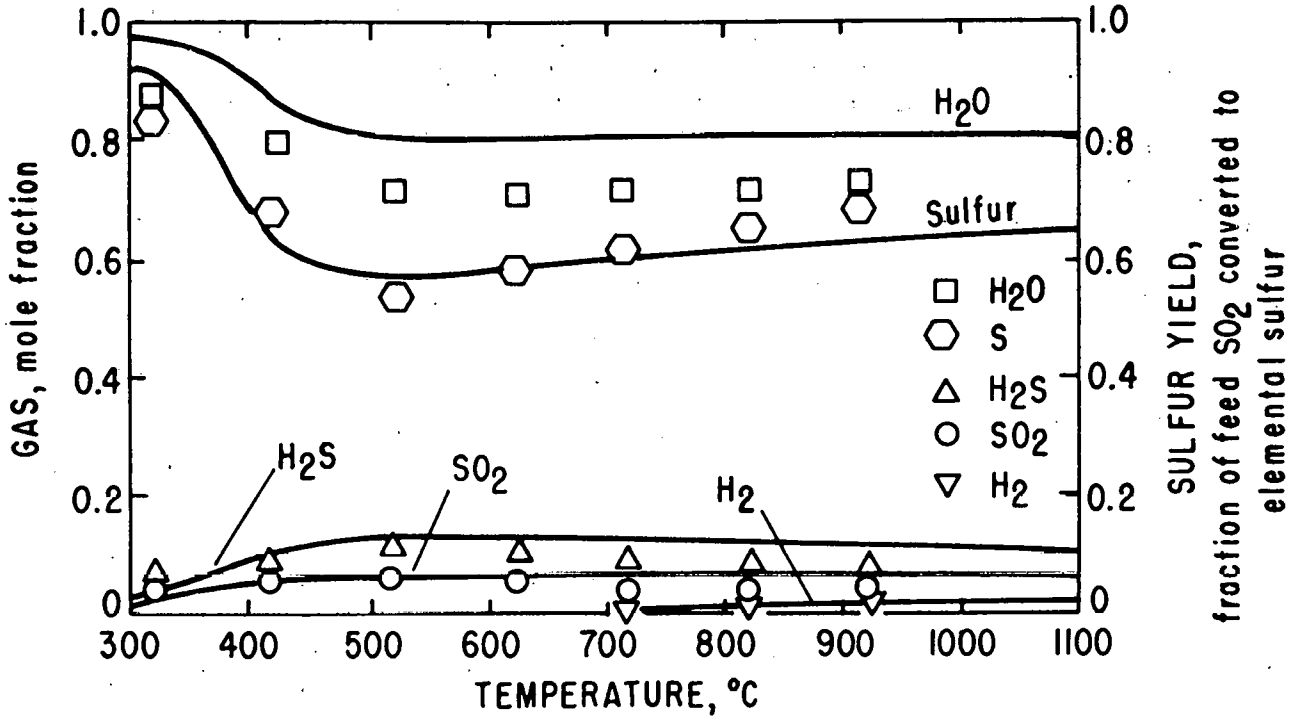

Fig. 6. Equilibrium Gas Compositions for the Reduction of SO_2 with Hydrogen at 1 atm. Symbols (calculated)--Murdock and Atwood; Curves--Lepsoe.[16] Reprinted with permission from Ind. Eng. Chem. Process Des. Dev. 13(3), 254 (1974). Copyright by the American Chemical Society.

Murdock and Atwood[18] also published kinetic data for reduction with hydrogen using an activated bauxite catalyst at 345-390°C. They obtained the following rate expression:

$$r_{s_1} = 1/2\ k_{H_2}\ P_{H_2} - k_{H_2S}(P_{H_2})^{3/2}(P_{SO_2})^{-1/2}$$

where r_{s_1} is the rate of sulfur production in mol (g of cat.)$^{-1}$ h^{-1}

$$k_{H_2} = 4800 \frac{\text{mol}}{(\text{g of cat.})\cdot\text{h}\cdot\text{atm}} \exp - \frac{16.3\ \text{kcal/mol K}}{RT}$$

and $$K_{H_2S} = 1.5 \times 10^8 \frac{\text{mol}}{(\text{g of cat.})\cdot\text{h}\cdot\text{atm}} \exp - \frac{34.3\ \text{kcal/mol K}}{RT}$$

For large values of space time, a more accurate but much more complex expression was obtained by Hsieh and Atwood.[19]

Reduction with Carbon Monoxide. In addition to Lepsoe's work,[16] others[17,20] have published thermodynamic data for reactions 3 and 9. Maadah and Maddox[21] and Kerr[22] give the equilibrium amounts of CO and COS from a Claus plant as a function of H_2S purity. Water hydrolyzes the toxic COS, reaction 12, but makes the thermodynamics less favorable. Okay and Short[23] give equilibrium compositions of COS for dilute conditions with and without water (Fig. 7).

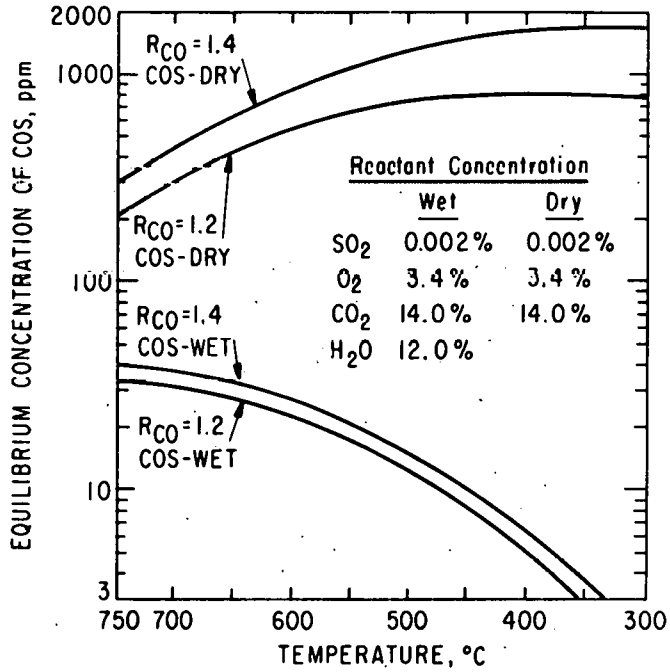

Fig. 7. Equilibrium Concentration of COS with and without Water in the Reaction System.

$$R_{CO} = (P_{CO} - P_{O_2})/2P_{O_2}$$

After Okay and Short.[23] Reprinted (as revised) with permission from Ind. Eng. Chem. Process Des. Dev. 12(3), 291 (1973). Copyright by the American Chemical Society.

Rate data are available for several catalysts used for reduction with carbon monoxide. Haas et al.[11] published rate data for several compositions of iron/alumina catalyst, as shown in Fig. 8 in which the space-time is the catalyst weight divided by the SO_2 mass feed rate. The feed contained 5% SO_2 and 10% CO. Okay and Short[23] and Wynn[24] obtained kinetic data for alumina catalysts with dilute SO_2 feeds, and Ryason and Harkins[25] obtained kinetic data with copper, silver, palladium, manganese, and nickel catalysts; they concluded that copper is the best.

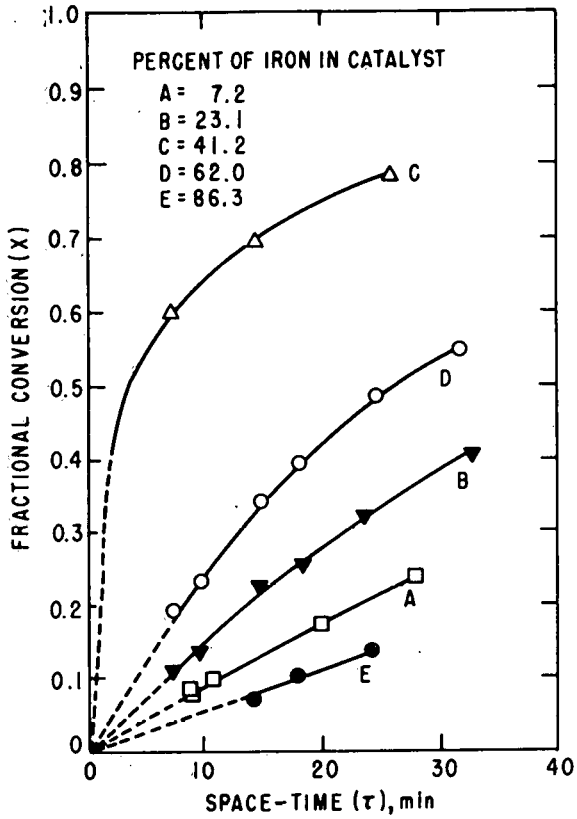

Fig. 8. Carbon Monoxide (10% CO, 5% SO_2) Reduction of SO_2. Rate data from various iron/alumina catalyst compositions. From Haas et al.[11]

Catalytic selectivity is a kinetic effect. A conventional bauxite catalyst has little effect on the hydrolysis of carbonyl sulfide, reaction 12. Consequently, excess COS in the feed tends to pass through a Claus reactor, polluting the effluent.[18,26] Cobalt molybdate catalysts are effective for COS hydrolysis and are used commercially in the first stage of Claus sulfur plants when the feed has a high COS content. George[26] published kinetic data on the hydrolysis of COS over cobalt molybdate, and Bazes et al.[27] published kinetic data on the SO_2 reduction reaction with CO, and found that the rate was controlled by pore diffusion with a variety of cobalt molybdate catalysts.

When the feed has a low COS content, it is desirable to use a catalyst on which the reduction reaction is much faster than the COS-forming reactions and so cobalt molybdate is not used. Haas and Khalafalla[28] found evidence that COS is a reactive intermediate when the iron/alumina catalyst is used. Happel et al.[29] noted that the metallic sulfides participated in COS production and looked for catalytic activity among metals which form especially stable oxides. Lanthanum oxide-titanium oxide compositions have the desired properties and catalyze SO_2 reduction at a higher rate than they

catalyze COS formation. Kundrath[30] has also published kinetic data on this system. It should be noted that the present commercial method of minimizing COS production is to operate with a slight excess of SO_2 in the feed. Water hydrolyzes COS, but it is rarely added in commercial operations because water lowers the activity of conventional catalysts.[23,31]

Reduction with Methane. Methane is a significant product from many coal gasifiers, and the reducing reactor should be capable of utilizing it. Helstrom and Atwood[35] found that CH_4 and SO_2 react on bauxite in the 500-600°C temperature range and obtained the following rate equation:

$$r_{CH_4} = \frac{P_{CH_4}\ B_1\ \exp(B_3/T)}{[1 + P_{SO_2}\ B_2\ \exp(B_4/T)]^n}$$

where r_{CH_4} is the rate of methane consumption, L/(kg of catalyst) (min); partial pressures, P, are in atmospheres. The parameter n is equal to 1 or 2, the number of sites assumed to be occupied by an adsorbed methane molecule. The following two sets of parameters are equally good kinetic predictors:

	Model	
Parameter	Single Site	Dual Site
n	1	2
B_1	4.49×10^3	2.2×10^4
B_2	6.85×10^{-4}	3.13×10^{-3}
B_3	-6.19×10^3	-7.85×10^3
B_4	1.15×10^4	8.85×10^3

Reduction with Hydrogen Sulfide. Lepsoe[16] and Doumani et al.[17] included H_2S in their thermodynamic work. Other authors[20-22,33] have made computer studies of extensive lists of reactions and have successfully predicted Claus plant product mixtures.

Kerr et al.[34] presented kinetic data for both bauxite and activated alumina catalysts. At about 235°C and with other conditions approximating industrial practice, the following expression was obtained for 2-4 mesh bauxite:

$$\frac{d[H_2S]}{dx} = \frac{24148}{v_a} \exp(-2526/T) \left\{ -[H_2S][SO_2] + \frac{[H_2S]_e\ [SO_2]_e\ [H_2O]\ [S_n]}{[H_2O]_e\ [S_n]_e} \right\}$$

where v_a is the the apparent linear gas velocity in cm/s, x is the distance into the catalyst bed, the brackets indicate fractional molar concentrations, and the subscript e refers to equilibrium values. For activated alumina, the pre-exponential term is about twice as high as for bauxite. George[26] has published kinetic data for the cobalt molybdate catalyst.

It appears that all reducing constituents of a coal gasifier effluent can be utilized. Reduction with H_2S is probably the most easily catalyzed reaction, and reduction with methane is the most difficult to catalyze. Bauxite and probably other catalysts are effective for all of the major coal gas constituents, although a higher temperature may be required to utilize methane than for the other gases.[9,32]

(5) Catalytic Properties of Coal Ash

In the absence of an expensive clean-up step, the coal gas may carry some ash into the catalyst bed. If the ash should block the catalyst pores or cause a large pressure drop, it would be unacceptable. However, the coal ash may have some desirable catalytic properties. Hendrickson[35] gives the following average analysis of U.S. coal ash determined by the Bureau of Mines. Silica has little catalytic value, but the alumina and iron oxide are

Compound	%
SiO_2	45.7
Al_2O_3	26.0
Fe_2O_3	18.1

important. In addition, bases such as calcium, magnesium, sodium, and potassium oxides (which are prominent ash constituents) have catalytic value. Kaakinen et al.[36] reported the compositions of ashes collected at various points in a power plant. Aluminum and iron concentrations showed little variation, although trace elements varied considerably. From coal mine to coal mine, ash compositions are extremely variable, but it seems likely that some ash compositions have catalytic value.

Measurements show that coal ash has a low surface area. Cabrera and Gray[37] found surface areas of only about 5 m^2/g, and when the residual carbon was oxidized, the remaining area was only 0.1 to 1.0 m^2/g. Combustion probably sinters the structure. Conventional alumina catalysts are available with 200-400 m^2/g surface area, and bauxite also has a high surface area. A reactor using ash for the catalyst would have to be larger than one using a conventional catalyst, but the ash is available at no cost. Catalyst deactivation would not be a problem because deactivated catalyst could be discarded. Furthermore, because of the sintering effect of combustion, ash produced in lower temperature processes such as fluidized-bed combustion may have a larger surface area. In this connection, Beckman[38] reported that incompletely consumed anthracite coal from the Foster-Wheeler SO_2 reduction reactor had good adsorption properties, indicative of a high surface area.

(6) Reduction with Coke

Foster-Wheeler states that coke can be used in lieu of anthracite coal. This method has been used in Europe for a very long time. Lepsoe[16] discussed the thermodynamics of SO_2 reduction with coke.

Cokes vary greatly in reactivity, with nonmetallurgical cokes generally better.[39] Lepsoe[16] investigated the kinetics for a particular type of metallurgical coke. One difficulty is an accurate assessment of the kinetic effect of coke surface area while the coke is being consumed. Macak and Pick[40] developed a model to predict the reactive surface area during coke consumption and performed several kinetic investigations. Spectrally pure carbon and three cokes of differing ash content were investigated. Reactivity increased with increasing ash content (Fig. 9). In addition, they investigated the effects of individual ash constituents in "synthetic" cokes; each such coke contained only one ash constituent. Each synthetic coke was made by mixing a powdered metal oxide, powdered low-ash coke, and pitch, and then carbonizing the mixture. Ash constituents were categorized in three groups according to how each affected the reactivity of coke for SO_2 reduction:

Group 1. The reaction rate was constant and all of the carbon was consumed. Activation energies are 40.9 kcal/mol for coke containing Fe_2O_3, and 58.2 kcal/mol for coke containing CaO.

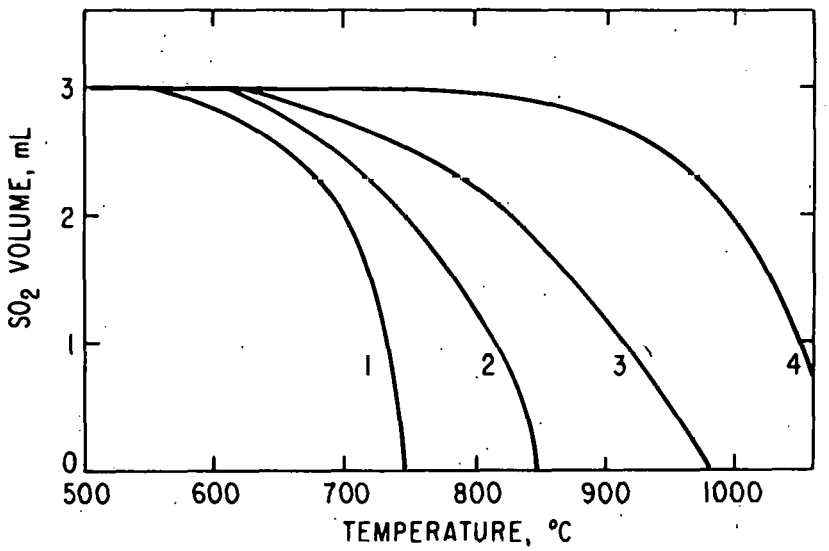

Fig. 9. Reactivity of Prepared Carboniferous Materials (in terms of mL of unconverted SO_2 remaining from a 3-mL dose). 1 - metallurgical coke, 14.3% ash; 2 - 'Stampfmasse', 7.9% ash; 3 - petroleum coke, ('Pechkoks'), 0.5% ash; 4 - Spectrally pure carbon, 0.0006% ash. Specific surface area ranged from 0.7 m^2/g ('Stampfmasse') to 1.3 m^2/g (spectrally pure carbon). After Macak and Pick.[40]

Group 2. The reaction rate fell rapidly in the first part of the runs, then became constant until the carbon was consumed. The activation energy was 71.6 kcal/mol K for MgO.

Group 3. The reaction rate fell rapidly to zero, and the remaining coke was not consumed. Activation energies could not be measured. The group included petroleum coke, control samples with no added model ash constituent, and cokes containing Al_2O_3 and SiO_2.

The results were explained in terms of a carbon-deactivating or passivating reaction. This results from a direct chemical interaction of SO_2 with the carbon:

$$SO_2 + C = \text{passivated carbon} \qquad r_1$$

The reaction suggested for sulfur production is a two-step reaction, with the SO_2 first reacting with the metal oxide:

$$SO_2 + MO = \text{Intermediate} \qquad r_2$$

$$\text{Intermediate} + C = CO_2 + 1/2\ S_2 + MO \qquad r_3$$

The kinetic results of the different ash constituent groups are consistent with the following rate relationships:

Group 1: minimum r_2, $r_3 >> r_1$

Group 2: minimum r_2, $r_3 \approx r_1$

Group 3: r_2 or $r_3 = 0$

In general, the results of this study agree with the results of the catalysis studies cited earlier. Of the substances found to enhance coke reactivity when incorporated into coke, iron is a well-known SO_2 reduction catalyst; calcium and magnesium are expected to have reduction catalytic activity because of their basicity.

(7) Sulfur Condensation

The kinds of processes considered here produce sulfur in the gas phase from which the sulfur is later condensed: The peculiar physical properties of sulfur complicate condensation and recovery. Sulfur vapor is composed largely of S_2 molecules only at fairly high temperatures and low system vapor pressure (Fig. 10).[41] Near the condensation point, sulfur vapor consists of S_8 rings. This causes sulfur to have an unusual equilibrium vapor pressure curve. Meyer[41] gives equilibrium vapor pressures (Table 8). Mist can form in the condenser, but Sawyer et al.[42] report that the loss could

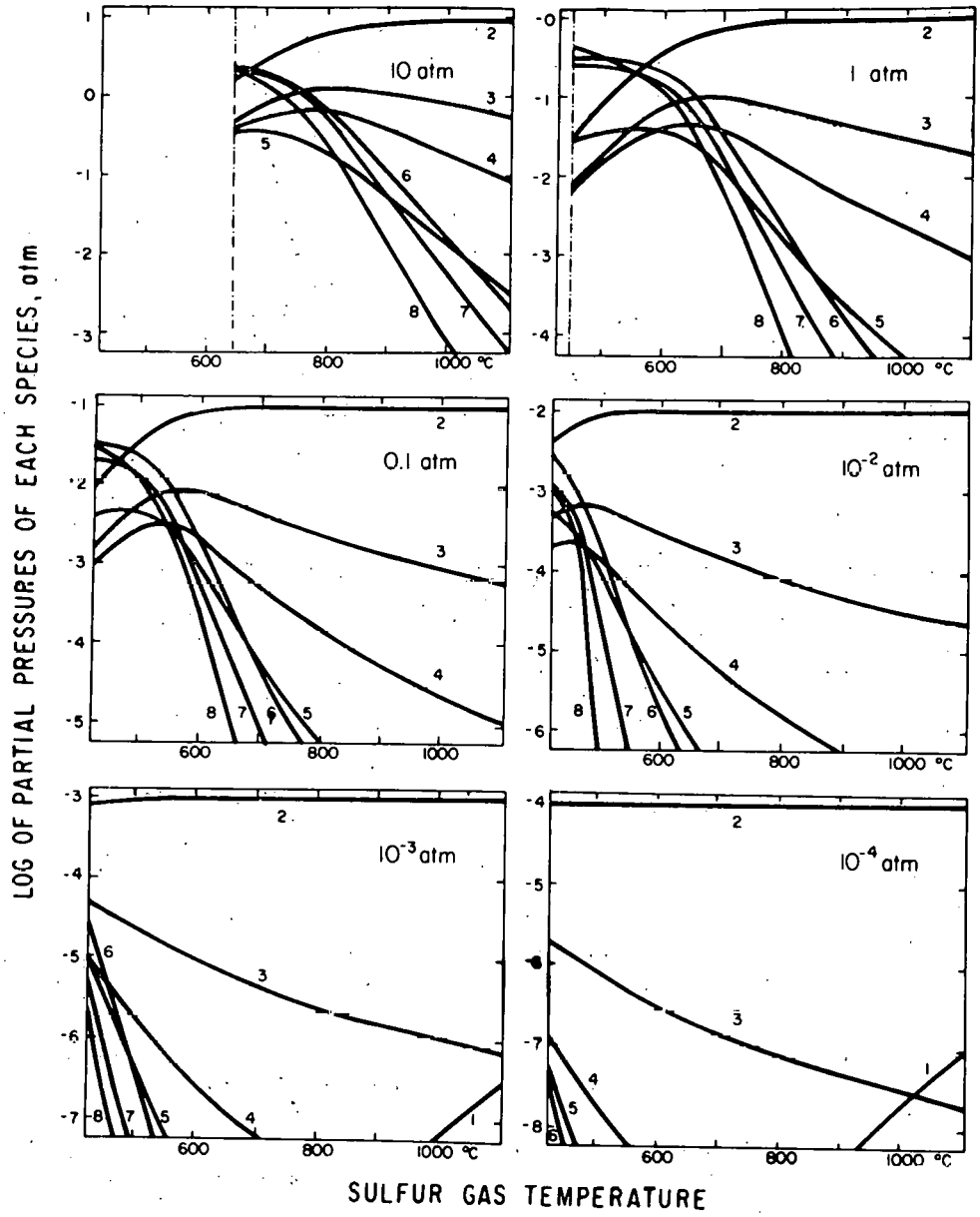

Fig. 10. Partial Pressures of Sulfur Species at Six Pressures (after Rau, 1976). From Meyer.[41] Each number on a curve refers to the number of sulfur atoms per molecule. At the upper right of each graph is the system vapor pressure in atmospheres.

be held to less than 0.1% by condensing just above the melting point and using a mist separator. The melting points of most sulfur allotropes lie between 108 and 130°C. However, the liquid sulfur has a viscosity maximum of 93,000 cP at 187°C. For this reason, sulfur processors avoid temperatures between 170°C and 230°C.[32] The vapor pressure increases sharply above 230°C, and so careful temperature control is also necessary for collection at 230°C.

Table 8. Equilibrium Vapor Pressures of Elemental Sulfur at Various Temperatures[41]

P,[a] torr	T, °C	P,[b] atm	T, °C
10^{-5}	39.0	1	444.61
10^{-4}	58.8	2	495
10^{-3}	81.1	5	574
10^{-2}	106.9	10	644
10^{-1}	141	20	721
1	186	40	800
10	244.9	50	833
100	328	100	936
760	444.61	200	1035

[a] 1 torr = 133.3 Pa

[b] 1 atm = 101.325 kPa

c. Thermodynamics for Combined Regeneration and Sulfur Production

Following the literature review, some thermodynamic parameters were checked to see if the number of required processing steps indicated in Fig. 3 could be reduced.

The calculations were made using a NASA computer program which predicts an equilibrium product distribution by minimizing the free energy. The input represented a hypothetical regeneration scheme in which spent lime sorbent and coal would be put into a reactor, and regenerated sorbent and a gas stream containing elemental sulfur would come out. A hydrogen to carbon ratio of 0.83 (the value for Sewickley coal) was used, and it was assumed that the sulfated lime contained enough $CaCO_3$ to maintain the equilibrium vapor pressure of CO_2. Several values of total system pressure were tried, as well as variations from the stoichiometric ratio of reductant to calcium sulfate. The best obtainable mole fractions of S_2 are listed in Table 9, for a total system pressure of 5 atm (500 kPa) and the stoichiometric ratio of reductant to calcium sulfate.

Since the gas from a reactor for simultaneous regeneration and sulfur production would contain SO_2 and reductants in addition to elemental sulfur, it is interesting to calculate how much additional sulfur could be recovered from the SO_2 in the effluent. It would be partially cooled, then allowed to react catalytically before entering a sulfur condenser. The equilibrium gas composition at 950°C (Table 9) would contain SO_2 and the reductants H_2S, CO, and H_2 in almost the stoichiometric relationship. The same computer program was applied to the 950°C gas mixture at 5 atm, with the results shown in Table 10. The sulfur content would still be very low because with so much water in the mix, the SO_2 would convert to H_2S.

Table 9. Thermodynamic Equilibrium Mole Fractions in the Gas Phase for Direct Reduction of Sulfated Lime with Sewickley Coal. Total system pressure, 5 atm.

Temp, °C	CO_2	CO	H_2	H_2O	H_2S	SO_2	S_2
900	0.14	0.0015	0.0072	0.85	0.0013	0.0019	0.000009
950	0.28	0.0037	0.0063	0.70	0.0015	0.0052	0.000028
1000	0.54	0.0085	0.0042	0.43	0.0011	0.0134	0.000080
1050	0.74	0.0139	0.0022	0.21	0.0007	0.0318	0.000214

Table 10. Thermodynamic Equilibrium Mole Fractions in the Gas Phase for a Regenerator Off-Gas. Total system pressure, 5 atm.

Temp, °C	CO_2	CO	H_2	H_2S	H_2O	SO_2	S_2
950	0.28	0.0037	0.0063	0.0015	0.70	0.0052	0.00003
900	0.28	0.0027	0.0054	0.0021	0.70	0.0046	0.00004
850	0.28	0.0019	0.0044	0.0027	0.70	0.0040	0.00004
800	0.28	0.0012	0.0034	0.0032	0.71	0.0035	0.00004
750	0.28	0.0008	0.0025	0.0037	0.71	0.0030	0.00003
650	0.28	0.0002	0.0011	0.0044	0.71	0.0024	0.00003

To calculate whether different solids compositions would yield significantly better results, the compositions of Occidental Research char and of a hypothetical low-hydrogen coke were studied, using the same computer program and a variety of temperatures and pressures. The results showed that only a very slight improvement in gas stream sulfur content could be expected as a result of different solid compositions. The stability of CaS is much greater than the stability of CaO, and so any system containing CaO and sulfur will have a low equilibrium pressure of sulfur and sulfur-containing species.

Comparing Tables 9 and 10 with Table 8 shows that some of the sulfur formed could be condensed out by cooling the gas. However, since the amounts condensed out would be small, a gas recycle system would be necessary to desulfurize a large amount of lime. Unfortunately, maintaining the temperature difference between reaction temperature (900-1100°C) and sulfur condensation temperature (about 130°C) would be costly, and only a small fraction would be condensed out of the gas stream. There seems to be no evidence that elemental sulfur is an intermediate in the reduction of calcium sulfate to calcium sulfide, and so it does not appear likely that sulfur could be produced in a non-equilibrium reactor.

d. Experimental

The first objective of the experimental work was to produce high-quality sulfur, using materials available at the combustor or sorbent regenerator. Two chemical reducing agents are readily available, (1) coal and (2) carbon contained in the ash from the combustor. Because the ash is a fine powder, it would cause a large pressure drop in the SO_2 stream, and experiments were performed to see whether a large pressure drop could be avoided by pelletization of the ash. Ash or ash-coal mixtures were used as the chemical reducing agent in a series of experiments to relate the sulfur purity to the composition of the reducing agent. Also, the relative carbon reactivity and the SO_2 conversion kinetics were measured in a small laboratory differential reactor.

(1) Equipment and Materials

Several types of laboratory equipment were used in the tests. Pelletization was attempted in a small Stokes Pennwalt model 511-6 laboratory pelletizer and in a hydraulic press. The SO_2 reactor consisted of a quartz U-tube which held a fixed bed of the reducing agent. The feed stream containing sulfur dioxide flowed through the reactor, then into a condenser for the removal of elemental sulfur. A gas chromatograph inlet port was located downstream from the sulfur condenser, and a bypass line allowed sampling of the feed stream, as shown in Fig. 11. The gas chromatograph was a Varian model 1420 for which operating conditions are given in Table 11. An HP 3373 integrator was used to measure the chromatogram peak areas.

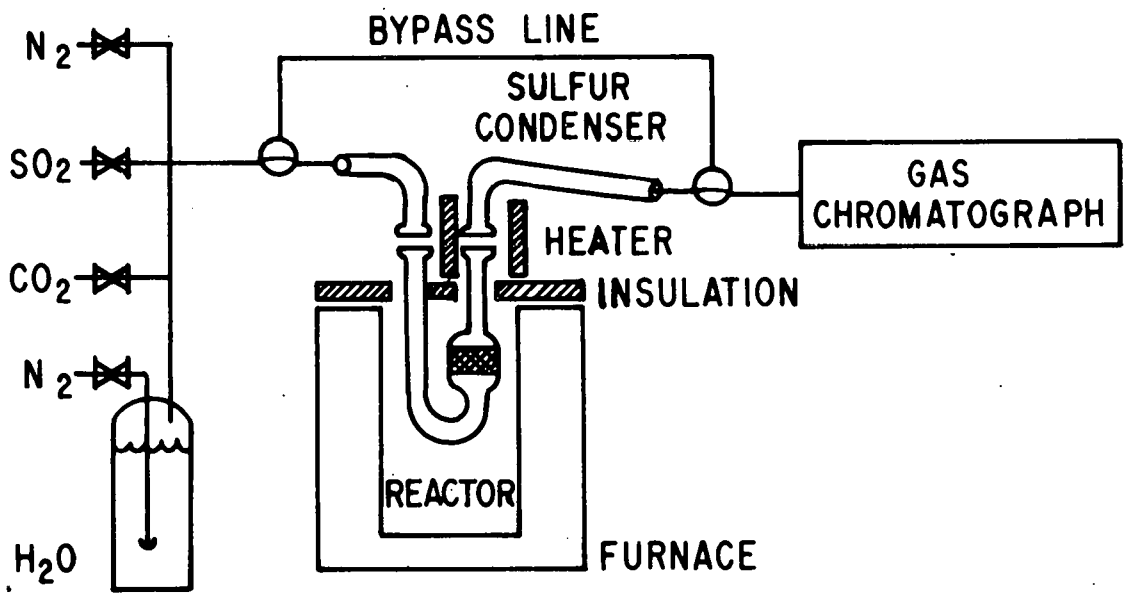

Fig. 11. Schematic Diagram of Sulfur Dioxide Reduction Apparatus

Table 11. Operating Conditions for Gas Chromatograph

Column and packing	3.4-m by 0.3-cm-OD stainless steel column packed with 80/100 mesh treated Porapak QS for 2.7 m, followed by 100/120 mesh Porapak T for 0.7 m.
Column temperature	110°C isothermal
Carrier gas	Helium at 30 mL/min
Sample volume	0.1 mL (atmospheric pressure)
Detector	Thermal conductivity bridge
Detector temperature	230°C
Detector current	220 mA

The main reductant used for converting SO_2 to elemental sulfur was the carbon contained in ash collected from the atmospheric PDU fluidized-bed combustor. The ash was obtained from the cyclones during CT-1, a 100-h combustor run using Sewickley coal. The ash composition is given in Table 12, and the Sewickley coal composition is given in Table 13. In runs in which

Table 12. Composition of Ash Collected in the Cyclones during Run CT-1

Substance	wt %
Carbon, C	35.0
Ferric oxide, Fe_2O_3	15.7
Lime, CaO	8.3
Sulfur Trioxide, SO_3	4.6
Other	36.4

coal-ash mixtures were used as reductant, finely powdered Sewickley coal was added to the ash. For the carbon reactivity measurements described below, a petroleum coke was ground to -200 mesh prior to its use as a reductant.

Table 13. Composition of Sewickley Coal

Proximate Analysis		Ultimate Analysis	
Moisture	1.11%	Moisture	1.11%
Ash	19.06%	Carbon	64.88%
Volatile matter	36.56%	Hydrogen	4.41%
Fixed carbon	43.27%	Nitrogen	1.04%
		Sulfur	5.46%
		Oxygen	4.00%
		Chlorine	0.04%
		Ash	19.06%

In a run in which there were separate coal and ash beds, large coal particles of -6 +100 mesh were placed in the reactor upstream from the catalyst (i.e., ash) bed. Carbon-free ash for the latter bed was prepared by oxidation of ash from run CT-1. To avoid sintering of the ash, this oxidation was carried out in a low-flow-rate air stream at 750°C.

The gaseous feed for the carbon reactivity tests and the kinetic measurements consisted of 9.55% SO_2 in N_2. For the run using separate coal and ash beds, the gaseous feed was a simulated regenerator off-gas containing 8% SO_2, 10% H_2O, 16% CO_2, and 66% N_2. This composition was achieved by controlling the flows through calibrated rotameters and by passing the N_2 through a water bubbler at 54°C.

(2) Use of Ash and Ash-Coal Mixtures

Ash from the ANL atmospheric-pressure fluidizied-bed combustor typically contains 30-40% carbon. This carboniferous material consists of fine particles of char originating from the coal used in the combustor. They are partially devolatilized in the combustion chamber and transported in the gas stream to the cyclones without becoming completely oxidized. They are collected in the cyclone separators along with mineral ash constituents and fines from attrition of the lime bed material.

The quantities of ash required for reduction of the sulfur dioxide absorbed during two 100-h combustor runs, CT-1 and CT-2, were calculated. It was assumed that all sulfur in the bed overflow material would be converted to SO_2 in a regenerator and that 75% of the carbon in the ash could be utilized

for converting SO_2 to elemental sulfur. The results showed that only 25 to 30% of the ash collected would actually be required. However, because there are important economic and safety incentives for raising combustion efficiency above 99%, combustion efficiency will undoubtedly be improved in more advanced fluidized-bed combustors, and there will be less carbon in the ash. If combustion efficiency exceeds about 96%, there would not generally be enough carbon available in the ash for converting the SO_2 to elemental sulfur.

To obtain sufficient carbon, it may be possible to add coal to the ash in order to avoid the usual problems encountered with the use of coal alone. One such problem is reactor plugging caused by swelling of the coal when it is heated, a property typical of many Eastern coals. However, when a mixture is used, ash may contain a sufficient volume of voids to offset the effect of coal swelling and thereby prevent reactor plugging. Also, coal volatiles evolve from coal when it is heated, contaminating the sulfur product. In a reduction reactor using coal alone; the volatiles are not eliminated by reaction with SO_2. In the presence of the additional surface area provided by ash, however, more of the coal volatile matter may react with the sulfur dioxide, preventing contamination of the product sulfur. A series of experiments were made at 550-750°C with ash and ash-coal mixtures to explore the feasibility of this approach, to obtain preliminary kinetic information, and to measure the purity of the product sulfur. Results are presented in following subsections.

(3) Pelletization

A problem encountered in the runs with ash was the large pressure loss (which can be a severe economic restriction) encountered by the gas stream flowing through the packed bed of fine solids. Figure 12 shows the pressure losses encountered at various approach velocities by a stream of SO_2/N_2 flowing through a shallow packed bed of ash. At higher temperatures, the pressure loss would be slightly higher.

Pressure drops can be reduced by using pelletized material, and pelletization of both ash and ash-coal mixtures containing up to 8% coal) was attempted. The maximum pressure of a laboratory pelletizer was used, but the pellets were not cohesive and broke readily. Subsequently, the ash and ash-8% coal mixtures were subjected to a pressure of 380,000 kPa (55,000 psi) in a press, still without cohesion.

The use of ash-coal mixtures containing up to 17% coal did not cause the reactor (Fig. 11) to become plugged. Following each run of the series, the reductant bed was examined for signs of caking. The material was firmly packed, but was easily removed from the reactor.

(4) Reactivity of the Carbon Contained in the Ash

The ash used in this study had high levels of the minerals which were observed to enhance carbon reactivity in the study by Macak and Pick.[40] Carbon reactivity tests were performed in a laboratory differential

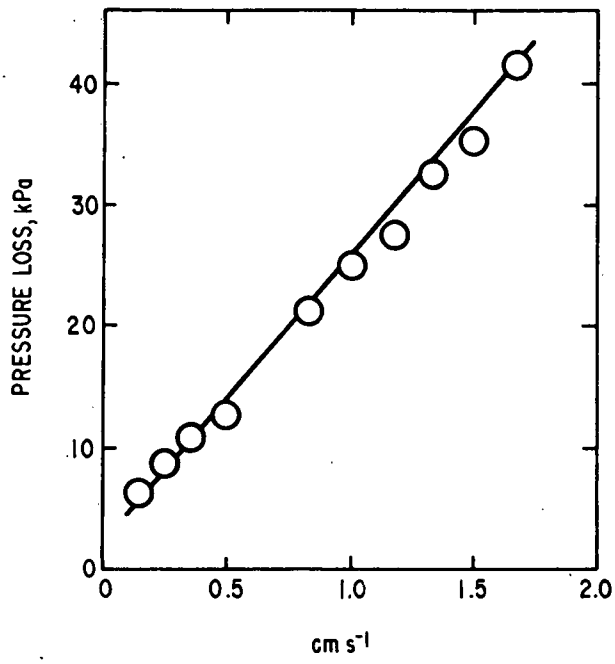

Fig. 12. Pressure Loss of a Gas Stream Containing 9.55% SO_2 in N_2 when Passed through a 3-cm Packed Bed of Ash at 600°C.

reactor, using the carbon in ash, coke mixed with the ash mineral matter, and coke mixed with an inert material. The ash mineral matter was previously used ash from which nearly all of the carbon had been consumed. The inert material was alpha alumina, a ceramic of low surface area obtained by heating another form of alumina above 1000°C.

A set of standard conditions, given in Table 14, was selected for the carbon reactivity tests. A sample was placed in the reactor and was heated to reaction temperature under nitrogen flow. Then the nitrogen was replaced with the gas containing SO_2 to measure the conversion of SO_2 to products. Periodically, the temperature was increased, and the SO_2 conversion measurement was repeated.

Table 14. Standard Conditions for Carbon Reactivity Tests

Sample size, carbon concentration	3 g, 30-35% carbon
Gas feed:	9.55% SO_2 in N_2
Temperature:	Various, 450-850°C
Gas feed rate:	5.0×10^{-4} L/s
Apparent contact time:	12 s
Carbon depletion during each run:	approximately 5%

The extent of conversion is indicated by the SO_2 level in the gas stream (shown in Fig. 13) after passing through the differential reactor. The carbon in the ash reacts with the SO_2 at a substantially lower temperature than does the carbon in the coke. At a given temperature, the extents of reaction with SO_2 of the mixture of coke and carbon-free ash and the mixture of coke and alpha alumina were about the same.

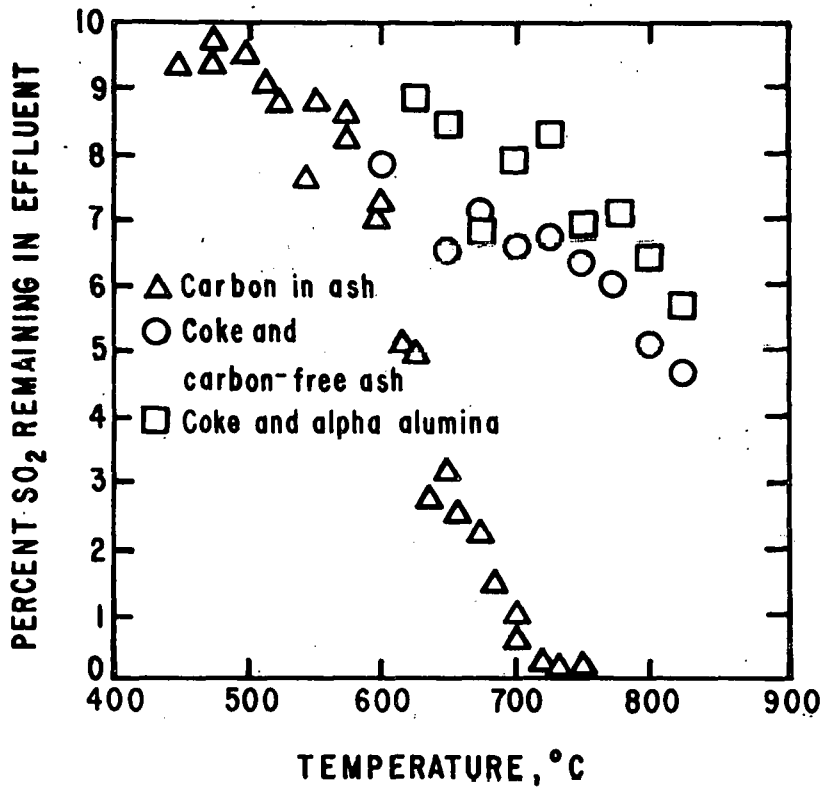

Fig. 13. Reactivity for Reduction of SO_2 to Sulfur, Measured by SO_2 Consumption.

(5) Kinetic Measurements

In work done in a laboratory differential reactor, it was difficult to obtain a reproducible steady state condition for measurement of the rate of reaction of SO_2 and carbon. When the reductant samples were first brought to reaction temperature, the reaction rates were very high, but they decreased rapidly while the reaction proceeded at constant temperature. Consistent rates were obtained only after reaction had proceeded for several hours, often overnight. The rates obtained in this manner are shown in Fig. 14, an Arrhenius plot which indicates an activation energy of about 30 kcal/mol.

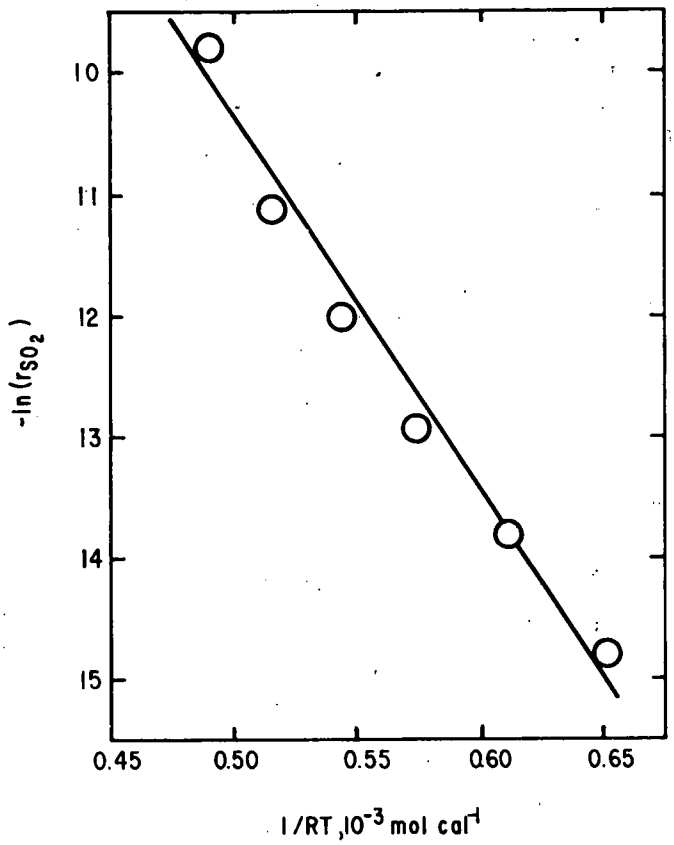

Fig. 14. Rate vs. 1/RT for the Reaction between SO_2 and the Carbon in Ash and Ash-Coal Mixtures. Reaction rate was measured after devolatilization at reaction temperature.

(6) Composition of Sulfur Made by Reaction of SO_2 with Ash and Ash-Coal Mixtures

The product sulfur was carried by the gas stream into the sulfur condenser (Fig. 11) where it collected on the walls. Following each run, the sulfur was removed from the condenser by carbon disulfide dissolution and placed in sample bottles; then the carbon disulfide was removed by evaporation. The samples were analyzed by Analytical Chemistry Department personnel,* and the results are summarized in Table 15.

Commercially available grades of sulfur contain less than 1% carbon impurities. Sulfur meeting or approaching this quality was obtained in the runs made at temperatures between 650 and 750°C and with about 3% or less coal in the mixture.

*R. M. Crooks, E. Street, J. P. Faris, and K. J. Jensen.

Table 15. Composition of Sulfur Made with Ash and Ash-Coal Mixtures

Run No.	Temp, °C	Bed Comp, %		Product					
		Ash	Coal	S, %	C, %	H, %	Na, ppm	K, ppm	Ca, ppm
19	550	100	0	n.d.	3.3	0.1	350	40	500
14	550	92.6	7.4	81.8	8.3	1.0	800	40	500
7	600	100	0	97.3	1.7	0.3	35	<10	50
16	600	97.1	2.9		2.1	0.2	75	12	100
12	600	82.6	17.4	70.3	24.3	2.5	300	25	500
17	650	100	0	97.9	0.8	0.0	T[a]	0	40
13	650	99	1	98.0	0.8	0.1	40	<10	75
5	650	92.6	7.4	97.5	1.1	0.1	T	<10	T
24	650	100	0	99.6	0.2	0.1	T	T	40
6	700	97.1	2.9	98.6	0.7	0.1	T	10	25
20	700	100	0	98.7	0.5	0.1	250	T	150
P-1	750	100	0	98.9	0.9	0.1	<5	25	T
P-2	750	100	0	98.4	0.5	0.1	6	25	T
22	750	100	0	99.3	0.5	0.1	50	T	100

[a]T indicates trace.

(7) Use of Coal and Ash in Separate Beds

Coal volatiles contaminating the sulfur (reported above) may originate from coal particles or from incompletely devolatilized char located near the exit end of the reductant bed. To increase the percent coal in the reactor (so that there is adequate reductant) without sacrificing sulfur quality, a run was made using a coal bed upstream from a carbon-free ash bed. With this arrangement, all of the coal volatiles would enter the ash bed which would function as a catalyst for the reaction of volatiles with SO_2.

About 16 g of carbon-free ash was placed in the bottom of the U-tube reactor, and 5 g coal was put on top of the ash on the intake side; thus, the simulated regenerator off-gas passed through the coal bed and then through the ash which functioned as a catalyst for the reaction of SO_2 with the coal volatiles. To avoid any sudden, excessive evolution of volatiles, the 750°C furnace was raised slowly to surround the coal bed. The composition of the sulfur product from this run is shown in Table 16.

Table 16. Composition of Sulfur Made with Separate Coal and Carbon-Free Ash Beds

Temp, °C	Bed Comp, %		Product					
	Ash	Coal	S, %	C, %	H, %	Na, ppm	K, ppm	Ca, ppm
750	76	24	98.5	0.2	0.1	T	15	100

This is an important result, because it indicates that high-quality product sulfur can be produced with coal in a suitable reactor. Coal should be fed to the system continuously, and the SO_2 stream should contact the freshly fed coal first. The resulting mixture of SO_2 and coal volatile matter must next contact coal char or ash to eliminate the coal volatile matter by reaction with the remaining SO_2.

It should be possible to develop a reator concept incorporating these features. A similar problem is encountered in coal gasification, where it is desirable to produce a gas stream free of condensible coal volatile matter. Colaluca et al.[43] reported success in overcoming the problem by gasifying in a series of fluidized beds. A similar system could probably be devised for this reaction.

e. Conclusions

Because of thermodynamic constraints, it is not practical to combine the regeneration of spent lime sorbent with the production of sulfur.

A high-quality sulfur can be made from the carbon in the ash from fluidized-bed combustion runs, which is much more reactive with SO_2 than is a petroleum coke. However, carbon is not likely to be available in the ash from more advanced fluidized-bed combustors. If combustion efficiencies can not be raised above about 96% without resorting to recycle, sufficient carbon will be available in the ash; if ash recycle would be necessary, a portion of the recycle stream could probably be withdrawn for sulfur production.

When mixtures of Sewickley coal and Sewickley coal ash are used, reactor plugging does not occur if mixtures contain no more than 17% coal. However, the sulfur product is poor when 17% coal is used. High-quality sulfur can be made with ash-coal mixtures only if the coal fraction is about 3% or less. When a larger coal fraction was used the sulfur product was contaminated with coal volatiles which condensed with the sulfur.

A much higher overall coal fraction can be used for the production of a high-quality sulfur if the coal and ash are in separate beds (rather than mixed), with the ash utilized as a catalyst bed for the reaction of SO_2 with coal volatiles.

The use of a packed bed of ash results in a large pressure drop in the gas stream that would be very costly to maintain on a commercial scale. Since the ash does not pelletize readily, other means of reducing the pressure loss need to be found.

f. Recommendations and Future Work

It may be possible to utilize coal, as the reductant for high-quality-sulfur production in a series of fluidized-bed reactors. Both coal

and the regenerator off-gas would enter the first reactor, where coal devolatilization would occur. With a long coal residence time in this reactor, fresh coal would be quickly diluted in the fluidized bed (which would consist mostly of devolatilized coal or char), and this dilution might prevent agglomeration.

The char and/or coal ash and the gas stream would travel to additional fluidized-bed reactors downstream where, in the presence of ash, the SO_2 would react with coal volatiles picked up in the first reactor. Carbon contained in the char would also be utilized. It might be necessary to use sand in the bed to help retain the ash. This system of reactors would be similar to the reactors used for gasifying coal without producing coal liquids which was described by Colaluca et al.[43]

In any further development of this sulfur recovery process, it is recommended that laboratory-scale experiments be performed to test the feasibility of converting SO_2 to elemental sulfur with coal in a series of small fluidized beds with continuous feeding of coal.

Further development of sulfur recovery processes in this laboratory is to be deferred until it can be shown that regeneration is justified on economic or environmental grounds. Recently, the development of processes to enhance the reactivity of limestone for use in fluidized-bed combustors has made significant progress. As Smyk[44] has shown, enhancement of limestone reactivity and of once-through usage are economically preferable to regeneration. As a result, efforts in the immediate future are to be concentrated on enhancement of limestone reactivity.

2. Alternative Regeneration Process Development

a. Rotary Kiln Regeneration
(D. C. Moulton and F. F. Nunes)

Previous emission-control studies[46] have shown that spent limestone sorbents can be regenerated by the use of reducing agents at high temperatures. Rotary kilns are being evaluated for use as regeneration reactors. Externally fired rotary kilns are capable of producing a concentrated SO_2 stream, which can be economically converted to elemental sulfur, a desirable final form because it is easily handled and stored. It is much more expensive to convert a dilute than a concentrated SO_2 stream.

Studies were conducted with two laboratory kilns. A small kiln was constructed from a 26-mm-ID tube of fused silica surrounded by an annular electric furnace. Mixtures of char and sulfated limestone were heated in a rotating kiln, with the flow of nitrogen carrier gas controlled to obtain the maximum SO_2 concentration in the off-gas. A more detailed description is given in a previous annual report.[45] The second kiln is a large laboratory-scale kiln, a Bartlett-Snow 16.5-cm-ID indirect gas-fired kiln made of HH alloy stainless steel. The experimental work with both kilns has been completed.

(1) Data Analysis

Analysis of the data has been completed, and details are included in a topical report.[47] Several empirical rate equations were found to have limited agreement with the kiln results. Application of the shrinking-core reaction rate model to the rotary kiln data provided fairly good agreement over the entire range of operating conditions.

The empirical rate equations indicated that the rate constant had no significant temperature dependence. Chemical reaction rate constants have strong temperature dependence, while physical processes such as diffusion have very little temperature dependence. It appears that the rate of reaction was limited by diffusion.

Application of the shrinking-core model leads to different mathematical forms, depending on the assumptions made. Different assumptions can be tested by seeing how well their mathematic predictions agree with the data. If diffusion is limiting, it is of interest to know whether the limiting diffusion occurs within the particle or exterior to the particle. If diffusion exterior to the particle is important, the regeneration rate can be increased by better gas-solid mixing.

The shrinking-core model was applied to the rotary kiln for each of the following assumptions:

1. The reaction rate was entirely due to diffusion within the particle (interior diffusion).

2. The reaction rate was entirely due to diffusion between the particle and the surrounding carrier gas stream (external diffusion).

Unfortunately, the two resulting mathematical expressions agree equally well with the results. Interior diffusion is generally a slow process because molecular motion within the solid is hindered. However, there is evidence that external diffusion was also significant because changes in operating parameters which would reduce the external diffusional resistance caused a reduction in the observed overall diffusional resistance. For example, increasing the kiln rotation rate to give better solids-gas mixing decreased the diffusional resistance. An increased rotation rate would be expected to decrease external diffusional resistance but would have no effect on internal diffusional resistance.

(2) Materials of Construction

During the kiln experiments, it became apparent that the materials of construction were not compatible with the reaction conditions. When stainless steel test specimens were placed in a simulated kiln atmosphere, there was very rapid chemical attack. A scale developed that contained nickel oxide and nickel sulfide and which partially flaked off when the test specimens were cooled. During kiln operation, the H. H. alloy kiln tube was severely

damaged--the inner surface became sulfided and flaked off into the product. The mixing fins (made of type 316 stainless steel) became warped, then covered with scale, and eventually broke into pieces.

(3) Results and Conclusions

Regeneration can be accomplished in externally fired rotary kilns, but severe conditions are required for high regeneration levels. At 1060°C, about 85% of the calcium sulfate was converted to calcium oxide, but at 1000°C, less than 50% was converted; at 960°C, conversion was less than 25%.

Also, a concentrated SO_2 stream can be obtained, but only at high temperatures. At 1060°C, SO_2 concentrations were in excess of 20%. Less concentrated streams were obtained at lower temperatures. For example, at 1000°C, SO_2 concentration was less than 7% and by extrapolation, the limit appeared to be below 11%.

High conversion of calcium sulfate to calcium oxide and a concentrated SO_2 stream could not be achieved simultaneously. High sulfate conversion required a low solids to gas feed ratio, but a concentrated SO_2 stream required a high solids to gas feed ratio.

The shrinking-core reaction rate model can be used to correlate the kinetic data. It appears to be useful in predicting sulfate conversion and percent SO_2 in the off-gas under various operating conditions. Data from this model can be used as a basis for comparing assumptions about the reaction. It can also be used to compare diffusional resistance to the reaction, which changes when the operating conditions or the feedstock is changed.

Use of the shrinking-core model did not help to distinguish the rate-controlling step. Interior diffusion within the particle seems likely to be the rate-controlling step, but there is also evidence that exterior diffusion between the particle and the nearby gas stream is important. If exterior diffusion is significant, the kinetics can be improved by better mixing--i.e., by more rapid rotation or by using a different reactor design (such as a fluidized bed, which has excellent mixing characteristics).

The materials of construction are woefully inadequate. The H. H. alloy has excellent resistance to reducing gases at high temperature, but chemical attack by SO_2 is very rapid. No other metals appear to be significantly better. Use of a nonmetal would be an unsatisfactory alternative because poor heat conduction would cause a large drop in efficiency.

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