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MASTER

REGENERATION OF SULFATED LIMESTONE FROM FBCs

Quarterly Report
October—December 1978

by

Irving Johnson, W. M. Swift, R. B. Snyder,
J. F. Lenc, D. S. Moulton, F. F. Nunes, G. W. Smith,
E. B. Smyk, F. G. Teats, and A. A. Jonke

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Prepared for the U. S. DEPARTMENT OF ENERGY
under Contract W-31-109-Eng-38

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Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161
Price: Printed Copy $5.25; Microfiche $3.00

Distribution Category:
Coal Conversion and Utilization--
Direct Combustion of Coal
(UC-90e)

ANL/CEN/FE-79-2

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Argonne, Illinois 60439

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Chemical Engineering Division

Prepared for the
U. S. Department of Energy
under Contract No. W-31-109-Eng-38
and the
U. S. Environmental Protection Agency
under Agreement IAG-D5-E681

Previous reports in this series

ANL/CEN/FE-77-10
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ANL/CEN/FE-78-5
ANL/CEN/FE-78-13

BIBLIOGRAPHIC DATA SHEET	1. Report No. ANL/CEN/FE-79-2	2.	3. Recipient's Accession No.

4. Title and Subtitle

Regeneration of Sulfated Limestone From FBCs

5. Report Date 1979

6.

7. Author(s) I. Johnson, W.M. Swift, R.B. Snyder, J.F. Lenc, D.S.Moulton, F.F. Nunes, G.W. Smith, E.B. Smyk, F.G. Teats, A.A. Jonke

8. Performing Organization Rept. No. ANL/CEN/FE-79-2

9. Performing Organization Name and Address

Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

10. Project/Task/Work Unit No.

11. Contract/Grant No.
W31-109-ENG-38 (DOE)
IAG-D5-E681 (EPA)

12. Sponsoring Organization Name and Address

U. S. Department of Energy
and
U. S. Environmental Protection Agency

13. Type of Report & Period Covered
October-December 1978

14.

15. Supplementary Notes

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Operational characteristics are reported for a process development-scale atmospheric fluidized-bed combustor which has been put into use for corrosion studies, and the exposure conditions for the first three 100-h corrosion runs are reported. Limestone used in these runs included untreated limestone and limestone treated with 0.3 mol % $CaCl_2$ or 0.5 mol % NaCl.

17. Key Words and Document Analysis. 17a. Descriptors

Additive
Air Pollution
Bauxite
Calcium Chlorides
Calcium Oxides
Carbon Monoxide
Coal
Coal Gasification
Coke
Combustion
Desulfurization
Dolomite
Fluidized-Bed Combustion
Hydrogen
Hydrogen Sulfides
Limestone
Materials Testing
Methane
Sodium Chlorides
Sulfur Oxides
Vapor Pressure

17b. Identifiers/Open-Ended Terms

Carbonyl Sulfide
Coal Ash
Corrosion Probes
Corrosion Tests
Sorbent Regeneration
Sorbents
Sorbent Regenerator Configuration
SO_2 Reduction Catalysts
Sulfation Enhancers
Sulfur, Elemental

17c. COSATI Field/Group 13 B

18. Availability Statement	19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages
	20. Security Class (This Page UNCLASSIFIED	22. Price

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ABSTRACT

These studies are concerned with the development of processes for the regeneration of sulfated limestone from fluidized-bed combustors (FBC) and with the evaluation of corrosion when limestone sorbents treated with various salts (to increase their SO_2 reactivity) are used in FBCs.

The results of a cyclic combustion (sulfation)--regeneration study of Germany Valley limestone are reported. A thermodynamic analysis was made of the reductive decomposition regeneration process to examine the interrelationship of: SO_2 concentration in the off-gas, temperature, pressure, oxidizing/reducing conditions, coal/sorbent ratio, feed gas oxygen concentration, and sorbent composition. A literature review was made on processes for the conversion of SO_2 to elemental sulfur.

Operational characteristics are reported for a process development-scale atmospheric fluidized-bed combustor which has been put into use for corrosion studies, and the exposure conditions for the first three 100-h corrosion runs are reported. Limestone used in these runs included untreated limestone and limestone treated with 0.3 mol % $CaCl_2$ or 0.5 mol % NaCl.

SUMMARY

A. Fluidized-Bed Reductive Decomposition Studies

Cyclic Studies. Germany Valley limestone was tested for performance in reducing SO_2 emissions from PFBCs. In a three-cycle combustion-regeneration study, the limestone-SO_2/O_2 reactivity in the combustor did not change appreciably and in the second and third cycles was low. Calcium utilization was about 8%. Regeneration was excellent--above 90% in the three cycles. However, because of the low calcium utilization of Germany Valley limestone, this stone is not an economically viable choice since a large regenerator would be required if this stone were used.

Thermodynamic Analysis of Process. A thermodynamic analysis was performed of the one-step reductive decomposition process for regenerating partially sulfated limestone sorbent (obtained from a fluidized-bed combustor). In this process, coal is used as the source of both sensible heat and reducing gases. Among the variables considered were temperature, pressure, oxidizing/reducing conditions, coal/sorbent ratios, feed gas oxygen concentration, partially sulfated sorbent compositions. A maximum SO_2 concentration of 16% was predicted for a full-sized regenerator operated under normal solids and gas preheat conditions.

B. Sulfur Recovery Process Studies

Reducing Sulfated Limestone with Coal to Produce Elemental Sulfur.

Sulfur production processes are examined for their applicability to the fluidized-bed combustor system. Sulfur dioxide that has been produced in a lime regenerator downstream from a combustor is to be reduced to elemental sulfur. Of most interest are processes which use coal as the reductant and as the source of process heat. One process which uses coal directly is presently under commercial development. Thermodynamic calculations show that a system producing elemental sulfur directly in a regenerator would be uneconomic because of the extremely low yield possible when calcium oxide is present. The reactivity of carboniferous materials with sulfur dioxide is greatly affected by the ash composition and content. The process may be improved by utilizing the ash or other materials of known catalytic value.

An alternative is coal gasification to produce a reducing gas which subsequently reacts with sulfur dioxide on a catalyst in a different vessel. Kinetic data are available for each of the probable constituents of a coal gasifier effluent: hydrogen, carbon monoxide, methane, and hydrogen sulfide.

D. Corrosion Studies

Effects of Limestone Sulfation Accelerators on Corrosion Rates of Metals in an AFBC. The recently constructed, automated PDU-scale, atmospheric-pressure, fluidized-bed coal combustion facility (AFBC) is being used in an experimental program to measure the corrosion of materials of construction in the presence of sulfation enhancers.

Before corrosion experiments were conducted in the new AFBC, the effects on SO_2 retention by Grove limestone (No. 1359) of adding low concentrations (1.0 mol % or less) of $CaCl_2$ or NaCl were evaluated in a series of 31 runs. Percent sulfur retentions and percent calcium utilizations as a function of the Ca/S mole ratio are reported.

In these runs, the degree of sulfation enhancement due to the addition of $CaCl_2$ or NaCl was generally lower than in laboratory-scale experiments previously reported. The differences in the two sets of data are thought to be due to the different manners of conducting the two series of experiments. The laboratory-scale experiments were carried out with a simulated flue gas and no coal combustion. Consequently, no coal ash constituents were present in the reactor. In contrast, combustion experiments were performed in the new AFBC. Further investigations are planned to explain the disparity between the two sets of data.

A series of four runs were conducted in the new AFBC to compare its performance with that of an older atmospheric-pressure fluidized-bed combustor under similar operating conditions. A major difference in the two sets of experiments was in the sulfur content of the coals. The Sewickley coal used in the recent runs contained 5.46% S, compared with 3.7% S for the Illinois coal used in the previously reported runs. Percent sulfur retentions as a function of Ca/S mole ratio for these four recent runs are reported. Sulfur retentions were in general agreement with those of previous atmospheric-pressure, fluidized-bed combustion experiments. At a Ca/S mole ratio of 3, sulfur retention was about 80% in the recent run series, compared with about 87% in the previous run series. Carbon, sulfur, and calcium material balances for 4.5-h steady state periods of each of the four runs are presented. Carbon balances ranged from 118 to 128%, sulfur balances ranged from 78 to 101%, and calcium balances from 96 to 114%. Combustion efficiencies varied from 86 to 88%.

Three 100-h corrosion test runs (CT-1, -2, and -3) were completed in the new AFBC. Operating conditions for the runs are reported. In each run, seven corrosion probes, each holding seven metal specimens, were installed at various locations in the bed and freeboard sections of the combustor. Three of the probes in a set were of the air-cooled type and the four remaining probes were of the uncooled coupon type. The types of metal specimens, their locations in the combustor, and the temperature for each of the seven corrosion probes used in each run are reported.

Except for minor problems, the new AFBC facility performed satisfactorily during the 100-h tests. Methods are being investigated of preventing recurrence of these problems in future tests.

The sorbent used in the three runs was Grove limestone. There was no salt addition in Run CT-1, about 0.3 mol % $CaCl_2$ in Run CT-2, and about 0.5 mol % NaCl in Run CT-3. The Ca/S mole ratio in each run was adjusted to maintain a nominal 700 ppm SO_2 in the dry off-gas. The resultant Ca/S mole ratios were 3.4, 3.5, and 3.6 for Runs CT-1, CT-2, and CT-3, respectively. Neither the addition of $CaCl_2$ in Run CT-2 nor the addition of NaCl in Run CT-3 enhanced the sulfation of the Grove limestone sorbent although enhanced sulfation had been expected from the results of the aforementioned laboratory-scale experiments.

Samples of the various solids output streams from the three 100-h corrosion test runs are being analyzed to determine the accuracy of the observed sulfur retentions obtained by monitoring SO_2 in the flue gas. The effects of salt addition on the corrosion of the metal specimens from all three runs are being evaluated by the Materials Science Division of ANL.

TASK A. FLUIDIZED-BED REDUCTIVE DECOMPOSITION STUDIES

1. Cyclic Studies

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

The results of cyclic combustion/regeneration experiments to evaluate the reactivity and attrition resistance of two limestones over repeated utilization cycles have been reported earlier.[1] In both sets of experiments, there was a gradual loss of reactivity of the sorbent (i.e., sulfur retention) at the late utilization cycles. However, regenerability of the sorbents was unaffected over the ten combustion/regeneration cycles comprising each set of experiments.

The two sorbents tested in the earlier cyclic experiments were Tymochtee dolomite and Greer limestone. Both Tymochtee in comparison with other dolomites and Greer in comparison with other limestones exhibit relatively high reactivities for sulfur retention on a once-through basis. Thus, even though the results of the experiments indicate that limestone requirements could be substantially reduced by regeneration and recycle of the sorbents, the dollar savings from the lower limestone usage (as compared with a once-through process) may not equal the cost of the regeneration process.

A number of limestones and dolomites are considerably less reactive, however, than the sorbents previously tested under cyclic conditions. Relatively large amounts of many of these stones would be required for once-through operation making once-through use less economic. Under such circumstances (but depending upon the availability of reactive stones nearby), regeneration may be considerably more attractive. There is even reason to believe that the reactivity of certain unreactive stones for sulfur retention may actually increase during the first few utilization cycles. Then there would be potential for a very significant percentage reduction in limestone requirements in comparison with a once-through basis.

Tests are being conducted, therefore, to evaluate four limestones under cyclic combustion/regeneration conditions. The scope of the tests will be reduced considerably from the ten cycles used in the first two series of experiments. In general, each limestone will be tested in three combustion/regeneration cycles with either high-pressure (about 810 kPa) or low-pressure (303 kPa or 405 kPa) combustion.

a. Equipment

The fluidized-bed combustion equipment and instrumentation of the PDU (process development unit) at Argonne consist 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 solids removal from the flue gas; associated heating and cooling arrangements and controls; and temperature- and pressure-sensing and display devices and a gas-analysis system. A simplified schematic flowsheet of the combustion equipment is presented in Fig. 1. Details of the PDU combustor design have been given previously.[1]

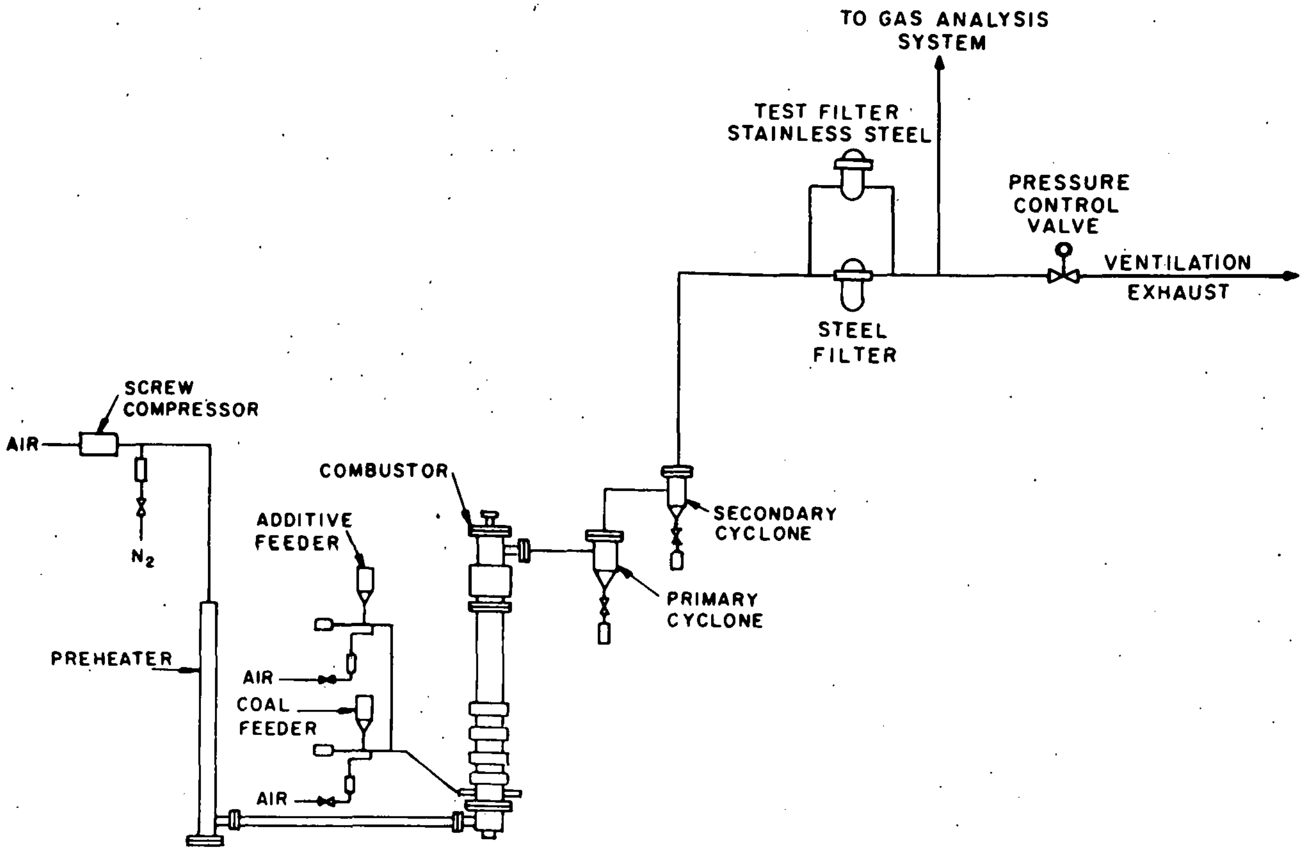

Fig. 1. Simplified Equipment Flow Sheet of PDU Fluidized-Bed Combustor and Associated Equipment. The "additive feeder" is actually a "sorbent feeder."

The flue gas (off-gas) is sampled continuously and is analyzed for the components of primary importance. Nitrogen oxide and total NO_x are analized using a chemiluminescent analyzer; sulfur dioxide, methane, carbon monoxide, and carbon dioxide determinations are made using infrared analyzers; oxygen is monitored using a paramagentic analyzer; and total hydrocarbons are analyzed by flame ionization. Prior to and during each experiment, standard gas mixtures of flue-gas constituents in nitrogen are used to check the response of each analytical instrument.

Figure 2 is a schematic diagram 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) in the regenerator is regulated by an overflow pipe that is external to the fluidized-bed. The pressurized, fluidized-bed reactor is lined with a 4.8-cm-thick castable refractory. The coal and the sulfated sorbent are metered separately (for independent control) to a common

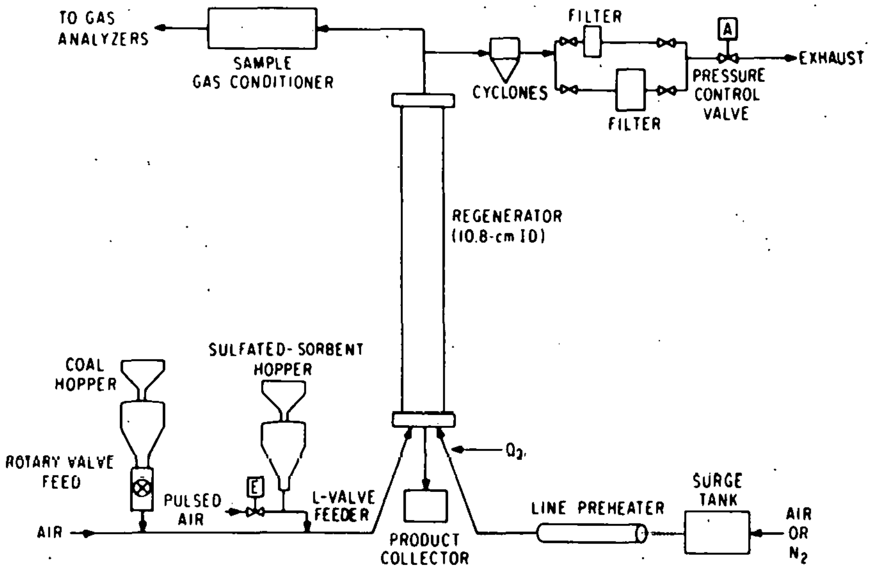

Fig. 2. PDU-Scale Sorbent Regeneration System

pneumatic transport line, which discharges into the fluidized bed above the gas distributor.

Other components of the experimental system are (1) an electrically heated pipe heat exchanger for preheating some of the fluidizing gas and for preheating air (used in startup only) to about 400°C and (2) a solids-cleanup system for the off-gas. Pertinent constituents (SO_2, O_2, CO, H_2, CH_4, and NO) in the off-gas are continuously analyzed.

b. Procedure

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

c. Cyclic Tests with Germany Valley Limestone

A series of cyclic tests has been completed to evaluate reactivity changes in Germany Valley limestone during cyclic utilization in which combustion was at high pressure. Limestones are generally considered unacceptable for use in PFBCs on a once-through basis. These tests were designed to evaluate the use of a limestone pressurized combustor with the sorbent regenerated at atmospheric pressure.

Germany Valley is a high-purity limestone which sulfates to a relatively low extent. 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, and the balance N_2. From these results, it was projected that for AFBC, approximately 1-1.3 kg of limestone/kg of coal would be required. The chemical composition of Germany Valley limestone is given in Table 1.

Table 1. Chemical Composition of Germany Valley Limestone

Derived Component	wt %
$CaCO_3$	97.8
$MgCO_3$	0.6
SiO_2	0.2
Fe_2O_3	0.1
Al_2O_3	1.8
Na_2O	0.3

Combustion Cycle Results. Conditions for the PDU-scale combustion experiments were nominally: a bed temperature of 900°C, a system pressure of 810 kPa, a fluidizing-gas velocity of 0.8 m/s, 3% O_2 in the combustor flue gas, and Sewickley coal combusted. Two batches of Sewickley coal were used; the first batch (used during the first combustion cycle) contained about 4.3% S, the second batch (used in the second and third combustion cycles) contained about 5.5% S.

For each of the three combustion cycles, the limestone feed rate was adjusted to obtain an SO_2 concentration of about 700 ppm in the flue gas, which corresponds to about 83% sulfur retention (the EPA requirement for Sewickley coal). Thus, reactivity of the limestone during the three cycles was represented by the amount of limestone required to achieve 83% sulfur retention during each combustion cycle.

Table 2 summarizes the experimental conditions and test results for the three combustion cycle experiments. On a mass basis, the kg of sorbent required per kg of coal decreased from about 1.23 in the first combustion cycle to about 1.06 in the third combustion cycle. Thus, 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 once-through requirements (a reasonable estimate based on sorbent savings projected

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

Coal: Sewickley	System Pressure: 810 kPa
Combustion Temperature: 900°C	Sorbent Particle Size: -10 +50 mesh
Fluidizing-Gas Velocity: 0.3 m/s	Excess Combustion Air: about 17%

Combustion Cycle	Feed Rate		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], %
1	15.1	18.5	1.23	8.9	700	85/72	0	8.1	8.1
2	12.7	14.1	1.11	10.2	618	88/96	0.6[f]	10.0	9.4
3	12.6	13.4	1.06	9.4	681	86/66	1.2	8.2	7.0

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

[b] 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 in product minus sorbent utilization in feed.

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

from previous cyclic tests). Thus, actual limestone consumption could be reduced to about 0.25 kg of limestone (0.2 times 1.23) per kg of coal.

Evaluation of the test data for indicated changes in limestone reactivity over the three combustion cycles gives mixed results. Based on the flue gas analyses, sulfur retention during each of the three combustion experiments was of the order of 85 to 88%. The CaO/S mole ratio was higher in both the second and third combustion cycles than in the first, indicating that the reactivity of the sorbent decreased after the first combustion cycle.

The last column in Table 2, which represents the increase in sorbent utilization during each combustion cycle, indicates that the reactivity of the sorbent increased in the second combustion cycle and then decreased in the third combustion cycle. Increased reactivity of an unreactive stone had been considered a possibility. However, the increase in sorbent utilization to 9.4% in the second combustion cycle is only based on an estimate of sorbent utilization in the limestone feed for that experiment. Thus, the indicated increase in reactivity during the second cycle is questionable.

On the basis of these results, it is uncertain whether the reactivity of Germany Valley limestone changes during three utilization cycles. It is clear, however, that limestone reactivity did not increase significantly during the first few utilization cycles (such an increase was considered a possibility due to heat and calcination effects in the first regeneration cycle).

Attrition of the Germany Valley limestone was very low in each of the three combustion experiments. In the first cycle, attrition was about 4.5% of the sorbent feed. In each of the second and third cycles, attrition of the sorbent feed amounted only to about 0.5%.

As mentioned above, the high CaO/S ratio required with Germany Valley limestone to meet the SO_2 emissions 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 to 9.4%, Table 2) has economic implications for the regeneration process in terms of large reactor size, low SO_2 levels achievable from the regenerator, and the quantity of sorbent that would have to be recycled.

Regeneration Cycle Results. The sulfated limestone was regenerated in the fluid-bed regenerator. Sewickley coal was used as both fuel and reductant. Table 3 gives the performance for Germany Valley limestone for three regeneration cycles. Percent sulfur in the feed stream (to the regenerator) is shown in column 2. In all cycles, the amount of sulfur was low in comparison to the sulfur contents of Tymochtee dolomite and Greer limestone in the earlier cyclic studies. The percent sulfur in the feed was larger in cycle 2 than in cycle 1, and then decreased in cycle 3.

In column 19, the percentages of Ca as $CaSO_4$ in the feed (calcium utilizations) were 6.4, 12.5, and 8.7% for the three cycles. The percent

Table 3. Conditions and Results for Three Regeneration Cycles

1	2 S in Limestone Feed, %	3 Limestone Feed Rate, kg/h	4 Coal Feed Rate, kg/h	5 O_2 in Fluidizing Gas, %	6 Temp, °C	7 S in Regenerated Limestone Product Overflow, %	8 S in Regenerated Limestone (Primary Cyclone), %	9 Ca in Limestone Feed, %	10 Ca in Regenerated Limestone Product Overflow, %	11 Ca in Regenerated Limestone (Primary Cyclone), %
RGVHP1	2.0	13	4.8	34.5	1090	0.29	2.9	38.9	61.5	14.1
RGVHP2	4.9	13.5	2.7	31.8	1090	0.58	1.6	49.6	61.1	29.9
RGVHP3	3.6	18	3.5	36.5	1070	0.28	1.4	51.6	61.1	11.7

	12 Si in Product, %	13 Product Flow Rate, kg/h	14 Product to Primary Cyclone, kg/h	15 Fluidizing Gas Velocity, m/s	16 SO_2 in Off-Gas, %	17 O_2 in Off-Gas, %	18 Reducing Gas in Off-Gas, %	19 Ca as $CaSO_4$ in Feed, %	20 Ca as $CaSO_4$ in Product, %	21 Regeneration Based on Solids Analysis, %	22 SO_2 in Off-Gas (based on Solids Analysis), %
RGVHP1	3.0	5	8.4	1.55	0.5	2.5	0.2	6.4	0.6	91	2.1
RGVHP2	4.3	10	0.9	1.22	2.2	0.1	0.6	12.5	1.2	90.5	4.6
RGVHP3	4.9	16	1.5	1.08	3.8	0.4	0.7	8.7	0.6	93.4	5.4

sulfur in the regenerated material was low (column 2). The percent regeneration of $CaSO_4$ to CaO was excellent (column 21 gives the percent regeneration for each cycle). In all cycles, better than 90% conversion of $CaSO_4$ to CaO was obtained.

The measured percent SO_2 in the off-gas increased from 0.5 to 3.8 in cycles 1 to 3 (column 16). The first cycle had a low SO_2 concentration in the off-gas due to the low sulfur content of the feed material and a high elutriation rate. In cycles 2 and 3, SO_2 concentrations in the off-gas were 2.2 and 3.8%. The higher SO_2 concentration in the third cycle was due to (1) the higher limestone feed rate and (2) the higher oxygen concentration in the fluidizing gas and thus lower requirement for fluidizing gas. The projected SO_2 concentrations in the off-gas, based on solids analysis, are given in column 22 and are 2.1, 4.6, and 5.4% for cycles 1, 2, and 3. If the solids analyses are accurate, the SO_2 analyzer (column 16) was reading low.

The reducing gas concentrations in all cycles (column 18) were low, 0.2-0.7%, in comparison with 3% in previous cyclic experiments. There was also some oxygen in the off-gas (column 17); nevertheless, regeneration was high.

By use of the ANL mass and energy constrained model,[2] it is estimated that the SO_2 concentrations in the off-gas from a "full-size" regenerator would be 8.3% and 9.9% for stones containing 2% and 5% sulfur, respectively. The average sulfur content of the feed stream for the three cycles is 3.5%, but would be lower for a continuously operated combustor-regenerator. Thus, a 7-8% SO_2 concentration in the off-gas could probably be realized, using Germany Valley limestone. However, the solids circulation rate would be two to three times higher than that for Greer limestone so that regeneration of Germany Valley would be less viable on an economic basis.

2. Thermodynamic Analysis of Process

(E. B. Smyk and R. B. Snyder)

Studies are being performed to determine the thermodynamic limitations of the one-step reductive decomposition process for regenerating partially sulfated limestone from fluidized-bed combustion. A NASA-supplied code[3] was used to calculate the equilibrium compositions of all constituents in a given system by the principle of minimization of system total free energy. Temperature, pressure, oxidizing/reducing conditions, coal to sorbent ratio, feed gas oxygen concentration, and sorbent composition were varied. The extent of regeneration and the SO_2 concentration in the flue gas were determined.

In previous work,[4] SO_2 partial pressures were calculated in the system, CaO, $CaCO_3$, $CaSO_4$, CaS, CO, CO_2, SO_2, at various temperatures and CO/CO_2 ratios. The equilibrium concentrations of COS, CS_2, CH_4, H_2, H_2S, SH, SO, SO_3, S_2, H_2O, and O_2 and their effect on the previously calculated equilibrium concentrations have also been determined. Nevertheless, the new results agree quite closely with the previous results. Results are presented for the four sets of regeneration conditions given in Table 4.

Table 4. Regeneration Conditions for Cases Investigated

Case	Solids Feed Temp, K	Gas Feed Temp, K	O_2 Conc.in Gas Feed, %
1	1116	672	21
2	1255	922	21
3	1116	672	100
4	1373	1373	100

In all cases, the partially sulfated sorbent was Greer limestone containing 5.2% S. Material and energy balances were made in order to determine how much coal would be needed for heating and reaction with the sorbent. The calculations were done for five levels of oxidizing-reducing conditions--at 50, 100, 200, 500, and 1000 kPa pressures and reaction temperatures between 1223 K and 1393 K. In each case, results are presented for the oxidizing-reducing condition which produced a maximum SO_2 concentration in the flue gas.

Case 1 is illustrated in Figs. 3 and 4. This case, presented as the baseline condition, represents the best guess of the conditions at which a full-sized facility would operate. Figure 3 demonstrates that increasing the pressure has a deleterious effect on the extent of regeneration, whereas increasing the temperature has a positive effect. The maximum extent of regeneration achievable is only about 87% because some CaS is formed at these reducing conditions. Conditions which are more oxidizing produce a higher extent of regeneration, but not as high a maximum SO_2 concentration as for

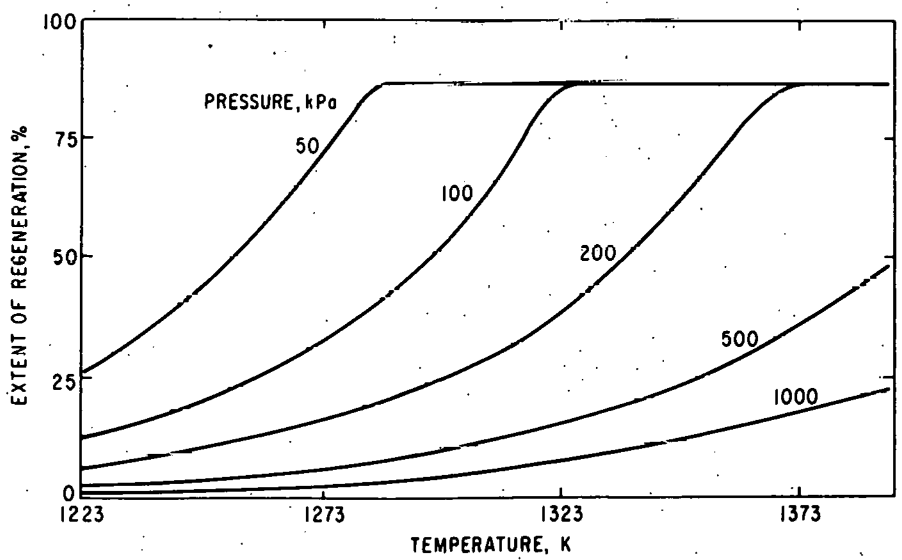

Fig. 3. Extent of Regeneration vs. Temperature and Pressure. Case 1

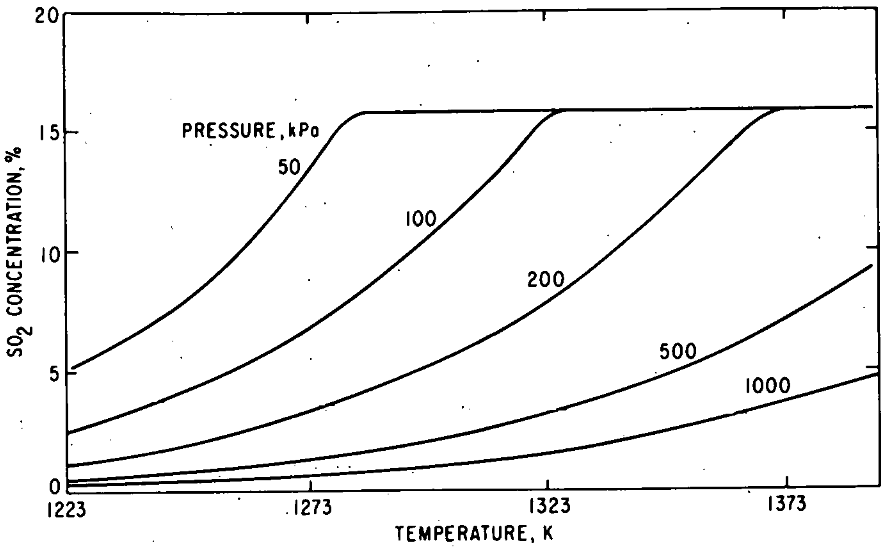

Fig. 4. SO_2 Concentration vs. Temperature and Pressure. Case 1

Case 1 because additional air (necessary to have conditions which are more oxidizing) dilutes the gas. It can be seen that the maximum extent of regeneration can be achieved at 1283 K at 50 kPa, at 1323 K at 100 kPa, and at 1373 K at 200 kPa. At 500 kPa and 1000 kPa, the maximum extent of regeneration is not achieved at temperatures of interest. A maximum SO_2 concentration of about 16% is predicted (Fig. 4).

In Case 2 there is some preheating of the gas and solids fed to the regenerator. Therefore, less coal is burned to provide the sensible heat necessary. In Fig. 5, trends for extent of regeneration in relation to temperature and pressure are the same as in Fig. 3. However, the maximum extents of regeneration at each pressure are reached at higher temperatures. Figure 6 shows that the maximum SO_2 concentration predicted for Case 2 is over 29%. Because of the higher concentrations of SO_2 (there is less dilution by combustion products), the equilibrium of the reaction presented below (a simplified view of the regeneration process)

$$CaSO_4 + CO \rightleftarrows CaO + SO_2 + CO_2$$

is driven to the left. To drive the reaction further to the right, a higher temperature is necessary. Maximum extent of regeneration at 50 kPa is not reached till 1323 K and is not reached at 100 kPa till 1373 K. At 200, 500, and 1000 kPa, the maximum extent of regeneration is not achieved at the temperatures of interest.

To illustrate an important point, Figs. 4 and 6 may be compared. At 50 kPa, the maximum SO_2 concentration is thermodynamically limited below 1283 K and material balance limited (i.e., by the concentration of inerts) above 1283 K (Fig. 4). At a given pressure, thermodynamic limitations apply at temperatures below the point of inflection (the point at which the curve becomes

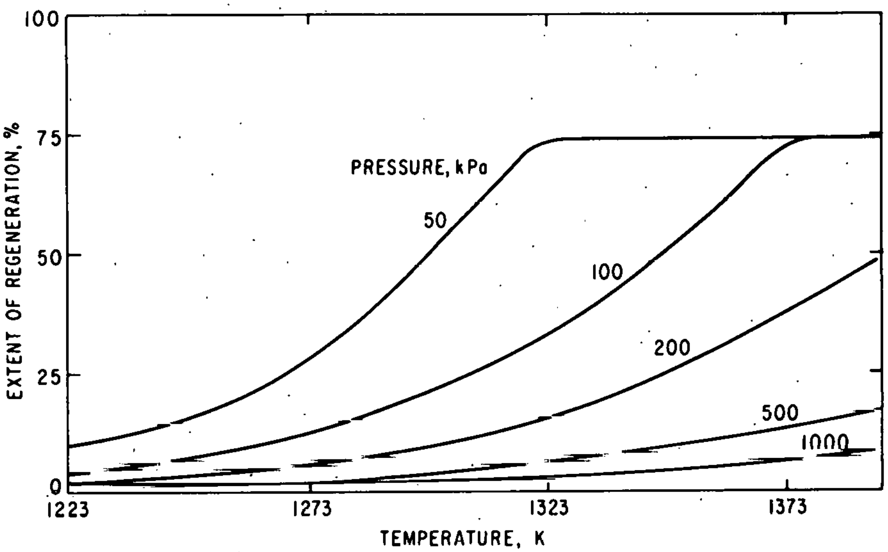

Fig. 5. Extent of Regeneration vs. Temperature and Pressure. Case 2

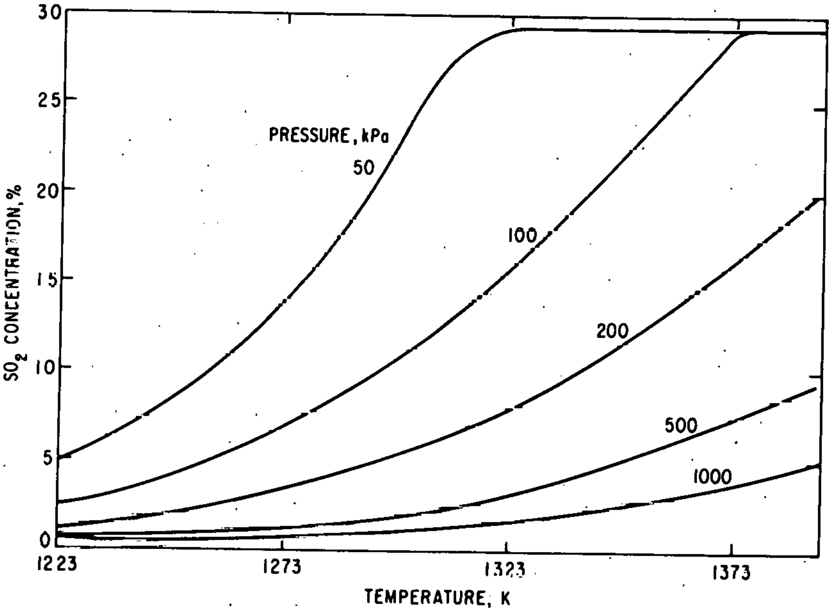

Fig. 6. SO_2 Concentration vs. Temperature and Pressure. Case 2

parallel to the x axis) and above this temperature, material balance limits apply. Therefore, at a given pressure, for a temperature of concern below the inflection point in both Figs. 4 and 6, the SO_2 concentration will be the same under both conditions. For example, at a pressure of 100 kPa and a temperature of 1313 K, a SO_2 concentration of 13.5% is predicted for both

Condition 1 (Fig. 4) and Condition 2 (Fig. 6). Where thermodynamic limitations apply, this will be true at all conditions postulated. To generalize, at a given temperature and pressure, the SO_2 concentration will be identical for all cases that are thermodynamically limited.

In Case 3, the solids feed and gas feed temperatures are the same as in Case 1 (solids feed 1116 K; gas feed, 672 K). However, instead of air (21% oxygen) being used as the feed gas, pure oxygen is employed. Since no nitrogen is present, there is less flue gas dilution. Figure 7 shows the extent of regeneration versus temperature and pressure at these conditions. It may be noted that the maximum extent of regeneration approaches 100% at 50 and 100 kPa. This is not peculiar to Case 3.

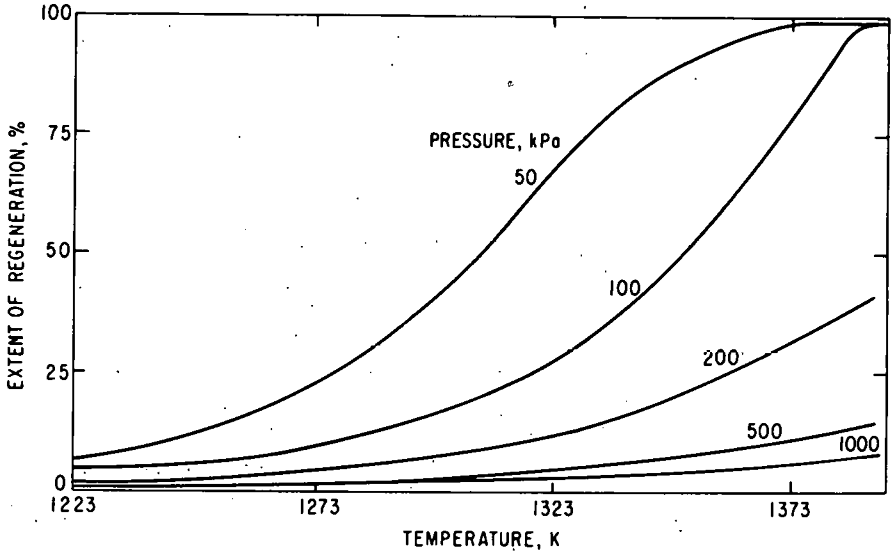

Fig. 7. Extent of Regeneration vs. Temperature and Pressure. Case 3

In other cases, the oxidizing-reducing conditions which resulted in maximum extent of regeneration did not result in a maximum SO_2 concentration. However, in Case 3, the maximum concentration of SO_2 and the maximum extent of regeneration were obtained at the same oxidizing-reducing conditions. The maximum extent of regeneration is not reached until 1353 K at 50 kPa and not until 1393 K at 100 kPa. At 200 kPa, 500 kPa, and 1000 kPa, the maximum extent of regeneration is not achieved at the temperatures of interest. Figure 8 predicts a maximum SO_2 concentration of about 40%. In Case 4, the feed solids and feed gas are both preheated to 1373 K, and the feed gas consists of 100% oxygen. It can be seen in Fig. 9 that maximum extent of regeneration at 50 kPa is achieved when the temperature rises to 1373 K but is not achieved at 100, 200, 500, and 1000 kPa at the temperatures of interest. A maximum SO_2 concentration of about 50% is predicted in Fig. 10.

As the analysis proceeds from Case 1 through Case 4, the predicted maximum concentration of SO_2 increases. At the same time, the concentration of dilution gases (primarily the N_2 associated with combustion air) decreases.

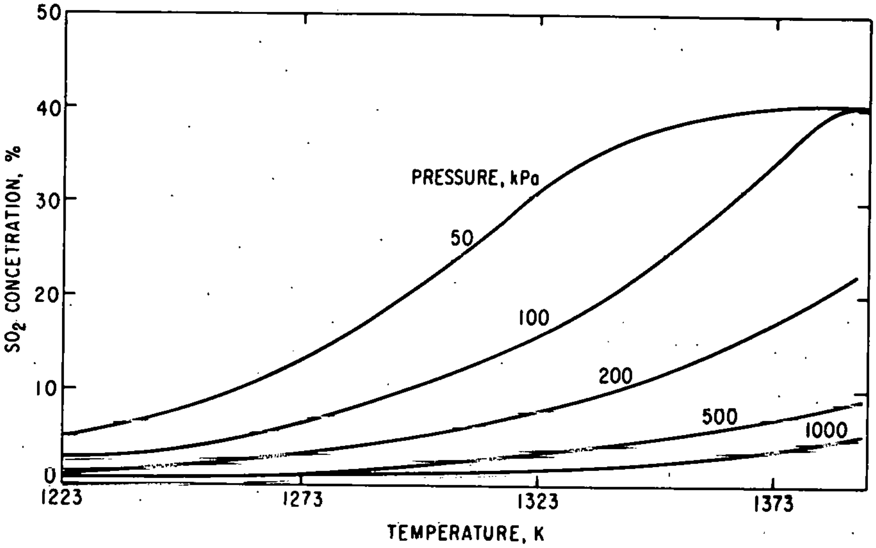

Fig. 8. SO$_2$ Concentration vs. Temperature and Pressure. Case 3

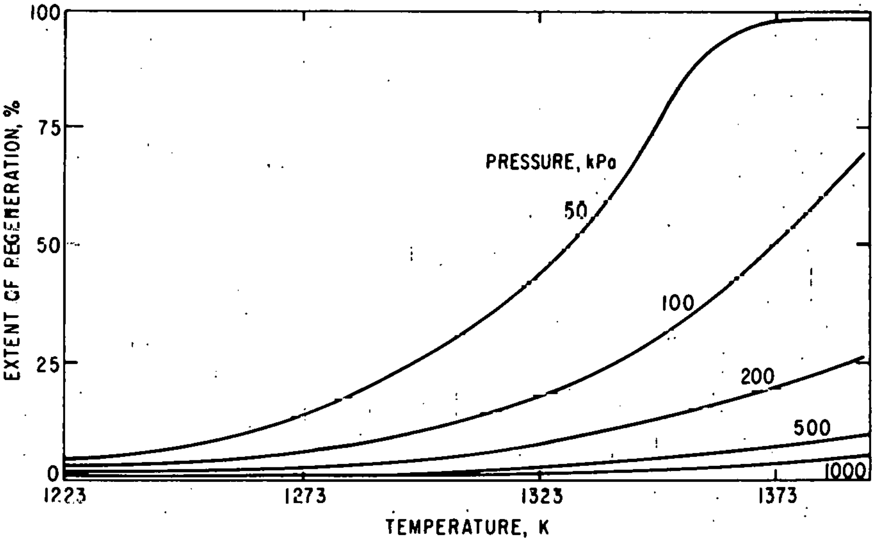

Fig. 9. Extent of Regeneration vs. Temperature and Pressure. Case 4

Therefore, higher temperatures are necessary to drive the reaction towards completion and to produce these higher concentrations of SO$_2$ and CO$_2$ (possible only when there is less dilution). Therefore, at a given pressure, a much higher temperature is necessary in Case 4 to get an extent of regeneration equivalent to that in Case 1.

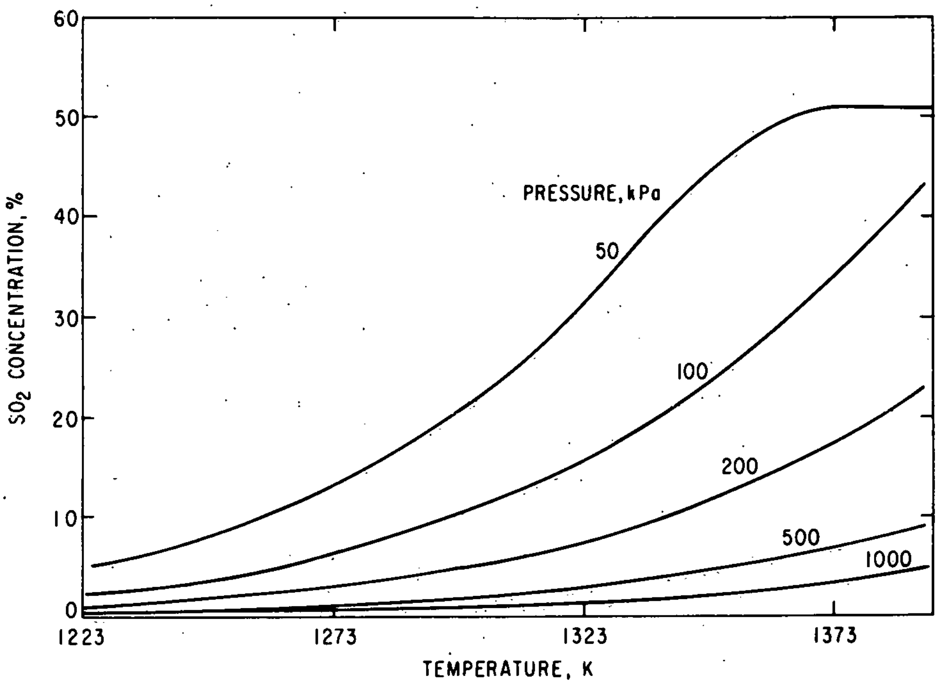

Fig. 10. SO_2 Concentration vs. Temperature and Pressure. Case 4

Further work will be concerned with analyzing experimental data to see how closely thermodynamic equilibrium is approached and with developing a general scheme for determining the maximum extent of regeneration and SO_2 concentration obtainable with a given regeneration system configuration.

TASK B. SULFUR RECOVERY PROCESS STUDIES

1. Reducing Sulfated Limestone with Coal to Produce Elemental Sulfur

(D. S. Moulton, E. B. Smyk, and C. A. Froelich*)

a. Introduction

Many processes for producing sulfur from SO_2 are described in the voluminous literature on sulfur production, but most are not readily applicable to the fluidized-bed combustor system. In such a system, the lime sorbent from a combustor, containing concentrated sulfur, would be regenerated in a sulfur production process. Figure 11 shows a general processing scheme with the maximum number of steps believed necessary and indicates that coal would be used as the reducing agent and for process heat for both regeneration and conversion of SO_2 to sulfur. Sulfur producing processes which require substantially more processing steps than are indicated in Fig. 11 are outside the scope of this discussion.

Regeneration processes under development at ANL produce a stream containing 8-15% SO_2. There are some problems if SO_2 is directly reduced with coal; alternatives include the use of coal gas and the use of coke.

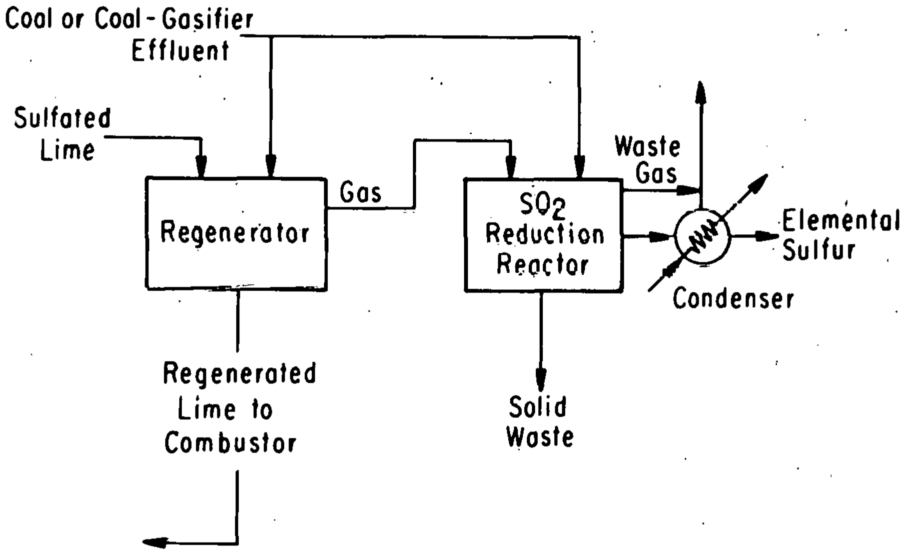

Fig. 11. Schematic of a General Form of Processing to Regenerate Sorbent and Produce Sulfur

b. SO_2 Reduction Using Coal

Reduction with coal has recently been developed as part of the Bergbau-Forschung/Foster Wheeler process. A stream containing SO_2 and steam

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*Undergraduate research associate

enters the bottom of a coal bed at 600-650°C[5] 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.[5,6]

Operating parameters control the product composition. As shown in Fig. 12, overall conversion of SO_2 increases with increasing steam content;[7] 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,[8] the gas residence time is 3-8 s, and the coal residence time is 12 to 20 h.

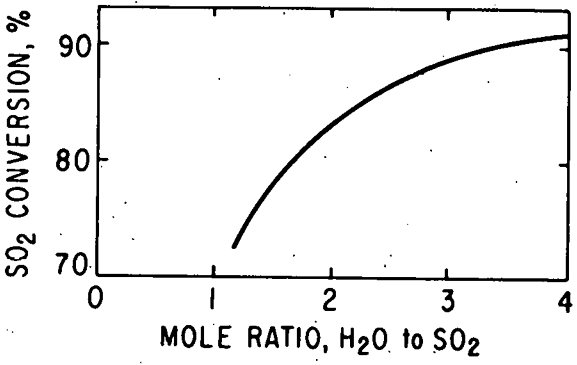

Fig. 12.

Relationship between Sulfur Dioxide Conversion to Sulfur and the Water to Sulfur Dioxide Ratio. All other parameters are constant. After Steiner[7]

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.

$$C + SO_2 = CO_2 + 1/2\ S_2 \tag{1}$$

$$C + H_2O = CO + H_2 \tag{2}$$

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

$$2CO + SO_2 = 1/2\ S_2 + 2CO_2 \tag{3}$$

$$2H_2 + SO_2 = 1/2\ S_2 + 2H_2O \tag{4}$$

Foster Wheeler uses a 2 to 1 steam to SO_2 ratio, but this high a ratio may be largely due to water originating from their upstream adsorption process.[8]

Anthracite coal is used for the reduction. The advantages include the following:

1. Swelling and caking problems are minimized.
2. The anthracite volatile content, which contributes impurities to the sulfur product, is low.

3. Anthracite coal or coal ash may possess a catalytic effect.

Other coals can be used if they are first devolatilized.[8,9]

Coke was used as an SO_2 reductant for many years because the direct use of coal had some disadvantages. Anthracite coal was not universally available, and other coals caused product impurities. An alternative to direct reduction with coal, which avoids the expense of making coke, is (1) coal gasification and (2) SO_2 reduction with coal gas in separate reactors, with both of these reactors operated at optimum conditions so that better overall kinetics are possible. This procedure would require a catalyst (section d below), and both the SO_2 stream and the coal gas might require cleanup before reduction. The simplicity of direct reduction with coal is a great advantage, but where anthracite is unavailable, separate coal gasification and SO_2 reduction reactors may be the preferred route.

c. Coal Gasification

Several coal gasification processes are 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.[10,11] 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.[12] 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:

$$CH_4 + 2SO_2 = 2H_2O + CO_2 + S_2 \tag{5}$$

$$2H_2S + SO_2 = 2H_2O + 3/2\ S_2 \tag{6}$$

Other reactions occur, forming small amounts of undesirable products:

$$H_2 + 1/2\ S_2 = H_2S \tag{7}$$

$$H_2O + 1/4\ S_2 = H_2 + 1/2\ SO_2 \tag{8}$$

$$CO + 1/2\ S_2 = COS \tag{9}$$

$$CO_2 + 2H_2S = CS_2 + 2H_2 \tag{10}$$

$$2CO + S_2 = CS_2 + CO_2 \tag{11}$$

$$CO_2 + H_2S = COS + H_2O \tag{12}$$

$$2CO_2 + 3S = SO_2 + 2COS \tag{13}$$

$$H_2S + (x-1)S = H_2S_x \tag{14}$$

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[13] 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.[14] 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. 13). The optimum composition was especially effective for dilute reactant streams.

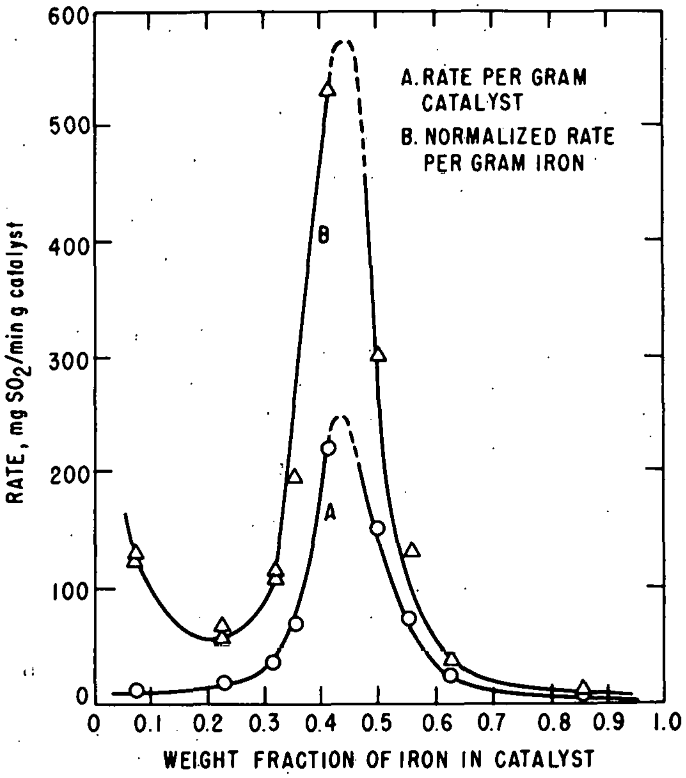

Fig. 13. Carbon Monoxide Reduction of SO_2. Dependence of SO_2 removal rate at 500°C on iron-alumina catalyst composition. From Haas et al.[14]

George[15] showed that the Claus reaction is catalyzed by bases in the activity order, Li > Na > K. It has been well established by Peri[16,17] 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[18] 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. The desirable characteristics of an SO_2 reduction catalyst include the following:

1. Metal sulfide, commonly iron
2. Strong base
3. High surface area (discussed below).

e. Reduction with Hydrogen

Lepsoe,[19] in 1938, presented a comprehensive thermodynamic treatment for reactions 3 through 11 with equilibrium constants for stoichiometric conditions. Doumani et al.[20] also published thermodynamic data on hydrogen reduction of SO_2 and described a process. A more recent analysis by Murdock and Atwood[21] included sulfur species not treated in earlier work. Their results, with Lepsoe's, are shown in Fig. 14.

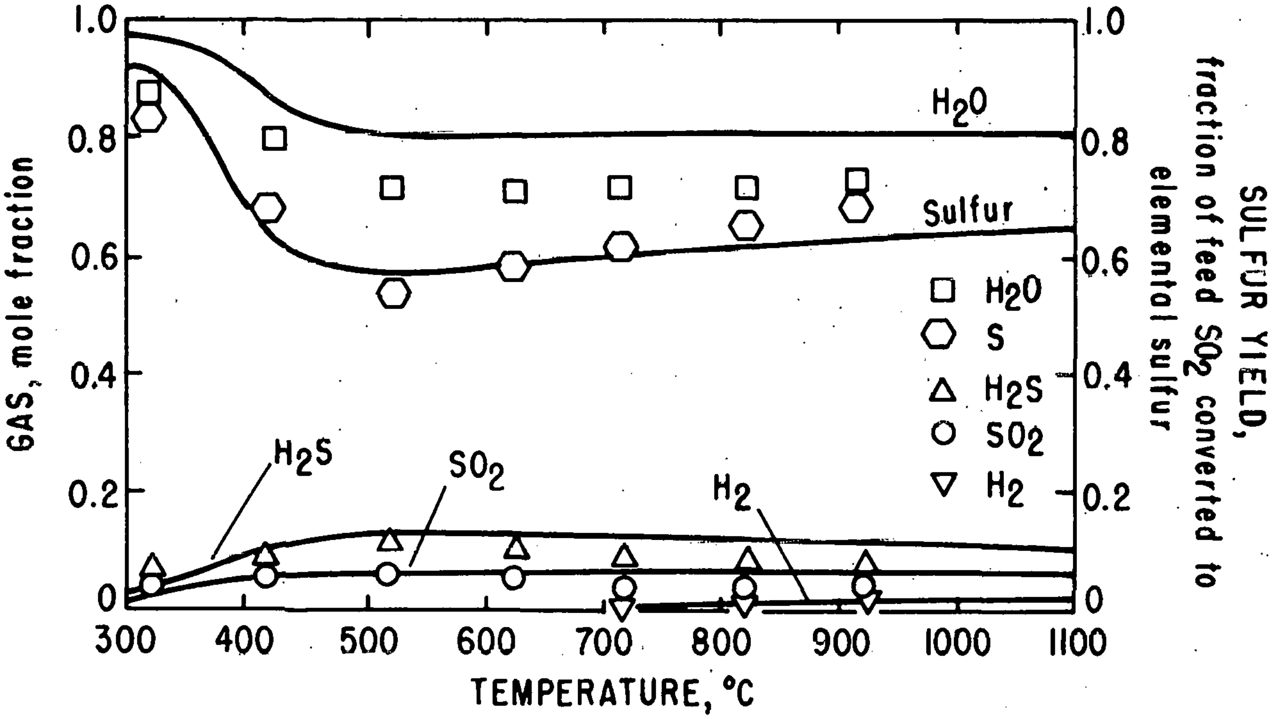

Fig. 14. Equilibrium Gas Compositions for the Reduction of SO_2 with Hydrogen at 1 atm. Symbols (calculated)--Murdock and Atwood[21]; Curves--Lepsoe.[19] Reprinted with permission from Ind. Eng. Chem. Process Des. Dev. 13(3), 254 (1974). Copyright by the American Chemical Society.

Murdock and Atwood[21] 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 $$K_{H_2S} = 1.5\text{x}10^{8}\ \frac{\text{mol}}{(\text{g of cat.})\cdot\text{h}\cdot\text{atm}}\ \exp\ -\ \frac{34.3\ \text{kcal/mol K}}{RT}$$

For large values of space time, a more accurate but much more complex expression was obtained by Hsieh and Atwood.[22]

f. Reduction with Carbon Monoxide

In addition to Lepsoe's work,[19] others[20,23] have published thermodynamic data for reactions 3 and 9. Maadah and Maddox[24] and Kerr[25] 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[26] give equilibrium compositions of CO for dilute conditions with and without water (Fig. 15).

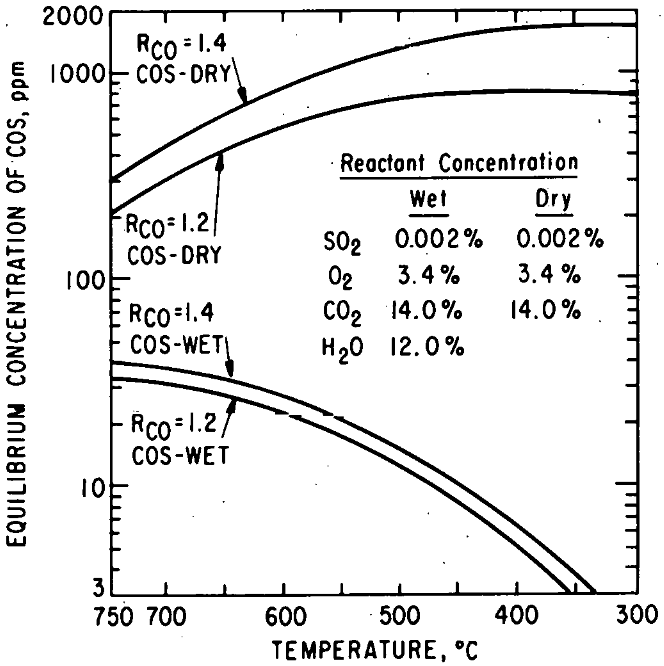

Fig. 15. Equilibrium Concentration of COS with and without Water in the Reaction System. $R_{CO} = (P_{CO} - P_{O_2})/2P_{SO_2}$. After Okay and Short.[26] Reprinted with permission from Ind. Eng. Chem. Process Des. Dev. 12(3), 291 (1973). Copyright by the American Chemical Society.

Rate data are available for several catalysts used for reduction with carbon monoxide. Haas et al.[14] published rate data for several compositions of iron/alumina catalyst, as shown in Fig. 16 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[26] and Wynn[27] obtained kinetic data for alumina catalysts with dilute SO_2 feeds, and Ryason and Harkins[28] obtained kinetic data with copper, silver, palladium, manganese, and nickel catalysts; they concluded that copper is the best.

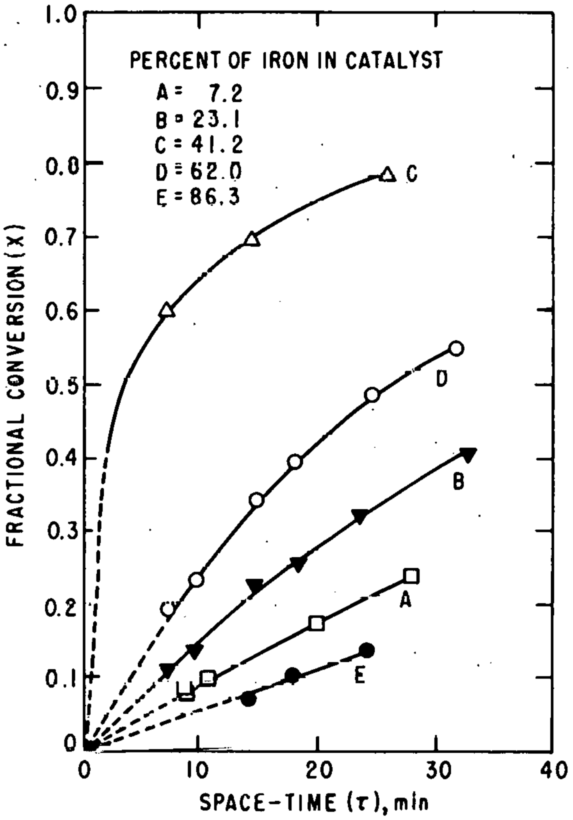

Fig. 16.

Carbon Monoxide (10% CO, 5% SO_2) Reduction of SO_2. Rate data for various iron/alumina catalyst compositions. From Haas et al.[14]

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.[21,29] 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[29] published kinetic data on the hydrolysis of COS over cobalt molybdate, and Bazes et al.[30] 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[31] found evidence that COS is a reactive intermediate when the iron/ alumina catalyst is used. Happel et al.[32] 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[33] 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.[26,34]

g. 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

h. Reduction with Hydrogen Sulfide

Lepsoe[19] and Doumani et al.[20] included H_2S in their thermodynamic work. Other authors[23-25,36] have made computer studies of extensive lists of reactions and have successfully predicted Claus plant product mixtures.

Kerr et al.[37] 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[29] 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 components, although a higher temperature may be required to utilize methane than for the other gases.[12,35]

i. 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[38] gives the following average analysis of U.S. coal ash determined by the Bureau of Mines.

Compound	%
SiO_2	45.7
Al_2O_3	26.0
Fe_2O_3	18.1

Silica has little catalytic value, but the alumina and iron oxide are important. In addition, bases such as calcium, magnesium, sodium, and potassium oxides (which are prominent ash constituents) have catalytic value. Kaakinen et al.[39] 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[40] found surface areas of only about 5 m^2/g; 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, and bauxite also has quite high surface area. Ash probably could not be used directly as the catalyst unless some process modification such as incomplete or low-temperature gasification would yield an ash with better surface properties while retaining other good catalytic properties. This is a possibility. A major cost in the Foster Wheeler system is for makeup carbon used in the flue gas SO_2 adsorber. Beckman[41] reported that incompletely consumed anthracite coal from the SO_2 reduction reactor had good adsorption properties and was being tested for use in the flue gas SO_2 adsorber.

j. 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[19] discussed the thermodynamics of SO_2 reduction with coke.

Cokes vary greatly in reactivity, with nonmetallurgical cokes generally better.[42] Lepsoe[19] 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[43] 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. 17). In addition, they investigated the effects of individual ash constituents in "synthetic" cokes; each such coke contained only one ash constituent. A 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 with SO_2:

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

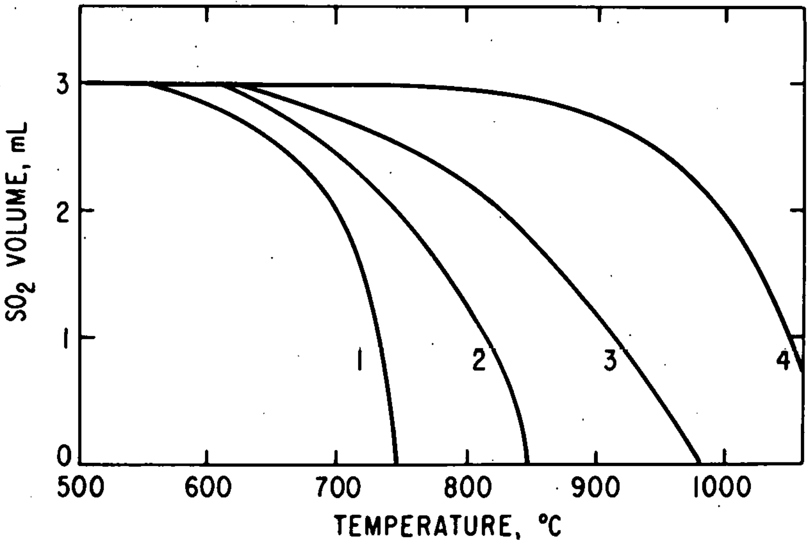

Fig. 17. Reactivity of Prepared Carboniferous Materials (in terms of mL of unconverted SO_2 remaining from a 3-mL dose). 1 - metallurgical coke, 14.3% ash; 2 - 'Stampfmasse', 7.9% ash; 3 - petroleum coke, ('Pechkoks'), 0.5% ash; 4 - Spectrally pure carbon, 0.0006% ash. Specific surface area ranged from 0.7 m^2/g ('Stampfmasse') to 1.3 m^2/g (spectrally pure carbon). After Macak and Pick.[43]

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 $r_2, r_3 \simeq r_1$

Group 3: r_2 or $r_3 = 0$

Of the substances found to enhance coke reactivity when incorporated into coke, iron is a well-known reduction catalyst; calcium and magnesium are expected to have reduction catalytic activity because of their basicity. It would be of interest to know if any of these substances would enhance the reactivity of coke or coal when they were only physically mixed together--for example, in a fluidized bed.

k. 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. 18).[44] Near the condensation point, sulfur vapor consists of S_8 rings. This causes sulfur to have an unusual temperature-vapor pressure relation. Meyer[44] gives equilibrium vapor pressures in Table 5. Mist can form in the condenser, but Sawyer et al.[45] report that the loss was 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

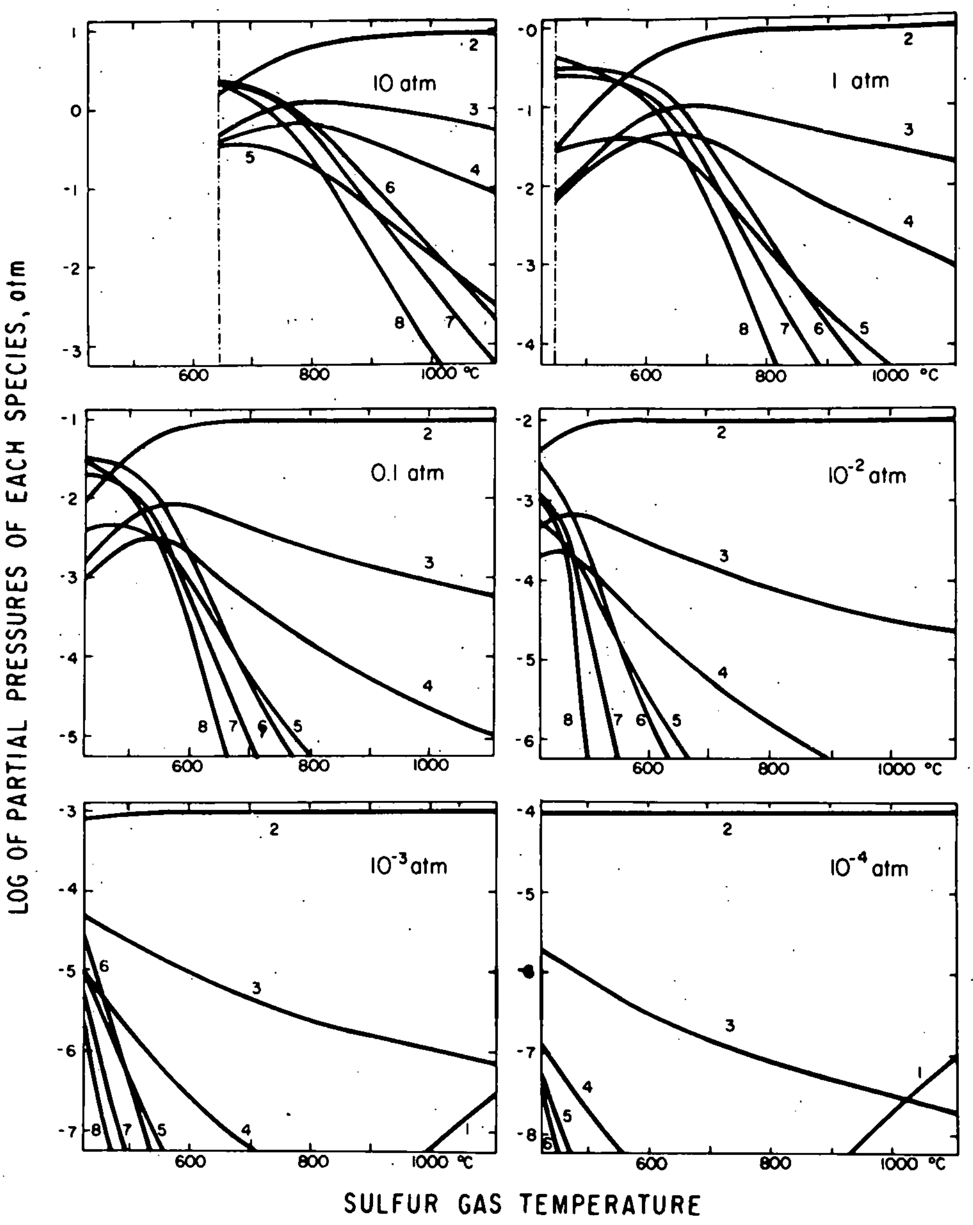

Fig. 18. Partial Pressures of Sulfur Species at Six Pressures (after Rau, 1976). From Meyer.[44] Each number on a curve refers to the number of sulfur atoms per molecule. At the upper right of each graph is the system vapor pressure in atmospheres.

187°C. For this reason, sulfur processors avoid temperatures between 170°C and 230°C.[34] The vapor pressure increases sharply above 230°C and so for efficient collection, careful temperature control is also necessary above 230°C.

Table 5. Equilibrium Vapor Pressures of Elemental Sulfur at Various Temperatures[44]

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

1. Regeneration/Sulfur Production Schemes

Perhaps the simplest regeneration scheme would be to put sulfated lime and coal into a reactor and to get out regenerated lime and a gas stream containing elemental sulfur and carbon dioxide. Computer thermodynamic calculations indicate that this would be possible but very difficult. For example, if $CH_{0.83}$ is selected as a carbon to hydrogen ratio typical of coal (the value for Sewickley coal) and if it is assumed that the sulfated lime contains sufficient $CaCO_3$ to maintain the equilibrium pressure of CO_2, the following reactions apparently limit S_2 production:

$$CaCO_3 = CaO + CO_2$$

$$CO_2 + CH_{0.83} = 2CO + 0.415\ H_2$$

$$H_2 + CO_2 = CO + H_2O$$

$$CO_2 + CaS = COS + CaO$$

$$COS = CO + 1/2\ S_2$$

Table 6 gives the thermodynamic equilibrium mole fractions in atmospheres for a total system pressure of 5 atm. The S_2 pressures given in Table 6 should be divided by four to get the S_8 partial pressures corresponding to condensation conditions. Comparison with Table 5 shows that some of the sulfur formed could be condensed out. 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 (900-1000°C) and sulfur condensation (about 130°C) would be costly and only a small fraction would be condensed out of the gas stream.

Table 6. Thermodynamic Equilibrium Mole Fractions in the Gas Phase for Direct Reduction of Sulfated Lime with Sewickley Coal. Total system pressure, 5 atm. Pressures in 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

Since the gas stream from a reaction 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 this source. The gas stream would be partially cooled, then allowed to react catalytically before entering a sulfur condenser. The equilibrium gas composition at 950°C (Table 6) 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 7. The sulfur content would still be very low because with so much hydrogen in the mix, the SO_2 would convert to H_2S.

Table 7. Thermodynamic Equilibrium Mole Fractions in Gas Phase for a Regenerator Off-Gas. Pressures in 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. 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. 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 nonequilibrium reactor. In conclusion, combined lime regeneration and elemental sulfur production is not practical because of thermodynamic constraints.

TASK D. CORROSION STUDIES

1. Effects of Limestone Sulfation Accelerators on Corrosion Rates of Metals in an AFBC

(J. F. Lenc, G. W. Smith, R. W. Mowry, F. G. Teats, F. F. Nunes,
S. D. Smith, and A. R. Pumphrey)

This investigation of corrosion rates is related to laboratory-scale work under way to increase the degree of sulfation of partially sulfated lime solids in a fluidized-bed combustor by means of additives (i.e., sulfation accelerators or enhancers). Sulfation enhancers such as NaCl, $CaCl_2$, and Na_2CO_3 added in small amounts to the lime solids increase both the rate and the extent of sulfation for many limestones. With increased SO_2 capacity of limestone, the quantity of lime solids required for the combustion process would be decreased. Such a decrease would lower the process cost and would reduce the environmental impact of solid waste disposal. However, there is concern that volatilization of these sulfation enhancers (alkali metal compounds) might cause unacceptable corrosion of the metal components of the combustion system. A separate laboratory-scale investigation of the corrosiveness of salts mixed with sulfated limestones is in progress.[46]

To measure the corrosion rates of metals of construction in the presence of sulfation enhancers in a PDU-scale unit, a new automated atmospheric-pressure fluidized-bed coal combustion facility (AFBC) was designed and constructed. The facility, including its automatic control system, was described in ANL/CEN/FE-78-13.

Before corrosion experiments were conducted in the new system, the effects on SO_2 retention of adding low concentrations (1.0 mol % or less) of $CaCl_2$ or NaCl were evaluated in a series of runs.

In this series of runs, Sewickley coal (either -6 +100 mesh or -12 +100 mesh) was combusted at a bed temperature of 850°C, a pressure of 101.3 kPa (1 atm), a fluidizing-gas velocity of 1 m/s, and a fluidized-bed height of 813 mm, with 3% O_2 in the dry off-gas. The above variables were maintained at the values stated in all of the runs; only the composition of the sorbent and the Ca/S mole ratio were altered. In all runs, Grove limestone (-10 +30 mesh), with or without $CaCl_2$ or NaCl addition, was the sorbent used.

A total of 31 runs were conducted in this series at Ca/S mole ratios ranging from 1.0 to 4.4. The percent sulfur retention and the percent calcium utilization for each of the 31 runs as a function of the $CaCl_2$ or NaCl concentration in the sorbent and the Ca/S mole ratios are listed in Table 8.

Three concentrations (∿0.1, ∿0.3, and ∿0.5 mol %) of $CaCl_2$ and two concentrations (∿0.5 and ∿1.0 mol %) of NaCl added to the Grove limestone were evaluated. Two methods were used to prepare the $CaCl_2$ or NaCl-containing Grove limestone. In the first method, which was used for preparing nominal 0.1 and 0.5 mol % $CaCl_2$ and nominal 0.5 and 1.0 mol % NaCl material, a batch of Grove limestone particles was spread in a shallow stainless steel tray. The particles were then sprayed with a water solution containing the weight

Table 8. Runs to Evaluate the Effects of CaCl$_2$ or NaCl Addition on Sulfur Retention of Grove Limestone (No. 1359)

Run Designation	Ca/S Mole Ratio	SO$_2$ in Off-Gas, ppm[a]	Sulfur Retention,[b] %	Calcium Utilization,[c] %
Grove limestone (1359) with no CaCl$_2$ or NaCl addition				
SAL-1A2	1.3	2200	37.1	28.5 (76.9)
SAL-9[d]	1.4	2100	40.0	28.6 (71.4)
SAL-11C1	2.1	1300	72.9	34.7 (47.6)
SAL-13	2.4	750	84.4	35.2 (41.7)
SAL-1B	2.6	1300	62.9	24.2 (38.5)
SAL-12	2.8	750	84.4	30.1 (35.7)
SAL-8[d]	3.0	450	87.1	29.0 (33.3)
SAL-11C2	3.4	700	85.4	25.1 (29.4)
SAL-10[d]	3.6	500	85.7	23.8 (27.8)
Grove limestone (1359) plus about 0.1 mol % CaCl$_2$[e]				
SAL-2B2	1.0	2300	34.3	34.3 (100)
SAL-2B1	1.6	1700	51.4	32.1 (62.5)
SAL-2A	2.6	1000	71.4	27.5 (38.5)
SAL-15	2.8	950	80.2	28.6 (35.7)
SAL-14	2.9	900	81.2	28.0 (34.5)
SAL-7[d]	3.0	450	87.1	29.0 (33.3)
SAL-6[d]	4.2	450	87.1	20.7 (23.8)
Grove limestone (1359) plus about 0.3 mol % CaCl$_2$[f]				
SAL-16A	1.2	2500	47.9	39.9 (83.3)
SAL-19	2.4	800	83.3	34.7 (41.7)
SAL-18	3.3	900	81.2	24.6 (30.3)
Grove limestone (1359) plus about 0.5 mol % CaCl$_2$[e]				
SAL-3B	1.4	1800	48.6	34.7 (71.4)
SAL-3A	1.9	1250	64.3	33.8 (52.6)
SAL-4	3.0	700	80.0	26.7 (33.3)
SAL-5	4.4	300	91.4	20.8 (22.7)

(contd)

Table 8. (contd)

Run Designation	Ca/S Mole Ratio	SO_2 in Off-Gas, ppm[a]	Sulfur Retention, %[b]	Calcium Utilization, %[c]
Grove limestone (1359) plus about 0.5 mol % NaCl[e]				
NAC-1	1.3	1800	62.5	48.1 (76.9)
NAC-3	2.2	1550	67.7	30.8 (45.4)
NAC-4	3.0	1100	77.1	25.7 (33.3)
NAC-2A	3.2	1400	70.8	22.1 (31.2)
Grove limestone (1359) plus about 1.0 mol % NaCl[e]				
NAC-8	1.3	2000	58.3	44.8 (76.9)
NAC-5	1.4	2400	50.0	35.7 (71.4)
NAC-6	2.0	1300	72.9	36.4 (50.0)
NAC-7	3.5	900	81.2	23.2 (28.6)

[a] Dry basis.

[b] Based on 3500 ppm SO_2 in dry off-gas if there had been zero sulfur retention for runs designated SAL-1 through SAL-10, inclusive, and 4800 ppm SO_2 in dry off-gas if there had been zero sulfur retention for the other runs. Sewickley coal (4.33% S, 70.75% C, heating value of 13018 Btu/lb, -6 +100 mesh) was used in runs SAL-1 through SAL-10, inclusive. Sewickley coal (5.46% S, 64.88% C, heating value of 11969 Btu/lb, -12 +100 mesh) was used in the remaining runs.

[c] Percentage of available calcium in the sorbent converted to $CaSO_4$. Number in parentheses indicates maximum percent calcium utilization based on the Ca/S mole ratio (reciprocal of the Ca/S mole ratio).

[d] This run was conducted following a run made with a higher $CaCl_2$ concentration in the sorbent.

[e] $CaCl_2$ or NaCl was added to the sorbent by a spraying method (see the text).

[f] $CaCl_2$ was added to the sorbent by a soaking method (see the text).

of $CaCl_2$ or NaCl that would give the desired concentration after evaporation of the water by air drying. In the second method, which was used for preparing nominal 0.3 mol % $CaCl_2$ material, a batch of Grove limestone particles was soaked in a heated water solution containing $CaCl_2$ in excess of that required to obtain the desired concentration. After soaking, excess $CaCl_2$ solution was drained from the limestone particles through a screen. The particles were then oven-dried at 232°C to evaporate residual water.

Examination of the data presented in Table 8 indicates that in this series of runs, sulfation enhancement due to the addition of the $CaCl_2$ or NaCl to Grove limestone sorbent was generally less than that obtained in previously reported laboratory-scale experiments.[47] For example, with 0.5% NaCl addition, calcium utilization was 22-48% in these runs and 52% in a laboratory-scale run; with 1% NaCl addition, calcium utilization was 23-45% in these runs and 45% in a laboratory-scale run. It is suspected that the differences in the two sets of data are due to different manners of conducting the two series of experiments. The laboratory-scale experiments were carried out with a simulated flue gas and no actual coal combustion occurred. As a consequence, no constituents of the coal ash were present in the reactor. In contrast, combustion runs were conducted in the AFBC. Further investigations are planned to explain the disparity between the two sets of data.

To compare the performance of the new AFBC with the performance of an older atmospheric-pressure fluidized-bed combustor, a series of four runs were conducted in the new unit. In these runs, a single batch of well-mixed Sewickley coal (-12 +100 mesh) was combusted at a bed temperature of 850°C, a pressure of 101.3 kPa (1 atm), a fluidizing-gas velocity of 1 m/s, a fluidized-bed height of 813 mm, and 3% O_2 in the dry off-gas. In the four runs, the sorbent was from the same batch of well-mixed Grove limestone (-10 +30 mesh) with no $CaCl_2$ or NaCl added. The above variables were maintained at the values stated, with only the Ca/S mole ratio altered.

The percent sulfur retention and the percent calcium utilization as a function of the Ca/S mole ratio for these four runs are listed in Table 9.

Table 9. Sulfur Retentions and Calcium Utilizations for Run Series SG

Run Designation[a]	Ca/S Mole Ratio	SO_2 in Off-Gas, ppm[b]	Sulfur Retention,[c] %	Calcium Utilization,[d] %
SG-2	1.3	3310	31.0	23.8 (76.9)
SG-3	2.1	1730	64.0	30.5 (47.6)
SG-4	2.9	1030	78.5	27.1 (35.5)
SG-1	3.2	760	84.2	26.3 (31.2)

[a] SG designates runs with Sewickley coal (5.46% S) and Grove limestone (95.3% $CaCO_3$) sorbent. Run numbers indicate the chronological order of the runs.

[b] Dry basis.

[c] Based on 4800 ppm SO_2 in dry off-gas at zero sulfur retention. (Sewickley coal, 5.46% S, 64.88% C, heating value of 11969 Btu/lb, -12 +100 mesh)

[d] Percentage of calcium in the sorbent converted to $CaSO_4$. Numbers in parentheses indicate maximum calcium utilizations based on Ca/S mole ratios (numbers in parentheses are equivalent to 100 times the reciprocals of the Ca/S mole ratios).

Figure 19 is a plot of the percent sulfur retention for the four runs as a function of the Ca/S mole ratio. The plot of sulfur retentions for this series is in general agreement with that for previous atmospheric-pressure fluidized-bed combustion experiments.[48] In the latter experiments, Illinois coal was combusted in a fluidized bed of Grove limestone (No. 1359). For a Ca/S mole ratio of 3, Fig. 19 shows a sulfur retention of about 80% for the recent run series, compared with about 87% for earlier reported experiments. A major difference in the two sets of experiments was the different sulfur contents of the coals. The Sewickley coal used in the recent runs contained 5.46% S, compared with 3.7% S for the Illinois coal used in the experiments in the old atmospheric-pressure combustor.

Carbon, sulfur, and calcium material balances as well as combustion efficiencies during a 4.5-h steady state period for each of the four runs are listed in Table 10. Carbon balances ranged from 118 to 128%, sulfur balances from 78 to 101%, and calcium balances, from 96 to 114%. Combustion efficiencies ranged from 86 to 88%.

The first three 100-h corrosion test runs (CT-1, -2, and -3) were successfully conducted in the new AFBC. In these runs, Sewickley coal (-12 +100 mesh) containing 5.46% S was combusted at a bed temperature of 850°C, a pressure of 101.3 kPa (1 atm), a fluidizing-gas velocity of 1 m/s, a fluidized-bed height of 813 mm, and 3% O_2 in the dry off-gas. The sorbent was Grove limestone (-10 +30 mesh) containing 95.3% $CaCO_3$ with and without $CaCl_2$ or NaCl addition. In the first run (CT-1), the Grove limestone sorbent contained no $CaCl_2$ or NaCl. The second run (CT-2) was made with about 0.3 mol % $CaCl_2$ in the sorbent, and the third run (CT-3) with about 0.5 mol % NaCl in the sorbent. The

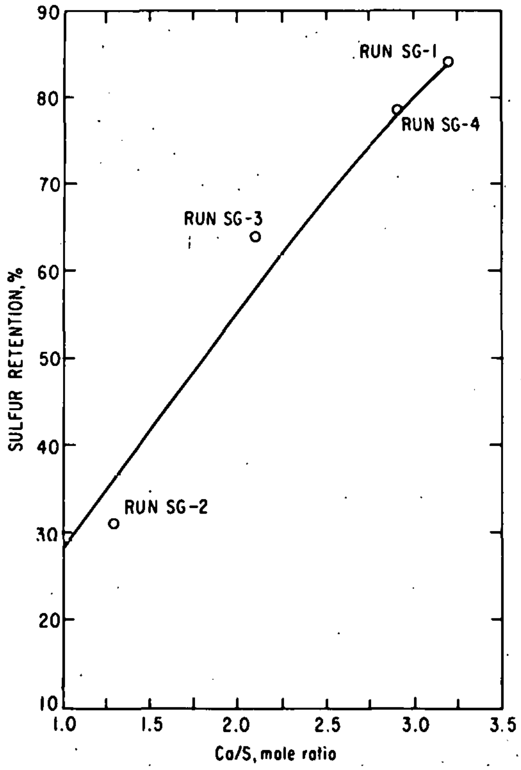

Fig. 19.

Sulfur Retention by Grove Limestone as a Function of Ca/S Mole Ratio. Temperature, 850°C; pressure, 101.3 kPa (1 atm); gas velocity, 1 m/s; coal, Sewickley (5.46% S), -12 +100 mesh; sorbent, Grove limestone (No. 1359, 95.3% $CaCO_3$, -10 +30 mesh).

Table 10. Carbon, Sulfur, and Calcium Material Balances and Combustion Efficiencies for 4.5-h Steady State Periods of SG Runs

Experimental Conditions

Temperature: 850°C
Pressure: 101.3 kPa
Gas Velocity: 1 m/s
Fluidized-Bed Height: 813 mm
Excess O_2: 3% (Dry off-gas)

Run Designation[a]	Ca/S Mole Ratio	Percent Accounted for			Combustion Efficiency,[b] %
		Carbon	Sulfur	Calcium	
SG-1	3.2	120	78	96	88
SG-2	1.3	118	101	114	88
SG-3	2.1	128	89	100	87
SG-4	2.9	127	93	99	86

[a] SG designates runs with Sewickley coal containing 5.46% S (-12 +100 mesh) and Grove limestone (No. 1359) sorbent containing 95.3% $CaCO_3$ (-10 +30 mesh).

[b] Defined as the percentage of total combustible carbon fed that was completely burned to CO_2.

Ca/S mole ratio in each of the three runs was adjusted to maintain about 700 ppm SO_2 in the dry off-gas in order to meet the EPA emission standard of 0.5 g SO_2/MJ (1.2 lb $SO_2/10^6$ Btu).

Seven corrosion probes, each holding seven metal specimens, were installed at various locations in the bed and freeboard sections of the combustor in each run. Three of the probes were of the air-cooled type shown schematically in Fig. 20. The four remaining probes were of the uncooled coupon type shown schematically in Fig. 21. Tables 11, 12, and 13 list the types of metal specimens, their locations, and the temperatures for each of the seven corrosion test runs.

The temperature of the air-cooled probe located in the freeboard section (Probe AC-3) was intended to be controlled at 649°C (1200°F) during the 100-h test runs. However, the highest actual temperature of this probe (observed in Run CT-3) was only 655°C (1211°F), and so no coolant air was used for this probe in the three runs.

Except for minor problems during the three 100-h corrosion test runs, performance of the new AFBC facility was very satisfactory. These problems were such that operating personnel were able to correct them without prematurely terminating any of the three runs. Methods of eliminating these problems in future tests are being investigated.

The Ca/S mole ratios required to maintain about 700 ppm SO_2 in the dry off-gas during each of the three 100-h corrosion test runs are presented in Table 14. Based on the Ca/S mole ratios listed in this table, it appears

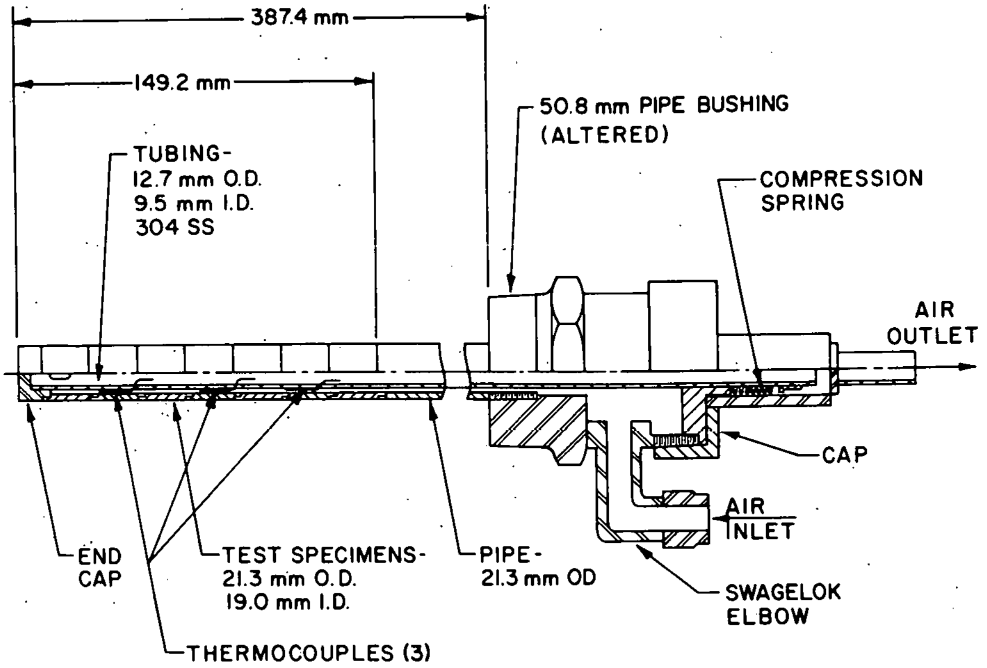

Fig. 20. Schematic of Air-Cooled Corrosion Probe. The test specimens (i.e., rings) form the outer tube of the probe.

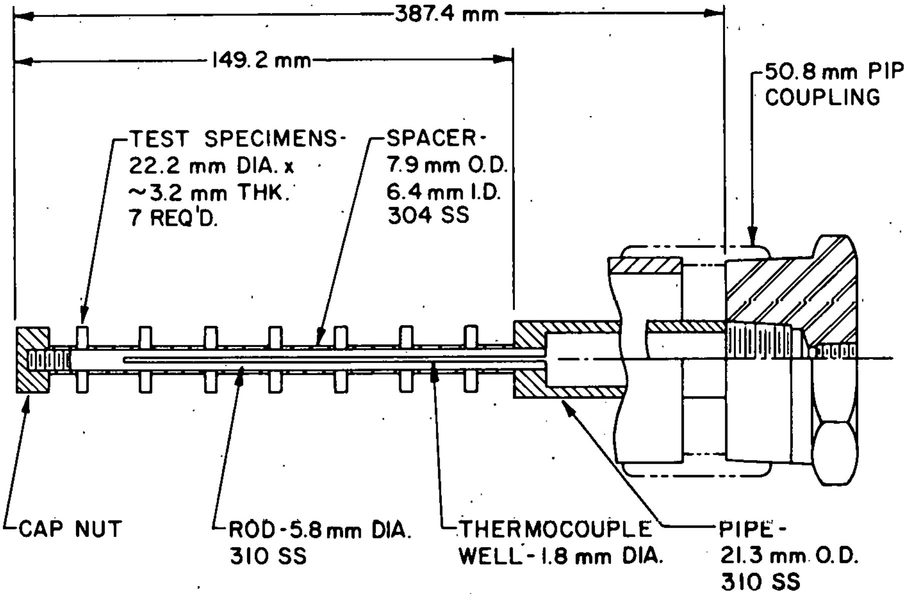

Fig. 21. Schematic of Uncooled, Coupon-Type Corrosion Probe

Table 11. Metal Types, Locations, and Temperatures of Corrosion Specimens for Run CT-1

Corrosion Probe Designation[a]	Metal Corrosion Specimens	Corrosion Probe Location	Temperature, °C
		<u>Bed Section</u>	
AC-1	304 SS, 309 SS, 316 SS, Incoloy 800, 2 1/4 Cr-1 Mo Steel, 9 Cr-1 Mo Steel, 446 Steel	50 cm above gas distributor plate	685-715
AC-2	Inconel 601, Inconel 617, RA 333, 309 SS, 310 SS, 321 SS, Incoloy 800	30 cm above gas distributor plate	660-720
C-1	Haynes 188, Inconel 601, Inconel 671, Hastelloy-X, RA 333, 310 SS, 347 SS	10 cm above gas distributor plate	840
C-2	Inconel 617, Inconel 625, Inconel 718, 304 SS, 310 SS, 316 SS, Incoloy 800	60 cm above gas distributor plate	840
		<u>Freeboard Section</u>	
AC-3[b]	Inconel 601, Inconel 617, RA 333, 309 SS, 310 SS, 321 SS, Incoloy 800	100 cm above top of bed	635
C-3	Haynes 188, Inconel 601, Inconel 617, Inconel 671, Hastelloy-X, RA 333, 310 SS	131 cm above top of bed	605
C-4	Haynes 188, Alloy 713 C, Inconel 738, 304 SS, 310 SS, 347 SS, Incoloy 800	39 cm above top of bed	670-675

[a] AC designates air-cooled probe.
C designates coupon probe, not cooled.

[b] No coolant air was required for this probe.

that the addition of either $CaCl_2$ or NaCl had no effect on the sulfation enhancement of Grove limestone. As discussed above, the difference between these results and those of previously reported laboratory-scale experiments is believed to be due to the different manners in which the two types of experimental data were generated. Hopefully, additional investigations will clarify the discrepancy.

Table 12. Metal Types, Locations, and Temperatures of Corrosion Specimens for Run CT-2

Corrosion Probe Designation[a]	Metal Corrosion Specimens	Corrosion Probe Location	Temperature, °C
		Bed Section	
AC-1	304 SS, 309 SS, 316 SS, Incoloy 800, 2 1/4 Cr-1 Mo Steel, 9 Cr-1 Mo Steel, 446 Steel	50 cm above gas distributor plate	540-565
AC-2	Inconel 601, Inconel 617, RA 333, 309 SS, 310 SS, 321 SS, Incoloy 800	30 cm above gas distributor plate	640-660
C-1	Haynes 188, Inconel 601, Inconel 671, Hastelloy-X, RA 333, 310 SS, 347 SS	60 cm above gas distributor plate	845-855
C-2	Inconel 617, Inconel 625, Inconel 718, 304 SS, 310 SS, 316 SS, Incoloy 800	10 cm above gas distributor plate	840-850
		Freeboard Section	
AC-3[b]	Inconel 601, Inconel 617, RA 333, 309 SS, 310 SS, 321 SS, Incoloy 800	100 cm above top of bed	610-650
C-3	Haynes 188, Inconel 601, Inconel 617, Inconel 671, Hastelloy-X, RA 333, 310 SS	131 cm above top of bed	590-695
C-4	Alloy 713 C, Inconel 738, Incoloy 800, HK-40 Alloy, HC Alloy, CA-40 Alloy, C-12 Alloy	39 cm above top of bed	700-730

[a] AC designates air-cooled probe.
C designates coupon probe, not cooled.

[b] No coolant air was required for this probe.

The various solids output streams from runs CT-1, -2, and -3 are being analyzed to determine the accuracy of the observed sulfur retentions obtained by monitoring SO_2 in the flue gas. The effects of salt addition on corrosion of the metal specimens from all three runs are being evaluated by the Materials Science Division of ANL.

Table 13. Metal Types, Locations, and Temperatures of Corrosion Specimens for Run CT-3

Corrosion Probe Designation[a]	Metal Corrosion Specimens	Corrosion Probe Location	Temperature, °C
		Bed Section	
AC-1	304 SS, 321 SS, 316 SS, Incoloy 800, 2 1/4 Cr-1 Mo Steel, 9 Cr-1 Mo Steel, 446 Steel	30 cm above gas distributor plate	620-640
AC-2	Inconel 601, Inconel 617, RA 333, 309 SS, 310 SS, 321 SS, 304 SS	50 cm above gas distributor plate	600-590
C-1	Haynes 188, Inconel 601, Inconel 671, Hastelloy-X, RA 333, 310 SS, 347 SS	60 cm above gas distributor plate	845-860
C-2	Inconel 617, Inconel 625, Inconel 718, 304 SS, 310 SS, 316 SS, Incoloy 800	10 cm above gas distributor plate	835-860
		Freeboard Section	
AC-3[b]	Inconel 601, Inconel 617, RA 333, 309 SS, 310 SS, 321 SS, Incoloy 800	100 cm above top of bed	645-655
C-3	Haynes 188, Inconel 601, Inconel 617, Inconel 671, Hastelloy-X, RA 333, 310 SS	131 cm above top of bed	610-615
C-4	Alloy 713 C, Inconel 738, Incoloy 800, HK-40 Alloy, HC Alloy, CA-40 Alloy, C-12 Alloy	39 cm above top of bed	720-730

[a] AC designates air-cooled probe.
C designates coupon probe, not cooled.

[b] No coolant air was required for this probe.

Table 14. Effects of Salt Addition on Calcium/Sulfur Ratios Required to Maintain about 700 ppm SO_2 in the Dry Off-Gas for Run Series CT

Experimental Conditions

Temperature: 850°C	Sorbent: Grove limestone (-10 +30 mesh) 95.3% $CaCO_3$
Pressure: 101.3 kPa	Fluidized-Bed Height: 813 mm
Gas Velocity: 1 m/s	Excess O_2: 3% (dry off-gas)
Coal: Sewickley (-12 +100 mesh) 5.46% S	

Run	Salt Addition	Ca/S Ratio
CT-1	None	3.4
CT-2	∿0.3 mol % $CaCl_2$	3.5
CT-3	∿0.5 mol % NaCl	3.6

REFERENCES

1. G. J. Vogel et al., Supportive Studies in Fluidized-Bed Combustion, Argonne National Laboratory Report ANL/CEN/FE-77-3, 1977.

2. G. J. Vogel et al., A Development Program on Pressurized Fluidized-Bed Combustion, Annual Report, July 1975-June 1976, Argonne National Laboratory Report ANL/ES/CEN-1016, p. 57.

3. Sanford Gordon and B. J. McBride, Computer Program for Calculation of Complex Chemical Equilibrium Compositions Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations, NASA Report NASA-58-273 (1971).

4. W. M. Swift et al., Decomposition of Calcium Sulfate: A Review of the Literature, Argonne National Laboratory Report ANL-76-122 (December 1976).

5. P. Steiner, U.S. Patent Spec. 53,238/73 (1975).

6. Evaluation of Regenerable Flue Gas Desulfurization Processes, Vol II, Electric Power Research Institute (Palo Alto, CA), Report EPRI-FP-272, pp. 61-62 (1968).

7. P. Steiner, H. Juntgen and K. Knoblauch, Adv. Chem. Ser. 139, 180, J. B. Pfeiffer, Ed. (1975).

8. Evaluation of Regenerable Flue Gas Desulfurization Processes, Vol. II, Electric Power Research Institute (Palo Alto, CA) Report EPRI-79-82, pp. 79-82 (1976).

9. W. F. Bischoff, Jr. et al., Chem. Eng. 82(1), 74 (1975).

10. H. C. Hottel and J. B. Howard, New Energy Technology, MIT Press, Cambridge, MA, pp. 103-157 (1971).

11. J. L. Johnson, Catal. Rev. 14(1), 131 (1976).

12. D. Bienstock et al., Sulfur Dioxide - Its Chemistry and Removal from Industrial Waste Gases, U.S. Bureau of Mines Information Circular 7836, pp. 27-34 (1958).

13. J. K. Chowdhury and R. M. Datta, J. Ind. Chem. Soc. 20, 253 (1943).

14. L. A. Haas et al., Removing Sulfur Dioxide by Carbon Monoxide Reduction, U.S. Bureau of Mines Report of Investigations 7483, Washington, D.C. (1971).

15. Z. M. George, Adv. Chem. Ser. 139, 75 (1975).

16. J. B. Peri, J. Phys. Chem. 69, 211 (1965).

17. J. B. Peri, J. Phys. Chem. 69, 220 (1965).

18. C. C. Chang, J. Catal. 53, 374 (1978).

19. R. Lepsoe, Ind. Eng. Chem. 30(1), 92 (1938).

20. T. F. Doumani *et al.*, Ind. Eng. Chem. 36(4), 329 (1944).

21. D. L. Murdock and G. A. Atwood, Ind. Eng. Chem., Process Des. Dev. 13(3), 254 (1974); D. L. Murdock, *Kinetics of the Reduction of Sulfur Dioxide by Hydrogen Over an Activated Bauxite Catalyst*, Doctoral thesis 73-23, 456 (Univ. Microfilms), University of Akron, Akron, Ohio (1973).

22. Y. Hsieh and G. A. Atwood, Ind. Eng. Chem., Process Des. Dev. 15(2),358 (1976).

23. A. Meisen and H. A. Bennett, Hydrocarbon Process 53(11), 171 (1974).

24. A. G. Maadah and R. N. Maddox, Hydrocarbon Process 57(8), 143 (1978).

25. R. K. Kerr, Energy Process./Can. 68(6), 28 (1976).

26. V. C. Okay and W. L. Short, Ind. Eng. Chem. Process Des. Dev. 12(3), 291 (1973).

27. W. L. Wynn, *Catalytic Reduction of Sulfur Dioxide by Carbon Monoxide*, thesis, Univ. of Pennsylvania, Philadelphia, (1977).

28. P. R. Ryason and J. Hankins, J. Air Pollut. Contr. Assoc. 17(12), 796 (1967).

29. Z. M. George, J. Catal. 32, 261 (1974).

30. J. G. I. Bazes *et al.*, Ind. Eng. Chem., Prod. Res. Dev. 14(4), 264 (1975).

31. L. A. Haas and S. E. Khalafalla, J. Catal. 29, 264 (1973).

32. J. Happel *et al.*, Ind. Eng. Chem. Prod. Res. Dev. 14(3), 154 (1975).

33. M. R. Kundrath, Ph.D. thesis, New York Univ. School of Eng. and Sci. (1974) in Diss. Abstr. Int. B, 35 (12 pt.1) 5874 (1975).

34. S. E. Khalafalla and L. A. Haas, Adv. Chem. Ser. 139, 60 (1975).

35. J. J. Helstrom and G. A. Atwood, Ind. Eng. Chem. Process Des. Dev. 17(2), 114 (1978).

36. R. K. Kerr and E. M. Berlie, Energy Process./Can. 69(6), 48 (1977).

37. R. K. Kerr *et al.*, Energy Process./Can. 69(1), 66 (1976).

38. T. A. Hendrickson (Compiler), *Synthetic Fuels Data Handbook*, Cameron Engineers Inc., Denver, CO, pp. 147-150 (1975).

39. J. W. Kaakinen et al., Environ. Sci. Technol. 9(9), 862 (1975).

40. J. G. Cabrera and M. N. Gray, Fuel 52, 213 (1973).

41. E. B. Beckman, The FW-BF System with Resox: A Status Report, presented at Fifth National Conf. on Energy and the Environment, Cincinnati, November 2, 1977.

42. D. Bienstock et al., Sulfur Dioxide - Its Chemistry and Removal From Industrial Waste Gases, U.S. Bureau of Mines Information Circular 7836, pp. 35-36 (1958).

43. J. Macak and P. Pick, Erdöl Kohle Erdgas Petrochem. Brennst. Chem. 26(6), 345 (1953).

44. B. Meyer, Sulfur Energy and Environment, Elsevier, New York, pp. 44, 60-62 (1977).

45. F. G. Sawyer et al., Ind. Eng. Chem. 42(10), 1938 (1944).

46. G. J. Vogel et al., Supportive Studies in Fluidized-Bed Combustion, Quarterly Report, July-September 1977, Argonne National Laboratory Report ANL/CEN/FE-77-8.

47. Irving Johnson et al., Support Studies in Fluidized-Bed Combustion, Quarterly Report, January-March 1978, Argonne National Laboratory Report ANL/CEN/FE-78-3.

48. A. A. Jonke et al., Reduction of Atmospheric Pollution by the Application of Fluidized-Bed Combustion, Annual Report, July 1970-June 1971, Argonne National Laboratory Report ANL/ES-CEN-1004.

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