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REDUCTION OF ATMOSPHERIC POLLUTION BY THE APPLICATION OF FLUIDIZED-BED COMBUSTION

Annual Report
July 1969—June 1970

by

A. A. Jonke, E. L. Carls, R. L. Jarry,
L. J. Anastasia, M. Haas, J. R. Pavlik, W. A. Murphy,
C. B. Schoffstoll, and G. N. Vargo

ARGONNE NATIONAL LABORATORY

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Meteorology

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Chemical Engineering Division

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ABSTRACT

Combustion of fossil fuels in a fluidized bed, to which particulate limestone is added to react with sulfur oxides, is being studied as a means of reducing the emission of SO_2 released during combustion. Coal has been burned in a 6-in.-dia bench-scale combustor to study (1) the effect on SO_2 removal of the limestone particle size, type of limestone, temperature, calcium to sulfur ratio, fluidized-bed depth, and recycle of elutriated flyash to the bed, (2) the extent of calcination and sulfation of limestone, and (3) factors affecting the NO concentration in the flue gas. In natural-gas combustion experiments, measurements were made of the extent of SO_2 removal, the NO level in the flue gas, and the combustion efficiency. Mathematical models have been developed to estimate (1) the extent of reaction of limestone with SO_2 during coal combustion and (2) the effect of nonuniform feeding of coal on combustion efficiency.

I. SUMMARY

Fluidized-bed combustion is being studied at Argonne National Laboratory as a method of reducing the quantity of atmospheric pollutants (oxides of sulfur and nitrogen) released during the combustion of fossil fuels. This work is being carried out under contract with the National Air Pollution Control Administration.

The concept of fluidized-bed combustion involves burning fuel in a fluidized bed of solids with simultaneous feeding of crushed or pulverized limestone to control sulfur dioxide emission. A fluidized-bed combustor offers, in addition to in situ control of SO_2 emission, high heat-transfer

rates and efficient contacting for gas-solids reactions. Also, combustion can be carried out at lower temperatures in a fluidized bed than in conventional combustors, and nitrogen oxide emission may be lowered.

The bench-scale stainless steel combustor employed in the ANL studies has a 6-in. diameter and 6-ft length; upstream from the combustor is a similarly sized preheater. Vibratory-screw feeders deliver the coal and the limestone additive into air-transport streams for injection into the fluidized-bed combustor. The flue gas from the combustor passes through primary and secondary cyclone separators and a glass-fiber final filter where entrained solids are removed. Infrared spectrometry and other suitable instrumental methods are used to measure concentrations of the components of the flue gas.

△

Work during the report period included bench-scale experiments with limestone additive of two particle sizes (44- μ m average diameter or smaller in several series of experiments and an average diameter of several hundred microns in other series). These experiments indicated the effects on SO₂ removal of (1) Ca/S mole ratio, (2) type of limestone material, (3) fluidized-bed depth, and (4) combustion temperature.

A series of bench-scale experiments was performed to compare SO₂ removal for pulverized limestone No. 1359 and Tymochtee dolomite additives. In these runs, the initial fluidized bed consisted of refractory alumina particles. Base-line reaction conditions were a combustion temperature of 1600°F, an average additive particle size of 25 μ m, a superficial gas velocity of 3 ft/sec, 10-20% excess air, a fluidized-bed depth of 2 ft, and addition rates giving a Ca/S mole ratio of 2.5 in the feed streams. With these conditions, the reduction in SO₂ concentration of the flue gas was higher for the dolomite than for the limestone, 90 and 83%, respectively. Variation of temperatures in the range 1550-1650°F had some effect on SO₂ removal by the pulverized limestone. Removals were 73, 83, and 77% at 1650, 1600, and 1550°F, respectively. An increase in superficial gas velocity from 3 to 9 ft/sec decreased SO₂ removals by about 10%. Decreasing the Ca/S mole ratio from 2.5 to 2.0 to 1.5 decreased SO₂ removals from 83 to 70 to 57%, respectively, at 1600°F.

Recycle to the combustor of a finely divided limestone-flyash mixture that had been elutriated from the bed did not increase SO₂ removal. This is contrary to expectations that SO₂ removal would be increased because of the additional reaction potential of the partially sulfated limestone contained in the elutriated solids. All reaction during the recycle experiments was apparently due to the addition of fresh limestone, and SO₂ removal was the same as that obtained in the absence of recycle.

Laboratory-scale tests were performed to compare the reactivity of partially sulfated limestone (elutriated with flyash) with the reactivity

of fresh limestone. Reactivities with SO_2 of these materials were similar. The failure of recycled material to increase SO_2 removal in the combustor is probably due to the short residence time of fine particles in the bed.

The extent of sulfation and calcination of material in the final alumina bed and of material in the solids collected overhead was determined by analysis. The results show that material retained in the fluid bed had the highest extent of CaO utilization (70%) and the greatest extent of calcination (~ 100). Material collected in the primary cyclone had the lowest CaO utilization (18%) and also the lowest extent of calcination ($\sim 75\%$). Material collected in the secondary cyclone was intermediate (CaO utilization of 43% and calcination of $\sim 90\%$). The low values for both sulfation and calcination of the material collected in the cyclones suggest that these materials were blown through the bed with little time for reaction and had a brief residence time.

Another series of bench-scale experiments was performed in which coarse-particle-size limestone was used for both the initial fluidized bed and the additive feed to determine the effects of operating variables at steady state. At steady state, the bed composition (i.e., Ca/S ratio) does not change with continued addition of fresh limestone and removal of reacted limestone. The time required to reach steady state is a function of bed weight and limestone feed rate. Calculations indicated that 95% of steady-state composition would be achieved in $2\frac{1}{2}$ bed changes, and that each bed change would require about 25 hr. The limestone bed material was therefore presulfated to nearly the expected steady-state level to shorten the experimental time.

These experiments were performed at a combustion temperature of 1600°F , with a superficial gas velocity of 3 ft/sec, a 2-ft-deep fluidized bed, and Ca/S mole ratios of 2.3-2.6. With three additives (limestone No. 1359, limestone No. 1360, and dolomite No. 1337) having particle sizes in the range 500-600 μm , SO_2 removals of 74-86% were achieved. The results indicate that SO_2 removal is relatively independent of the type of additive material used in these studies. Of particular interest in these experiments is that the use of large-particle-size limestone material in this mode of operation gave greater SO_2 removals than were obtained with fine limestone (average particle size, 25 μm) in experiments using an alumina bed. The presence of a large mass of limestone throughout the run and the longer retention of large-particle-size limestone in the bed are probably responsible for this result.

A marked effect of combustion temperature on SO_2 removal was noted for both a limestone (No. 1359) and a dolomite (No. 1337) in these experiments with calcined limestone beds. The experiments were performed over the temperature range 1400 - 1800°F . At a Ca/S mole ratio of 2.5 with limestone No. 1359, SO_2 removal at 1500 and 1550°F was 91%.

Lower SO_2 removals were observed at temperatures above and below this temperature range. The temperature effect when the dolomite was the additive was nearly identical.

The use of a fluidized-bed combustor for the combustion of natural gas was also investigated. Because a relatively low combustion temperature (1600°F) is feasible in this method of combustion, nitric oxide (NO) generation was held to the level dictated by the nitrogen fixation equilibrium, about 60 ppm. Although combustion efficiencies were only 94-99% in our experimental setup, a combustion efficiency greater than 99% can likely be achieved by more efficient distribution of natural gas in the fluidized bed.

In other natural-gas experiments, artificially generated SO_2 was reacted with limestone at 1600°F . The SO_2 removals were 95 to 99% at a low Ca/S mole ratio of 1.5. These excellent results were probably due to efficient distribution of the injected SO_2 in the combustor (as compared with coal-combustion experiments) and to an ash-free environment.

In other work, when a bed of partially sulfated limestone was heated, desorption of SO_2 started at slightly above 1700°F . At 1850°F and with an excess air level in the feed resulting in 1 vol % oxygen in the flue gas, SO_2 concentration in the flue gas was 5000 ppm. This high degree of SO_2 desorption at a relatively low temperature (previously, a temperature of about 2200°F had been thought necessary to obtain this effect) may have been due to localized reducing conditions in the bed at the low excess-air level employed.

A reduction of NO concentration in the flue gas, concomitant with a reduction in SO_2 concentration, has been noted upon addition of limestone to the fluidized bed. The lowering of NO concentration is probably related largely to the presence of sulfated limestone in the bed.

Attempts to decompose NO by adding metal oxides (Al_2O_3 , Co_3O_4 , and ZrO_2) as catalysts were not successful. In fact, when Co_3O_4 was tested, the NO concentration in the flue gas increased.

Flue gas from the fluidized-bed combustion of coal was analyzed for nitrogen oxide compounds by three independent analytical procedures. Nitric oxide was the only nitrogen oxide species present in significant quantity.

Modeling studies were also performed to predict the extent of SO_2 removal as a function of various operating parameters and to predict the mixing of coal particles injected into a fluidized-bed combustor.

A mathematical model was developed to predict the degree of SO_2 removal in a fluidized-bed coal combustor as a function of the operating parameters of bed height, superficial gas velocity, and limestone additive feed rate. Calculations were made illustrating the application of the model. In one comparison of the SO_2 removal predicted by the model with data generated in the bench-scale program, a greater SO_2 removal was predicted than was found experimentally. The discrepancy probably is a result of currently available kinetic data for the sulfation reaction not being applicable to the reaction environment in the fluidized bed, where a particle is exposed to varying conditions.

Models have been developed to predict the effects on SO_2 removal of nonuniform feeding of coal, which results in localized reducing or oxidizing conditions at points within and above a fluidized-bed combustor. These mathematical models predict coal concentration gradients within the bed for (1) coal injection at the base of the bed and (2) horizontal-jet coal injection and deep penetration into the bed. The models were applied to the operating conditions anticipated for a large fluidized-bed coal combustor. Results indicated that coal concentration in the bed would be more uniform if coal is injected horizontally in a jet with deep penetration into the bed than if coal is injected vertically from a point at the base of the bed.

II. INTRODUCTION

The combustion of fossil fuels, particularly coal, for the production of electrical power is the major source of sulfur dioxide air pollutant today. By the year 2000, the increased power demand could result in a fourfold increase in total emission of SO_2 unless stringent means are applied for SO_2 control. To combat this problem, extensive pollution-control research is under way involving 1) processes for the removal of sulfur dioxide from flue gases following combustion and 2) processes for the desulfurization of fuels prior to their combustion (i.e., physical separation of sulfur-containing constituents or gasification techniques to yield a sulfur-free fuel). Although various schemes have been shown to be technically feasible, none have yet provided the answer to the problem of increasing air pollution from SO_2 emission.

Fluidized-bed combustion, a relatively new combustion concept studied both in Europe and the United States during the past decade, is apparently a means of reducing atmospheric pollution. This concept involves introducing fuel and a SO_2 -reacting additive material such as limestone into a hot fluidized bed of solids in which boiler tubes are immersed. Since a fluidized bed is a highly efficient medium for carrying out gas-solid reactions, the emission of gaseous SO_2 released during combustion of fuel may be efficiently controlled by injecting into the bed a material that reacts with

the gaseous SO_2 . Combustion of fuel occurs simultaneously with in situ reaction of SO_2 with limestone in the fluidized bed.

Fluidized-bed combustion also has economic advantages over conventional combustion techniques. Due to the excellent heat-transfer characteristics and the possibly smaller size of fluidized-bed combustors, they are expected to have lower capital and operating costs than conventional units.

Much of the investigational work on fluidized-bed combustion has been conducted in European countries, where the original objective was to develop a combustion process for low-grade fuels such as high-ash coals and lignites.¹ In Great Britain, a study of the feasibility of fluidized-bed combustion for utility-size boilers was started in 1961. A large development program³ since 1961 by the British National Coal Board has progressed to the point where construction of a 20-MW prototype unit is being considered. Early fluidized-bed combustion studies in the United States were carried out by several industrial and government research laboratories. During recent years, the United States' effort has intensified because fluidized-bed combustion offers good prospects for effective air-pollution control. The current U.S. effort is under the direction of the National Air Pollution Control Administration (NAPCA), Public Health Service, U.S. Department of Health, Education, and Welfare. Expected applications of fluidized-bed combustors are for electric utilities and industrial steam generation.

A. Description of Fluidized-bed Combustion of Coal

The bed material in a fluidized-bed combustor for combustion of coal may consist of limestone, particulate alumina, granular ash, or other suitable refractory material. An upward flow of air distributed by a gas distributor plate at the bottom of the combustor expands the bed to a dense suspension. The entire fluidized mass is then heated to coal ignition temperature, and crushed coal is fed pneumatically into the bed at several locations near the bottom of the bed. The added coal, which constitutes only a small weight percent of the bed, disperses throughout the bed and burns at 1500-1800°F. The temperature is low enough to avoid softening and sintering of the ash, but high enough to give acceptable combustion efficiency. The combustion heat is transferred to steam tubes inside the combustor.

Most applications of the concept involve burning coal in shallow fluidized beds of large cross-sectional area. Typically, bed depths of 2-3 ft are employed, and air velocities in the bed are 3-15 ft/sec. Gas velocities at the lower end of this range are associated with applications to electric power generating systems, for which maximum heat-transfer coefficients and combustion efficiency are desired. The higher

gas velocities are associated with applications to industrial steam-generating systems, for which high heat-release rates and small boiler size are desired.

During coal combustion, a small fraction of the coal is elutriated in the gas and carried out of the bed before it is completely consumed. To reduce carbon losses in a commercial combustor, it would be necessary to recycle the flyash or to feed it to a second fluidized bed where combustion would be completed.

B. Control of Sulfur Oxide Emission

To control sulfur oxide emission, crushed limestone can be fed continuously to a fluidized bed, where it calcines to lime, then reacts with sulfur oxide to form calcium sulfate. At least two alternative modes of operation of a desulfurizing fluidized-bed combustor are possible.

In one mode of operation, coal and limestone are added to a bed composed of a mixture of partially sulfated limestone of relatively coarse particle size and any coarse ash produced by combustion of the fuel; the bed level is controlled by continuously withdrawing excess bed material. Since the limestone fed to the combustor becomes a principal constituent of the fluidized bed, the particle size of the limestone feed is primarily selected on the basis of combustor operating conditions, especially gas velocity. For this mode of operation, the particle size of the limestone is approximately the same as the coal particle size.

In the second mode of operation, the fuel is burned in a bed composed chiefly of ash or other refractory material, to which finely pulverized limestone is fed. Since the fine limestone particles are readily elutriated by the gas stream, they have a relatively short residence time in the bed. To improve reagent utilization efficiency and fuel combustion efficiency, a portion of the elutriated limestone and flyash can be recycled.

Since using limestone for reaction with SO_2 increases the quantity of solids that must be disposed of, investigations are being carried out at other sites on CaSO_4 regeneration whereby CaO could be obtained for reuse and the sulfur value recovered. Also being investigated at other sites is the utilization of mixtures of ash and sulfated limestone as soil conditioners and as raw material for cement manufacture.

Limestone is used to control sulfur oxide emission in types of combustors other than fluidized beds. However, efficient removal of SO_2 and high utilization of additive material are expected in fluidized-bed combustion systems using limestone additive material because of efficient gas-solids contacting and long solids residence time. Another advantage of a fluidized bed is that the combustion temperature is near the optimum temperature for the reaction between SO_2 and limestone.

C. ANL Program

In the ANL program, those operating characteristics of a fluidized-bed combustor for sulfur dioxide removal that are applicable to the design of utility- and industrial-sized units are being investigated. Bench-scale experimental work is being performed to investigate conditions whereby both a high degree of SO₂ removal from the flue gas and a high degree of limestone utilization can be achieved. In addition, a laboratory-scale program provides information (i.e., kinetic data) in support of the bench-scale work. Mathematical models were developed to predict (1) the effects of equipment operating parameters on the degree of SO₂ removal and (2) the solids-mixing characteristics of fluidized beds.

III. MATERIALS FOR BENCH-SCALE EXPERIMENTS

A. Coal

The coal used was a bituminous coal, Illinois Seam No. 6. This coal, which contains 4.5 wt % sulfur, is characterized in Table 1. Prior to use, it was air-dried and screened to -6 mesh (for high-gas-velocity experiments) or -14 mesh (for low-gas-velocity experiments).

TABLE 1. Characteristics of Coal^a
(Illinois Seam No. 6, Peabody Coal Company, Mine 10, Christian County, Illinois)

<u>Proximate Analysis, wt %</u>			
	<u>As Received</u>	<u>Dry Basis</u>	
Moisture	5.70	-	
Volatile Matter	41.00	43.50	
Fixed Carbon	40.97	43.37	
Ash	12.33	13.13	
Sulfur	4.57	4.84	
Heating Value, Btu/lb	11,546	12,245	
<u>Ultimate Analysis, wt %</u>			
Carbon	68.03	Sulfur	4.84
Hydrogen	4.96	Nitrogen	1.11
<u>Particle-size Distribution</u>			
<u>U.S. Screen Size</u>	<u>As Received, wt %</u>	<u>-6 Mesh Sieved, wt %</u>	<u>-14 Mesh Sieved, wt %</u>
+6	22.0	-	-
-6 +14	14.5	18.5	-
-14 +25	20.5	26.1	31.9
-25 +45	17.0	21.7	26.6
-45 +80	11.5	14.6	18.0
-80 +170	6.5	8.3	10.2
-170 +325	4.5	5.7	7.0
-325	4.0	5.1	6.3

^aSupplied by Commonwealth Edison Company, Chicago, Illinois.

B. Limestone Additive Materials

Additive materials (see Table 2) used in bench-scale experiments were limestone No. 1359 (M. J. Grove Lime Co., Stephens City, Virginia), limestone No. 1360 (Monmouth Stone Co., Monmouth, Illinois), dolomite No. 1337 (Charles Pfiser and Co., Gibsonburg, Ohio), and a dolomite (C. E. Duff and Sons, Huntsville, Ohio) from the Tymochtee formation of western Ohio.

TABLE 2. Composition of Additives Used
in Bench-scale Experiments

	No. 1359 Limestone	No. 1360 Limestone	No. 1337 Dolomite	Tymochtee Dolomite
<u>As Received</u>				
CaCO ₃ , wt %	97.8	69.8	53.4	49.3
MgCO ₃ , wt %	1.3	19.2	46.5	36.6
<u>Calcined Basis</u>				
CaO, wt %	97.0	76.4	57.0	44.6
MgO, wt %	1.1	17.9	42.2	32.7
		Major phase ^a Minor phase ^a		CaMg(CO ₃) ₂ SiO ₂

^aX-ray analysis furnished by Z. Tomczuk, Chemical Engineering Division. The observed pattern agrees well with the ASTM standard pattern for dolomite from Haley, Ross Twp., Ontario, Canada, April 1970.

C. Miscellaneous Materials

In some bench-scale experiments, the initial bed material was refractory alumina (Alcoa T-61 tabular alumina).

Natural gas, sometimes containing added SO₂, was burned in the fluidized-bed combustor in one series of experiments. Two different samples of the natural gas are analyzed in Table 3. As seen, the elemental nitrogen content of the two samples varied greatly. This variation is a result of the utility company adding the quantity of nitrogen necessary to obtain a heat content of ~1040 Btu/ft³. The sulfur dioxide added in some natural-gas combustion experiments was a high-purity gas obtained from the Matheson Company.

TABLE 3. Analyses of Two Different Samples of Natural Gas

	Sample 1, Analysis ^a by Gas Chromatography, vol %	Sample 2, Analysis ^b by Mass Spectrometry, vol %		Sample 1, Analysis ^a by Gas Chromatography, vol %	Sample 2, Analysis ^b by Mass Spectrometry, vol %
CH ₄	88.15	92.5	O ₂	0.05	<0.03
C ₂ H ₆	5.38	3.5	Misc	0.07	<0.4
C ₃ H ₈	1.65	1.0	N ₂	3.64	1.6
C ₄ H ₁₀	0.43	<0.5 ^c	Heat content	1035 Btu/cu ft	
C ₅ H ₁₂	0.10	-	Specific gravity, 20°C/20°C	0.6	
CO ₂	0.36	0.8			
He	0.17	<0.05			

^aAnalysis by Northern Illinois Gas Co.^bAnalysis by Chemistry Division, Argonne National Laboratory.^cC₄ and higher hydrocarbons.

IV. BENCH-SCALE EQUIPMENT

A vertical fluidized-bed reactor (shown schematically in Fig. 1) is being used for bench-scale investigations at Argonne. It consists of three flanged sections of 6-in.-dia stainless steel pipe: a top 2-ft-long section, a middle 4-ft-long section (where combustion occurs), and an 8-in.-long bottom section (which contains the gas distributor plate). Surrounding the 4-ft section are four annular chambers (each 2½ in. high) through which an

air stream alone or a mixture of water dispersed in an air stream can be circulated to control the temperature in each zone. Figure 2 is a photograph of the bench-scale equipment.

Fig. 1. Fluidized-bed Reactor (Combustor)

Figure 3 is a simplified piping diagram of the bench-scale equipment. Air supplied to the unit is fed from a compressed-air supply and is metered through a flow control system consisting of a Taylor pressure transmitter, a flow recording and control device, and two orifice-flow control valve arrangements. The fluidizing air is passed through an electrical preheater (designed to preheat the inlet air to 1000°F). The air enters the reactor through a bubble-cap-type gas distributor mounted on the bottom flange of the reactor. Fifteen bubble caps are used, each with eight 1/16-in.-dia holes. The preheated inlet air and the auxiliary heaters on the reactor

Fig. 2. Bench-scale Fluidized-bed Reactor.
ANL Neg. No. 308-2251.

increase the temperature of the inert bed to the coal-ignition point.

Coal, additive, and recycled elutriated fines are transported from bin feeders to the combustor as a dilute phase in transport-air streams. The variable-drive bin feeders are mounted on scales to meter the quantity of solids fed into the transport air streams. The entrained solids are injected through a fitting into the fluidized bed at a point just above the gas distributor plate.

The off-gas from the combustor is passed through two high-efficiency cyclone separators in series and a glass-fiber final filter to separate elutriated solids from the gas stream. Solids collected in the cyclones can be recycled to the combustor.

A sample consisting of approximately one-twentieth of the total flue gas (0.5 scfm) is removed continuously through a 1/2-in.-dia stainless steel sample probe at either the upper portion of the bench-scale combustor or downstream from the secondary cyclone (see Fig. 4). The gas passed

Fig. 3. Simplified Piping Diagram of Bench-scale Equipment

Fig. 4. Gas Sampling and Analysis System

through a sintered-nickel filter to remove solids, then through first a water condenser, and then a refrigerator to remove water. A typical residual water content, as measured with an electrolytic hygrometer, is 3000 ppm. This level of water would not interfere with the measurement of high levels of flue-gas constituents. For example, 3000 ppm moisture in the gas gives a reading corresponding to ~ 30 ppm SO_2 and ~ 20 ppm NO . Moisture does not affect the oxygen analysis.

Continuous analyses for NO , SO_2 , CO , and CH_4 are carried out with infrared analyzers. Continuous measurement of oxygen is accomplished with a Hays paramagnetic oxygen analyzer. NO_x can be monitored continuously with a Mast coulometric analyzer. Intermittent analyses are made for CO_2 by gas chromatography. Figure 5 is a photograph of the instrument panel.

Fig. 5. Instrument Panel. ANL Neg. No. 308-2248.

V. PROCEDURE FOR BENCH-SCALE EXPERIMENTS

The startup procedure for bench-scale experiments starts with preheating the fluidized bed to approximately 1000°F by passing heated air through the bed and using resistance heaters installed on the combustor. Coal fed through a variable-drive volumetric screw feeder is then introduced into the bed by entrainment

in a transport air stream. Ignition occurs, and when the bed temperature has increased during a period of ~1 hr to 1600°F (or another selected temperature), the bed temperature is stabilized by means of air passed through the annular chambers around the middle section of the reactor.

After 1 hr of steady-state operation (i.e., with relatively constant levels of oxygen, sulfur dioxide, and nitric oxide levels in the flue gas), additive injection is initiated. During an experiment, the bed and overhead solids are sampled periodically. In experiments employing the recycle of fines, most of the elutriated solids removed from the gas stream by the primary cyclone are batch-fed into a variable-drive volumetric screw feeder and reintroduced into the bed.

VI. RESULTS AND DISCUSSION

A. Reduction in Emissions of SO₂

The major purpose of the bench-scale experimental program has been to evaluate various modes of operation of a fluidized-bed combustor incorporating the addition of limestone to control SO₂ emission. Combustion experiments performed with fine limestone additive and coarse limestone additive are described separately below.

In one mode of operation, pulverized limestone was fed to a fluidized bed of suitable inert refractory material in which coal was burned. For this mode of operation to be feasible, the limestone particles must be sufficiently reactive to react with SO₂ released in the fluidized bed before the limestone particles are elutriated out of the bed.

The second mode of operation was with additive materials of large particle size that largely were not elutriated and hence remained in the bed. When this mode of operation was continued employing a procedure for removing excess bed material, the starting material was displaced with partially reacted additive, and the fluidized bed at steady state consisted only of partially reacted additive. For this latter mode of operation to be feasible, the possibly lower reactivity of large particles must be compensated for by a greater mass of material being available in the fluidized bed for reaction with SO₂ and by an increased solids residence time.

In addition to coal combustion experiments with two sizes of additive particles, several experiments were performed with natural-gas fuel. In several of the natural-gas combustion runs, a stream of SO₂ was added to investigate (1) any effects of the absence of coal ash on SO₂ reaction with limestone and (2) the effect on SO₂ removal of the generation pattern of SO₂ within a fluidized bed.

The major variables investigated, in addition to particle size of the additive, included type of limestone additive employed, superficial gas velocity, operating with and without recycle of elutriated fines to the combustor, combustion temperature, and Ca/S mole ratio in the input feed.

The operating conditions and the variables studied in the several series of experiments are summarized in Table 4. The operating conditions and results for the individual experiments are presented in detail in Appendix A.

TABLE 4. Operating Conditions and Variables Studied in Several Series of Combustion Experiments

Experimental Series	Starting Bed Material	Additive	Additive Average Particle Size, μm	Fuel	Combustion Temp, $^{\circ}\text{F}$	Ca/S Mole Ratio	Superficial Gas Velocity, ft/sec	Variables Studied
SACC	Alumina	Limestone No. 1359	25, 600, 1400	Coal	1600	1.0-3.0	3, 9	a) Gas velocity b) Recycle of elutriated solids c) Additive particle size d) Size of starting bed particles
BC-1	Alumina	Limestone No. 1359	25	Coal	1600	1.2, 2.0	3	Presence of baffle plate
SA	Alumina	Limestone No. 1359	25 103	Coal	1550, 1650	0.6-4.2	3	a) Combustion temperature b) Additive particle size c) Ca/S mole ratio
BC-2 to -5	Alumina	Tymochtee Dolomite	<44 650	Coal	1600	0.6-2.1	3	a) Additive type b) Additive particle size c) Ca/S mole ratio
BC-6 to -10	Partially sulfated limestone	Limestone No. 1359 Limestone No. 1360 Dolomite No. 1337	615 630 540	Coal	1600 1600 1480-1800	2.2-2.6	~3	a) Limestone starting bed b) Combustion temperature
AR-1	Partially sulfated limestone	Limestone No. 1359	490	Coal	1400-1600	2.5	3	Combustion temperature
NG-1 and -2	Alumina	-	-	Natural Gas	1600, 1800	-	2.1-2.8	NO emissions during natural-gas combustion
NG-3 to -5	Alumina	Limestone No. 1359	25	Natural Gas	1600-1850	1.4-2.1	2.1-2.8	a) SO ₂ removal during natural-gas combustion b) Additive regeneration

1. Experiments with Pulverized Limestone (or Dolomite) and Fluidized Beds of Inert Solids

a. Ca/S Mole Ratio. For experiments in which pulverized limestone additive was used, the principal independent variable affecting the extent of reduction in SO₂ emissions has been found to be the quantity of limestone added relative to the sulfur contained in the coal. Figure 6 shows SO₂ removals for three experiments with various Ca/S mole ratios in the coal and additive feed streams. All these experiments were carried out at 1600°F, with 10-20% excess air, a superficial gas velocity of 3 ft/sec, and a fluidized-bed height of about 2 ft (additional data are presented in Table A.1). Under these operating conditions, when pulverized limestone No. 1359 (average particle size of 25 μm) and additive feed rates corresponding to Ca/S mole ratios of 2.2 to 3.0 were used, SO₂ removals of about 79% were achieved. The SO₂ removals correspond to overall CaO utilizations of 36 to 26%.

The statistical significance of the effect of Ca/S mole ratio on the extent of SO₂ removal is discussed in Subsection c of this section.

Fig. 6. Effect of Ca/S Mole Ratio on SO₂ Removal Using Pulverized Limestone No. 1359. (Expts. SACC-1, -5, and -9. Average particle size: 25 μ m; combustion temp: 1600°F; superficial gas velocity: 3 ft/sec; fluidized-bed depth: 2 ft.)

was % SO₂ removal (Y). The statistical design permitted three variables to be studied at two levels in four experiments.

The final regression equation took the form

$$Y = 27.3 + 22.3X_3 - 1.638X_3^2 \quad (1)$$

Here, *t*-values for the coefficients of X_3 and X_3^2 were 4.2 and 1.44, respectively. With 14 degrees of freedom, the coefficient of X_3 is still highly significant while that of X_3^2 is significant at approximately the 85% level.

Neither combustion temperature, X_1 , nor additive particle size, X_2 , produced significant improvement in the regression. Values of *t* for the coefficients of X_1 and X_2 indicated very low significance levels. Hence, these variables were not included in the regression equation.

*Regression analysis performed by Professor L. B. Koppel, Purdue University, consultant to Chemical Engineering Division.

b. Combustion Temperature.

The effect of combustion temperature within the range 1550-1650°F on the degree of SO₂ removal when pulverized (25- μ m) limestone No. 1359 was added to the fluidized-bed combustor is shown in Fig. 7. The data points for operation at 1600°F are replotted from Fig. 6. Data are shown for SA-1 and SA-2 at combustion temperatures of 1550 and 1650°F (see Table A.4). As seen from the data, varying the combustion temperature within the range of 1550-1650°F appears to have only a small effect.

c. Multiple-regression

Analysis* of Significance of Ca/S Mole Ratio, Combustion Temperature, and Particle Size of Limestone.

Multiple-regression techniques were used to analyze the data from SA-1 to SA-4 in order to determine the significance of three independent variables: combustion temperature (X_1) within the range of 1550-1650°F, additive average particle size (X_2) of 25 and 103 μ m, and Ca/S mole ratio in the feed (X_3) within the range of about 1 to 4. The dependent variable

Fig. 7. Effect of Combustion Temperature on SO_2 Removal Using Pulverized Limestone No. 1359. (Average particle size: 25 μm ; superficial gas velocity: 3 ft/sec; fluidized-bed depth: 2 ft.)

effect on SO_2 removal; some evidence of quadratic effects of the Ca/S mole ratio was obtained in the regression analysis. The effects of combustion temperature (1550-1650°F) and particle diameter (25 and 103 μm) are too small to be judged statistically significant.

d. Superficial Gas Velocity. The effect on SO_2 removal of superficial gas velocities of 3-9 ft/sec is shown in Fig. 8. The experiments for which data are plotted used limestone No. 1359 with an average particle size of 25 μm and were carried out at 1600°F with a fluidized-bed depth of about 2 ft. At a Ca/S mole ratio of 2, SO_2 removal from the flue gas decreased from 72 to 63% as a result of increasing the fluidizing gas velocity from 3 to 9 ft/sec.

e. Comparison of Limestone No. 1359 with Tymochtee Dolomite for SO_2 Removal. The effectiveness at 1600°F of Tymochtee dolomite for SO_2 removal (Table A.6) was compared with the effectiveness at 1600°F of the limestone used in experiments reported above. In the experiments with

The covariance matrix for the full linear regression

$$Y = a + b_1X_1 + b_2X_2 + b_3X_3$$

showed correlation coefficients between the independent variables X_1 , X_2 , and X_3 which never exceeded 0.06.

The standard error for Eq. 1 is 5.7. Thus, in approximate terms, replication of an experiment produces SO_2 removals that vary over a range ± 11 -12% for experiments SA-1 to SA-4. As indicated in the description of individual SA-series experiments (Appendix A, Section 2), feed rates for the 103- μm additive during SA-3 were known to be uniform for only relatively short time periods. SO_2 emission may not have reached steady-state levels in these short time periods; hence, results from experiment SA-3 may have a pronounced effect on the standard error.

Conclusions from the multiple-regression analysis are that, of the three variables tested in the statistical set of experiment, only the Ca/S mole ratio has a statistically significant

Fig. 8. Effect of Superficial Gas Velocity on SO_2 Removal Using Pulverized Limestone No. 1359. (Average particle size: $25\text{ }\mu\text{m}$; combustion temp: 1600°F ; bed depth: 2 ft.)

Tymochtee, the dolomite particles had an average size of $<44\text{ }\mu\text{m}$; the limestone experiments were with $25\text{-}\mu\text{m}$ limestone No. 1359. As shown in Fig. 9, reactivities (i.e., SO_2 removals) of these materials in this size range differed markedly. The Tymochtee dolomite had the greater effectiveness at all Ca/S mole ratios tested. However, the use of a dolomite is not desirable. The magnesium content of dolomite would be an additional waste burden, since MgO is inert towards reaction with SO_2 at these temperatures. (Appendix G presents calculated waste burdens and feeding requirements for limestone and dolomite as a function of sulfur content of the coal.)

Tests with Tymochtee dolomite of a larger particle size are discussed in Subsection VI.A.2.a.

f. Recycling of Elutriated Solids to the Combustor. In two experiments

(SACC-5 and -8) with $25\text{-}\mu\text{m}$ limestone No. 1359 and gas velocities of 3 and 9 ft/sec, solids that had been elutriated from the fluidized bed and collected in cyclone separators were recycled to the combustor via a screw feeder

Fig. 9

Comparison of SO_2 Removal with Pulverized Limestone No. 1359 and Tymochtee Dolomite (1600°F , 3 ft/sec, 2-ft fluidized bed)

and air transport system. These solids were known to contain unreacted CaO since the overall utilizations of CaO (see Table A.1) were below 40% [based on (1) feed rates of coal and limestone and (2) degree of SO₂ removal].

As shown in Table 5, recycle of elutriated solids during experiment SACC-5, which was conducted with a fluidizing-gas velocity of 3 ft/sec, had no beneficial effect, i.e., no further decrease in the emission of SO₂. In experiment SACC-8, conducted at 9 ft/sec, increased quantities of SO₂ appeared in the flue gas during periods of recycle. Presumably, the carbon contained in the elutriated fines burned, releasing additional SO₂. This was indicated by a decrease in the oxygen content of the flue gas while recycle was under way.

TABLE 5. Effect of Recycle of Elutriated Solids
on SO₂ Removal

Combustion temperature: 1600°F
Bed height: 2 ft (fluidized)

Expt.	Superficial Gas Velocity, ft/sec	Ca/S Mole Ratio	Reduction in SO ₂ Emission, %
SACC-5	3	2.2	79
SACC-5 (recycle)	3	2.2	79
SACC-8	9	1.0	39
SACC-8 (recycle)	9	1.0	33
SACC-8	9	2.4	69
SACC-8 (recycle)	9	2.4	71
SACC-8 (recycle)	9	2.4	64

Because recycle of elutriated solids did not further decrease SO₂ levels in the flue gas during bench-scale experiments, laboratory-scale experiments (see Appendix B) of relatively long duration were performed on material elutriated from the fluidized bed during bench-scale experiments. The major objective was to compare the reactivity of this material with that of fresh limestone. In addition, laboratory tests were performed to determine whether alteration of the physical condition of the elutriated material, e.g., by grinding or by exposure to a hydration-dehydration cycle, might make it more porous and reactive.

Results indicated that high utilizations (~85%) of CaO contained in the elutriated solids could be achieved and that the reactivity of the mixtures of flyash and partially sulfated limestone was essentially the same as that of fresh limestone, when calculated on the basis of unsulfated calcium. Neither grinding nor a hydration-dehydration cycle appeared to

offer a significant advantage. It is concluded that the inability of recycled material to affect SO_2 emission level in bench-scale experiments results from poor gas-solids contacting and from insufficient residence time for fine particles to react significantly.

g. Extent of Particle Calcination and Reaction. In some experiments, analyses for calcium, sulfur, and in some cases CO_3 were performed on samples from the fluidized bed, from elutriated material collected in the primary and secondary cyclone separators, and from the final filter. From the analyses, the extent of calcination of these materials was determined, as well as the extent of reaction with SO_2 .

During SACC-9, which used 25- μm limestone No. 1359 and was conducted at 1600°F with a superficial gas velocity of 3 ft/sec, the calcium and sulfur concentrations in the bed material increased with time (see Fig. 10). However, the Ca/S mole ratio in the bed (see Fig. 11) remained relatively constant at 1.5, which corresponds to a CaO utilization of 67% for additive material contained in the bed. The Ca/S mole ratio for solids collected in the primary cyclone was approximately 5, which represents a CaO utilization of 20%. Ca/S mole ratios for the finer solids collected in the secondary cyclone were 2 to 3, corresponding to CaO utilizations of 33 to 50%. For the finest material collected (on the process final filter), the Ca/S mole ratio was 1.3, which corresponds to a CaO utilization of 77%. Similar values for the various solids streams were found during experiments SA-1 to SA-4, which were conducted under similar conditions (see Table 6).

From carbonate analyses of samples of material from the fluidized bed and the two cyclones (experiments with 25- μm limestone No. 1359 conducted at superficial gas velocities of 3 ft/sec), the extent of limestone calcination was determined. The latter is plotted against extent

Fig. 10. Calcium and Sulfur Concentrations in the Fluidized Bed, Expt. SACC-9

Fig. 11. Ca/S Mole Ratios in Fluidized Bed and Elutriated Fines Samples, Expt. SACC-9

TABLE 6. Extent of Reaction of CaO in Various Solids Streams, Expts. SA-1 to SA-4

Limestone No. 1359 additive:		25 μ m	SA-1 and SA-2,
		103 μ m	SA-3 and SA-4
Combustion temperature:		1550°F	SA-1 and SA-4,
		1650°F	SA-2 and SA-3

Expt. SA-	Solids Stream Sampled	No. of Samples	Range of Ca/S Mole Ratios	Avg Ca/S Mole Ratio	Avg CaO Utiliz., %
1	Fluid bed	5	1.2-2.0	1.5	67
	Primary cyclone	5	4.0-6.5	5.3	19
	Secondary cyclone	2	2.0-2.3	2.2	45
	Final filter	1	-	1.3	77
2	Fluid bed	6	1.3-1.4	1.4	71
	Primary cyclone	4	4.8-7.2	6.3	16
	Secondary cyclone	3	1.8-3.0	2.6	38
	Final filter	1	-	1.6	62
3	Fluid bed	5	1.3-1.5	1.4	71
	Primary cyclone	4	1.5-6.3	4.1	24
	Secondary cyclone	4	2.0-2.5	2.2	45
	Final filter	1	-	0.7	>100
4	Fluid bed	3	1.3-1.4	1.4	71
	Primary cyclone	4	4.8-11.8	7.1	14
	Secondary cyclone	4	1.8-3.4	2.4	42

of CaO utilization in Fig. 12. These experiments were conducted at 1550-1650°F. The results show that material collected in the primary cyclone, which had the lowest extent of calcination, also had the lowest CaO utilization. Material retained in the fluidized bed, which had the highest extent of calcination, also had the highest extent of CaO utilization. Results for samples from the secondary cyclone were intermediate.

Fig. 12

Relationship of CaO Utilization to Extent of Limestone Calcination, Pulverized Limestone No. 1359 (3 ft/sec; 1550-1650°F)

The mean residence time of additive particles in the fluidized bed was calculated for SA-series experiments in which pulverized limestone additive and a superficial gas velocity of 3 ft/sec were used. (Mean residence time of additive particles is calculated by dividing the quantity of calcium contained in the fluidized bed at steady state by the rate at which calcium is introduced into the fluidized bed.) Additive feed rates were at several levels between 0.4 and 2.6 lb/hr during these experiments; because the feed rate was at each level for a relatively short time, steady-state levels of calcium may not have been achieved in the bed. With this limitation,

the overall average additive feed rate and the calcium content of the final bed were used to estimate a mean residence time for additive particles in the bed.

For experiments SA-1 and SA-2 with 25- μm additive, the average residence times were calculated to be 1.0 and 0.9 hr, respectively. For experiment SA-3 with 103- μm additive, the average residence time was calculated to be 1.3 hr. These mean residence times, which are relatively long, are not believed to accurately express average residence time of the bulk of the additive material introduced into the bed--that is, if residence times had been ~ 1 hr, the limestone should have been calcined and sulfated to a greater extent than was observed. Probably, a large proportion of the additive did not intermix with the bed material (as is evidenced by differing Ca/S ratios of bed material and elutriated solids), but was blown through the bed with little time for reaction.

h. Combustion of Natural Gas. Improved SO_2 removal was noted in experiments NG-3 and NG-4 in which the fuel was natural gas containing an added stream of SO_2 , rather than coal. The additive used in the two experiments was 25- μm limestone No. 1359. When natural gas spiked with SO_2 was burned, SO_2 removal was 92-99%; in comparison, 60-70% of the SO_2 was removed when coal was burned in experiments with similar Ca/S mole ratios of 1.5-2.1 in the feed streams.

In coal-combustion experiments, the flyash material present might interfere with the SO_2 -CaO reaction, contributing to poorer SO_2 removal. Therefore, in a gas-combustion experiment (NG-5) with a Ca/S mole ratio of 1.8, flyash was introduced at a rate equivalent to twice the rate of ash production during coal-combustion experiments, and SO_2 removal decreased from 95 to 90%. When flyash was introduced at three times the rate for coal combustion, SO_2 removal decreased to 84%. This effect was not due to the physical presence of more fines in the system, since SO_2 levels in the flue gas were not measurably affected by the introduction of finely divided alumina particles ($< 44 \mu\text{m}$).

The difference between SO_2 removals with flyash absent (NG-3) and flyash present (NG-5) appeared to be too small to account for the observed differences between SO_2 removals in coal-combustion experiments and natural-gas-combustion experiments. Probably of more significance is that SO_2 is introduced into the fluidized bed in different manners when different fuels were burned. In experiments with natural gas, SO_2 was introduced at or near the bottom of the fluidized bed. The greatest SO_2 removal in the series with natural gas, i.e., 99%, was observed during NG-3 in which SO_2 was premixed with the combustion air and introduced through the gas distributor. In NG-4, SO_2 was admitted through a side port adjacent to the natural gas inlet but above the air distributor, and SO_2 removal was 92%. In the coal-combustion experiments, some coal particles

could be carried to upper portions of the bed before they burned, releasing SO_2 . A theoretical discussion of the effects on SO_2 removal of generation pattern of SO_2 within the fluidized bed is incorporated into the mathematical model on SO_2 capture and is presented in Appendix C, Section 1.

2. Experiments with Large-particle-size Limestone or Dolomite

In the second mode of operation of the bench-scale equipment, large limestone additive particles were used that remained in the fluidized bed. At steady state, the fluidized bed would consist of a mixture of partially sulfated limestone and any ash particles too large to be elutriated. In some experiments, the starting bed was alumina; in another experiment, fresh limestone; and in yet others, partially sulfated limestone.

The time required for a fluidized bed to achieve steady-state composition is a function of bed weight and the rate at which large-size additive particles are fed into the fluidized bed. For the operating conditions employed in the bench-scale unit, the time required to achieve one bed change is of the order of 25 hr (assuming that no additive elutriates). It can be calculated that after $2\frac{1}{2}$ bed changes, bed composition is 95% of the final steady-state composition (assuming that feeding and bed takeoff are continuous and that solids mixing is complete). It is seen that the experimental times required to achieve steady-state conditions are quite long.

In an effort to shorten the experimental time, experiments were conducted with starting fluidized beds consisting of partially sulfated limestone additives of a composition close to that expected under steady-state operation. These beds were prepared by calcining a batch of limestone in the fluid-bed combustor, then sulfating the material by burning coal in the fluidized bed and introducing an added stream of SO_2 into the fluidizing air. Once the bed was prepared, the starting bed for a subsequent experiment was the final bed from the preceding experiment.

a. Comparison of Additive Materials. A series of experiments (BC-6 to BC-10, AR-1) was carried out to evaluate the relative effectiveness for SO_2 removal of limestone No. 1359, limestone No. 1360, and dolomite No. 1337, each with an average particle size of about 500-600 μm . The additive feed rates corresponded to Ca/S mole ratios of 2.3-2.6 in the feed, and the combustion temperature for either a portion of each run or the entire run was 1600°F. The SO_2 removal during operation at 1600°F ranged from 74 to 86% (see Table 7). The results indicate that the degree of SO_2 removal achieved was relatively independent of the type of additive material.

Figure 13 shows that the SO_2 removals achieved during the above experiments employing coarse limestone No. 1359 are similar to removals in earlier experiments with limestone No. 1359 of an average particle

size of 25 μm . Apparently, although the larger-sized additive particles have lower reactivity towards SO_2 than do small particles, the increased residence time of the larger particles in the fluidized bed and the larger mass of material in contact with the gas stream results in the same degree of SO_2 removal as with finer (more reactive) additive particles. The latter elutriate from the fluidized bed and hence have shorter contact times with the gas stream.

TABLE 7. SO_2 Removals Achieved with Six Types of Additive

Combustion temperature: 1600°F
Superficial gas velocity: ~3 ft/sec

Expt.	Additive Material		Average Particle Size, μm	Ca/S Mole Ratio	SO_2 Removal, %	CaO Utilization, %
	Type	No.				
BC-6	Limestone	1359	615	2.6	79	30
BC-7	Limestone	1359	615	2.3	83	36
BC-8	Limestone	1359	615	2.5	79	32
AR-1	Limestone	1359	615	2.5	86	34
BC-9	Limestone	1360	630	2.3	74	32
BC-10	Dolomite	1337	540	2.2	81	37

Fig. 13

Comparison of SO_2 Removal with Fine and Coarse Limestones

Operating conditions for experiments SACC-2 and SACC-3 (reported earlier in ANL/ES-CEN-1001) were Ca/S mole ratios of 2.4-2.6 and introduction of large-sized limestone additive particles (600 μm) into starting beds of alumina. The apparently steady levels of SO_2 in the flue gas for these experiments corresponded to SO_2 removals of about 50%, which are lower than in recent experiments employing starter beds of presulfated limestone. This may be attributed to steady-state conditions not being achieved in SACC-2 and SACC-3, even though the SO_2 level of the flue gas appeared to be constant. The calcium content of the bed during SACC-2 increased linearly with time up to a value of about 20 wt % (see Fig. 14). Sulfur in the bed increased slowly, as the run progressed, to a level of 3%. It was calculated that replacement of the entire alumina bed with partially reacted limestone would give a calcium concentration in the bed ranging between 29.4 wt % (as CaSO_4) and 71.5 wt % (as CaO).

stone would give a calcium concentration in the bed ranging between 29.4 wt % (as CaSO_4) and 71.5 wt % (as CaO).

Fig. 14. Calcium and Sulfur Contents of Solids Streams during Expt. SACC-2 with Large-particle Additive and Alumina Starter Bed

dolomite with an average particle diameter of 650 μ m was injected into an alumina starting bed at Ca/S mole ratios of 1.5 and 1.6. SO₂ removals were 78 and 87%, respectively. These data essentially reproduce literature data in which Tymochtee dolomite was injected into a fluidized bed of Tymochtee dolomite (at 1800°F) having an average particle size of ~800 μ m (see Fig. 15).

At a given Ca/S mole ratio, the CaO utilization with large particles of Tymochtee dolomite was higher than in other experiments with smaller-sized particles (<44 μ m) of Tymochtee dolomite (see Table A.6). The reasons for different relationships of particle size to CaO utilization for limestone and dolomite are not clear; however, the presence of MgO in the dolomite matrix may have kept the structure porous so that a larger fraction of the CaO in the large particle was sulfated. Also, elutriation and decreased residence time of fine dolomite particles probably contributed to their poorer sulfation. In experiments with limestone No. 1359, the fine particles probably contributed to their poorer sulfation. In experiments with limestone No. 1359, the fine particles were apparently reactive enough to compensate for their short particle residence time in the reactor.

The Ca/S mole ratios for the various solids streams in SACC-2 also are shown in Fig. 14. During the run, the larger additive particles remained in the fluidized bed, and Ca/S mole ratios in the bed decreased from an early maximum of 9.5 to a final value of ~5.5, corresponding to an overall CaO utilization of 18%. Solids from the primary cyclone in SACC-2 had a Ca/S mole ratio of ~3 (33% CaO utilization), solids from the secondary cyclone had a ratio of ~2.0 (50% utilization), and those from the final filter had a ratio of 1.4 (70% utilization).

The effectiveness of a dolomitic limestone that had been tested by other workers⁴ was also evaluated. In two experiments, BC-2 and BC-3, Tymochtee

Fig. 15. Effect of Ca/S Mole Feed Ratio on SO₂ Removal, ANL and Consolidation Coal Co. Data

b. Physical Characteristics of Partially Reacted Additive in Beds. Bed material for experiments with starter beds of partially sulfated limestone No. 1359 (BC-6, -7, -8) and limestone No. 1360 (BC-9) was

sampled, and the average tapped bulk density was 1.4 g/cc. During each of these experiments, some additive elutriated. However, chemical analyses (now in progress) to determine calcium and sulfur concentrations of the elutriated solids collected in the primary and secondary cyclones will indicate whether diminution of the additive particles occurred.

c. Effect of Combustion Temperature. Combustion temperatures between 1400 and 1800°F were observed to have a marked effect on the degree of SO₂ removal for dolomite No. 1337 and limestone No. 1359. After sustained operation at 1600°F with dolomite No. 1337 (BC-10), the combustion temperature was decreased to 1480°F. Thereupon, SO₂ removal increased from 81 to 91%. Later, the combustion temperature was increased to 1800°F, and SO₂ removal from the flue gas decreased to only 17%.

With limestone No. 1359 additive (experiment AR-1), the temperature range 1400-1600°F was explored; the temperature was increased 50°F at ~4-hr intervals. Limestone No. 1359 injected at a Ca/S mole ratio of 2.5 and at a coal-combustion temperature of 1500-1550°F

Fig. 16. Effect of Fluidized-bed Combustion Temperature on SO₂ Removal

appeared to be most effective for SO₂ control. SO₂ removal was 91%. SO₂ removal was poorer at temperatures above and below this temperature range. The effect of combustion temperature on SO₂ removal for both of these experiments is shown in Fig. 16, i.e., no apparent hysteresis effect of an increase or decrease in combustion temperature.

The data in Fig. 16 show clearly that the optimum temperature for sulfur retention is less than 1600°F when combustion is carried out in a bed of No. 1359 limestone or No. 1337 dolomite having an average particle size

of ~500 μm. In contrast, for pulverized limestone No. 1359 particles (25 μm), SO₂ removal was not improved significantly when the temperature was lowered from 1600 to 1550°F. This difference can be explained by recognizing that the capacity of pulverized limestone for reaction with SO₂ depends on the extent of calcination. For finely powdered limestone that is readily elutriated from the bed, the extent of calcination depends on bed temperature. Thus the optimum sulfur-retention temperature for pulverized limestone is not necessarily the same as for coarse limestone.

As reported in the literature,⁴ high sulfur removal was achieved using Tymochtee dolomite at 1800°F. This result seems to conflict

with the results of experiment BC-10, in which very poor sulfur removal was observed at 1800°F with dolomite No. 1337. These differences suggest that the optimum temperature may not be the same for all limestones (or dolomites). In work reported by Harrington, Borgwardt, and Potter,⁵ ten limestones were evaluated for reactivities at 1400, 1600, and 1800°F. Generally, reactivity increased as the temperature increased from 1400 to 1600°F. A further increase to 1800°F produced mixed results; four stones showed higher reactivities and six stones (including Nos. 1337 and 1359) showed lower reactivities at the higher temperatures. Tymochtee dolomite was not one of those tested.

The sensitivity of sulfur removal to bed temperature, illustrated in Fig. 16, is rather surprising. Increasing the temperature above 1550°F could have either a physical effect (closing of pores) or a chemical effect. Possible chemical explanations for the decreased sulfur retention at higher temperatures also were considered. The following is an example of the type of mechanism that might be operative:

In any fluidized bed, an emulsion phase and a gas bubble phase are present. Gas in excess of that required for minimum fluidization is in the bubble phase but also circulates between the bubble and the emulsion phase. The gas in the bubble phase is essentially not available for reaction with solid particles until it moves into the emulsion phase. In the lower portion of a fluid-bed coal combustor, oxygen in the emulsion phase reacts very rapidly with coal. All the oxygen in the emulsion phase is consumed, forming carbon monoxide. As the bubbles rise through the bed, air exchanges between the bubbles and the emulsion phase; in the upper part of the bed, the emulsion phase contains excess oxygen.

Thus, in the lower part of the combustor, the following reaction might occur:

In the upper part of the combustor, one or more of the following reactions might occur:

Reactions 2 and 3 would result in SO₂ being regenerated in the upper part of the combustor, seriously limiting the efficiency of the system for retention of sulfur. These SO₂ regeneration reactions are

highly temperature-dependent and might account for sulfur-retention efficiency being lower at higher temperatures. The above explanation, it must be emphasized, is highly speculative.

B. Reduction in Emissions of Nitrogen Oxides

Nitrogen oxides, principally nitric oxide (NO), are formed during the combustion of fossil fuels and are a major contributor to air pollution. The quantities of NO observed in the flue gas from high-temperature combustors can be accounted for by the equilibrium of the nitrogen-fixation reaction, $\frac{1}{2} \text{N}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{NO}$, between the nitrogen and oxygen in the fluidizing air. However, for fluidized-bed coal-combustion experiments, observed concentrations of NO have been far in excess of those expected on the basis of the above reaction equilibrium. At 1600°F (a common temperature for fluid-bed combustion), the equilibrium concentration of NO varies from 50 to 200 ppm, depending on the oxygen concentration; the latter, in turn, depends on the level of excess air employed. During combustion of coal in the bench-scale fluid-bed combustor, nitric oxide levels of 400-800 ppm have been measured.

A suggested explanation for these high NO concentrations is that the temperature of the combusting particles is significantly higher (1800-2100°F) than the 1600°F measured. An equally probable explanation is that the nitrogenous content of the coal (1-1.5 wt % in U.S. coals) is a source of NO and that the kinetics of NO decomposition are slow enough so that equilibrium levels are not achieved. A simple and direct demonstration that the nitrogenous content of the coal is the source of NO was described in the previous annual report (ANL/ES/CEN-1001). In that demonstration, an inert component (argon) was substituted for the nitrogen component of the fluidizing gas in the fluid bed. Substituting argon did not affect the nitric oxide level significantly, showing clearly that most of the NO had originated from the nitrogenous content of the coal.

It was also reported in the preceding annual report that NO concentrations were reduced concomitantly with SO₂ concentrations when limestone was added. The NO concentration was lowered by as much as 40% of its original concentration. However, it appeared from the data accumulated to that time that NO concentration in the flue gas could not be lowered below 400 ppm.

Various investigations have been performed to obtain information to explain the cause of the observed reduction in NO levels and possibly lead to a method of further decreasing NO levels in the flue gas from fluidized-bed combustion systems. In one investigation, the NO levels obtained upon combustion of a nitrogen-free fuel (natural gas) were measured; in another investigation, the influence on NO removal of fluid-bed operating parameters (including the potential catalytic effect of limestone or sulfated limestone in the fluidized bed) was studied; and still in another

investigation, the effect on NO levels of adding metal oxides to promote catalytic decomposition of NO in a bench-scale combustor was studied.

1. Influence of Fuel on NO Emission

Substantiation of the earlier conclusion that most of the NO is generated from the nitrogenous content of the coal was furnished by the results of a series of experiments with natural gas. In these experiments, in which the only source of nitrogen was the fluidizing air, the NO concentration observed in the flue gas (<100 ppm) was that expected from the nitrogen fixation equilibrium.

2. Influence on NO Removal of a Limestone Fluidized Bed and the Fluidized-bed Operating Conditions

Changes in nitric oxide concentration in the flue gas during the addition of limestone to a fluidized-bed combustor were observed in a series of coal-combustion experiments. The most significant reduction in NO emis-

Fig. 17. Effect of Calcium/Sulfur Mole Ratio on Nitric Oxide Removal, -325 Mesh (<44 μ m) Tymochtee Dolomite

sion (from an initial concentration of about 600 to 200-300 ppm) was achieved when the initial fluidized bed was composed entirely of limestone. An interesting observation pertaining to NO removal upon the addition of limestone was that NO concentration did not decrease immediately, but only after SO₂ removal had occurred. This suggests that the sulfate formed by the reaction between SO₂ and limestone may be responsible for NO removal. The influence of calcium sulfate on the reduction of NO concentration is also apparently indicated by results obtained with Tymochtee dolomite (see Fig. 17); the extent of NO removal was inversely proportional to the Ca/S mole ratio in the feed. With lower Ca/S mole ratios in the feed, higher concentrations of CaSO₄ would be expected in the bed. It had been observed that higher Ca/S mole ratios in the feed are associated with lower SO₂ levels in the

off-gas. Other data will be examined to determine if a relationship between SO₂ levels and NO levels in the flue gas is a causal factor in the observed NO removals, as has been suggested by Skopp.⁶

An analysis of a series of fluid-bed experiments showed that the degree of reduction in NO concentration was inversely proportional to the velocity of the fluidizing gas. These results are shown in Fig. 18, which indicates that the NO reduction in the flue gas was directly proportional to the gas residence time, indicating the possibility that the kinetics of decomposition control the levels of NO.

Fig. 18. Effect of Superficial Gas Velocity on Nitric Oxide Removal

that oxides of aluminum, cobalt, and zirconium appeared to be the most effective of the decomposition catalysts.

Experiments were conducted in the bench-scale fluidized-bed combustor by injecting particulate metal oxides into the fluidized-bed combustor at the location where coal and limestone additive were injected. In the first experiment, the solid catalysts used, in turn, were aluminum oxide (Al_2O_3), zirconium oxide (ZrO_2), and cobalt oxide (Co_3O_4 , cobaltous-cobaltic oxide). Except for zirconium oxide, which contained a percent or two of hafnium, these materials were reagent grade with purities greater than 99.9%.

Injection of Al_2O_3 or ZrO_2 into the fluidized bed at rates of several pounds per hour did not change the nitric oxide concentration in the flue gas. Injection of each material was continued for about one hour.

Injection of Co_3O_4 at a rate of about 4 lb/hr caused the nitric oxide concentration in the flue gas to increase rather than decrease. (The latter would be expected if NO were catalytically decomposed.) The NO concentration increased from about 700 ppm before injection to about 1400 ppm during injection. When Co_3O_4 injection was stopped, the NO concentration in the flue gas dropped back to nearly its original level. Upon reinstitution of catalyst injection, NO concentration in the flue gas immediately increased.

In a second experiment with Co_3O_4 , the NO and SO_2 concentrations in the flue gas were 600 and 1000 ppm, respectively, before catalyst

3. Addition of Metal Oxides to Promote Catalytic Decomposition

Catalytic decomposition was considered as a means of reducing nitric oxide emission. Reviews of the literature in the field of catalytic control of nitrogen oxides^{7,8} indicate that low reaction rates, instability of the catalyst at fluidized-bed temperatures, and catalyst poisoning by sulfur oxides are among the factors mitigating against in situ use of particulate catalysts. Nevertheless, the attractiveness of this approach for lowering NO emission, the fact that these catalysts had not been previously evaluated in a fluidized bed, and the simplicity of the testing procedures led to scoping tests being performed. The literature indicated

injection was started. When Co_3O_4 was first injected at a rate of about 4.5 lb/hr, NO concentration increased to about 1000 ppm. Co_3O_4 might act as a catalyst for the oxidation of nitrogen compounds in coal to NO, similarly to the catalytic oxidation of ammonia. In both experiments, the addition of metal oxide catalysts had no discernible effect on SO_2 concentration in the flue gas.

4. NO_2 Content of Off-gas

A suggested mechanism for the removal of NO concomitantly with the removal of SO_2 upon the introduction of limestone was based on the equilibrium reaction $\text{NO}_2 + \text{SO}_2 \rightleftharpoons \text{SO}_3 + \text{NO}$, which has been studied by British workers.⁹ If this reaction is involved, a decrease in SO_2 concentration could result in a corresponding decrease in NO concentration and an increase in NO_2 concentration. This reaction hypothesis was tested by determining the NO_2 content of the flue gas during a fluidized-bed combustion experiment. Three different analytical methods were used to assay the NO_2 content of the flue gas.

In one method, the phenoldisulfonic acid procedure,¹⁰ the concentration of nitrogen oxides in the flue gas was determined and the NO_2 value was obtained by difference, using the value for NO concentration determined simultaneously by means of the IR analyzer. A second method was the use of a mass spectrometer to determine the NO/ NO_2 mass ratio.* The third method for assaying NO_2 concentration in the flue gas used the Mast NO_2 analyzer, which is a continuous in-line instrument.¹¹

Samples of flue gas taken both before and during the addition of limestone in a coal-combustion experiment were analyzed. The results from all three methods indicated that the flue-gas samples contained essentially no NO_2 . For example, mass-spectrometric analysis indicated that the NO/ NO_2 ratio was at least 50/1 and probably much higher. Also, the Mast in-line NO_2 analyzer consistently indicated no NO_2 or, at the most, concentrations at the parts-per-million level. Of the three methods, the phenoldisulfonic acid method, which gives the NO_2 concentration by difference ($\text{NO}_2 = \text{NO}_x - \text{NO}$), seemed the least precise; both negative and positive values for the NO_2 concentration were obtained.

These results indicate that the NO_2 concentration in the flue gas from a fluidized-bed combustor is very small, which is in agreement with results for other types of coal combustors. Since NO_2 concentration does not change when limestone is added to the fluidized bed, the equilibrium reaction $\text{NO}_2 + \text{SO}_2 \rightleftharpoons \text{NO} + \text{SO}_3$ is apparently not operative in the observed reduction in NO concentration concomitantly with SO_2 removal.

*The mass-spectrometric analyses were kindly performed by Dr. E. Sloth of the Chemistry Division.

C. Miscellaneous

1. Mathematical Modeling

a. A Model for Predicting the Extent of Reaction of Limestone and SO₂ during Fluidized-bed Combustion of Coal (L. B. Koppel*). A mathematical model is being developed to predict the degree of SO₂ removal in fluidized-bed coal combustors as a function of the operating parameters of bed height, gas velocity, and additive feed rate. The model requires, as input, laboratory-scale kinetic data on the reaction of SO₂ and limestone materials. The generation pattern of SO₂ within the bed (i.e., the manner in which coal burns throughout the fluidized bed) possibly has a significant effect on the degree of SO₂ removal. Details of the model are presented in Appendix C, Section 1.

b. Modeling Studies of Coal Feeding for Fluidized-bed Combustors (J. Gabor and D. Ramaswami). Modeling studies were initiated to predict the mixing of coal particles in a fluidized-bed combustor. The initial model was based on the use of a diffusion coefficient to describe particle mixing. It was concluded that coal concentration in the bed is more uniform for horizontal jet coal injection with deep penetration into the bed than for feed injection at the base of the bed. Details of this model are contained in Appendix C, Section 2.

2. Combustion Efficiency

Combustion experiments, expressed as percent of the carbon in the feed that was completely burned, were determined during various bench-scale experiments. For coal-combustion experiments conducted at 1600°F with a superficial gas velocity of 3 ft/sec, 10-20% excess air, and no recycle of elutriated fines, the combustion efficiency ranged from 93.4 to 97.2%. Most (80-90%) of the unburned carbon left the system in elutriated solids. Details of the results are presented in Appendix D.

3. Material Balances

Material balances for sulfur, calcium, and carbon for four coal-combustion experiments ranged between 83 and 100%. Details are presented in Appendix E.

4. Alternative Methods of Calculating SO₂ Removal

The relationship between two methods of calculating SO₂ removal has been derived to determine whether values of SO₂ removal determined by the two methods differ significantly. SO₂ removal can be calculated (1) as the percent of sulfur fed that is not in the flue gas or (2) as the percent reduction

*L. B. Koppel, Purdue University, consultant to the Chemical Engineering Division, Argonne National Laboratory.

in SO₂ emission upon introducing additive. The calculation of SO₂ removal based on (1) SO₂ initially in the flue gas and (2) SO₂ in the flue gas upon introducing additive is more conservative than the calculation based on total sulfur in the feed. However, at levels of SO₂ removal greater than 80%, the difference between the two methods of calculation appear to be less than the experimental error. Details are presented in Appendix F.

5. Calculated Waste Burden from Limestone and Dolomite Additives

The quantity of additive feed needed and the amount of waste solids generated by the addition of various types and amounts of limestone and dolomite additives to a fluidized-bed combustor were calculated for coals of various ash and sulfur contents. If $1\frac{1}{2}$ times the stoichiometric amount of limestone were used for pollution control in burning a 10% ash coal containing 2% sulfur, the total quantity of waste solids would be doubled as compared with combustion without the limestone additive. The use of a dolomite would result in an even greater increase in total waste solids burden. Details are presented in Appendix G.

APPENDIX A

Detailed Description of Experiments

Presented here are details on operating conditions and results of experiments discussed in Section VI of this report.

1. SACC Series

A systematic experimental plan, designated the SACC series, was designed to investigate the reduction of SO₂ emissions by fluidized-bed combustion of coal at 1600°F under conditions applicable to conceptual designs of both utility-size power stations and industrial steam boilers. The principal variables studied were (1) the particle size of limestone No. 1359 additive, (2) the fluidizing-gas velocity, and (3) the recycle of elutriated fines.

Some experiments in the systematic plan (SACC-1 to SACC-4) were reported previously (ANL/ES-CEN-1001, p. 23); the operating conditions and results for the complete series of experiments are given in Table A.1.

TABLE A.1. Operating Conditions and Results, SACC Series of Experiments

Equipment:		6-in.-dia bench-scale combustor											
Starting bed:		13.2 kg alumina ^a											
Coal:		~4.5 wt % sulfur (as received) ^b											
Additive:		Limestone No. 1359 (98 wt % CaCO ₃ , 1.3 wt % MgCO ₃)											
Combustion Temperature:		1600°F											
Bed height:		15 in. static (~24 in. fluidized)											
Expt. SACC-	Superficial Gas Velocity, ft/sec	Additive Average Particle Size, μm	O ₂ in Flue Gas, vol %	Ca/S Mole Ratio	Recycle of Elutriated Fines	SO ₂ in Flue Gas, ppm		Reduction in SO ₂ Emission, %	CaO Utiliz., %	NO in Flue Gas, ppm		Reduction in NO Emission, %	
						Initial	Final			Initial	Final		
1	3	25	2.0	1.9	No	4000	1300	68	36	710	440	38	
2	3	600	3.8	2.4	No	3400	1600	53	22	600	400	33	
3	3	600	2.9	2.6	No	3600	1700	52	20	560	400	29	
5	3	25	3.2	2.2	No	3700	800	79	36	595	420	29	
5R	3	25	3.2	2.2	Yes	3700	800	79	36	595	420	29	
9	3	25	3.5	1.7	No	3900	1400	64	38	705	500	29	
9	3	25	1.5	1.2	No	3900	2290	41	34	705	400	43	
9	3	25	2.5	1.7	No	3900	1380	65	38	705	460	35	
9	3	25	3.0	3.0	No	3900	800	79	26	705	500	29	
6	9	25	3.5	1.3	No	4050	2000	51	39	550	420	24	
6	9	25	3.3	1.7	No	-	1650	59	34	550	400	27	
7	9	1400	2.3	1.6	No	4070	3350	18	11	680	550	19	
8	9	25	3.5	1.0	No	3950	2400	39	39	610	520	15	
8R	9	25	3.0	1.0	Yes	3950	2650	33	33	610	510	16	
8R	9	25	2.5	2.4	Yes	3950	1150	71	30	610	510	16	
8	9	25	2.5	2.4	No	4350	1350	69	29	570	470	17	
8R	9	25	1.5	2.4	Yes	4350	1550	64	27	570	420	26	

^aAlumina particle size: 30 and 14 mesh for experiments at 3 and 9 ft/sec, respectively.

^bCoal particle size: -14 and -6 mesh for experiments at 3 and 9 ft/sec, respectively.

2. SA Series

An additional series of bench-scale experiments (SA-1 to SA-4) with limestone No. 1359 was statistically designed to investigate the effects of additive particle size (25- and 103- μ m average), bed temperature (1550 and 1650°F), and additive feed rate (Ca/S ratios of 1-4). In these experiments, the superficial gas velocity was maintained at ~3 ft/sec.

The statistical design was a Plackett-Burman design,^{12,14} which permits three variables to be studied at two levels in four experiments. The statistical design is shown in Table A.2, in which the high level of a variable is coded by "+" and the low level by "-." The general form of the coding equation¹⁴ is

$$X = \frac{(\text{experimental level of variable}) - (\text{midvalue of variable})}{\text{unit change}};$$

e.g., in experiment SA-1,

$$X(\text{Temp}) = \frac{1500 - \frac{1550 + 1650}{2}}{\frac{1650 - 1550}{2}} = \frac{1550 - 1600}{50} = -1.$$

The effect of a variable on a result is simply the difference between the average value of the result with the variable at the high level and the average value with the variable at the low level,¹² e.g., from Table A.2,

$$E_{\text{Temp}} = \frac{Y_2 + Y_3}{2} - \frac{Y_1 + Y_4}{2},$$

or

$$E_{\text{Temp}} = \frac{Y_2 + Y_3 - Y_1 - Y_4}{2}.$$

TABLE A.2. Statistical Design, SA Series Experiments

Equipment:	6-in.-dia fluidized-bed combustor
Coal:	~4.5 wt % sulfur
Additive:	Limestone No. 1359
Bed height:	15 in. static (24 in. fluidized)
Superficial gas velocity:	3.0 ft/sec
Excess air:	~2.0%

Variables:

1. Combustion Temperature: (+) 1650°F
(-) 1550°F
2. Additive particle size: (+) -80 +325 mesh
(177 to 44 μm)
(-) -325 mesh (25 μm)
3. Ca/S mole ratio in feed: (+) high level
(-) low level

Expt.	Combustion Temp	Additive Particle Size	Ca/S	Result
SA-1	-	-	+	Y ₁
SA-2	+	-	-	Y ₂
SA-3	+	+	+	Y ₃
SA-4	-	+	-	Y ₄
(Repeat one experiment)				Y ₅

One source of uncertainty is the experimental error, which can be estimated from the results of replicate experiments.¹³ For example, if the design in Table A.2 is used, with experiment SA-1 repeated as experiment SA-5,

$$\text{Variance} = \sigma^2 = \frac{\sum_{i=1}^n (Y_i - \bar{Y})^2}{n - 1} = \frac{(Y_1 - Y_5)^2}{2}.$$

The significance of an effect can then be determined by the Student's t-test¹² as: $t = E/\sigma$. The tabulated values of t can now be entered with one degree of freedom to obtain the probability of finding an effect with the given magnitude purely by chance.

The larger-particle limestone additive had an average particle size of 103 μm and the particle size distribution given in Table A.3. The 25- μm limestone was the same as that used in the SACC series.

TABLE A.3. Particle-size Distribution for
Limestone No. 1359
(average particle size = 103 μm)

U.S. Mesh	wt %	U.S. Mesh	wt %
-80 +100	15.8	-170 +200	14.1
-100 +120	14.6	-200 +325	12.6
-120 +170	34.1	-325	8.8

The operating conditions and results for the SA series of experiments are given in Table A.4. The results for experiment SA-3 are considered tentative, because steady-state conditions with constant additive feed rates were maintained only for periods of less than one hour.

TABLE A.4. Operating Conditions and Results, Expts. SA-1 to SA-4

Equipment: 6-in.-dia fluidized-bed combustor
Coal: -14 mesh, 4.5 wt % S
Additive: Limestone No. 1359 (97.8 wt % CaCO_3)
Starting bed: 13.2 kg sintered alumina (30-mesh Alcoa T-61)
Bed height: 15 in. static (24 in. fluidized)
Superficial gas velocity: 3 ft/sec

Expt. SA-	Combustion Temp, °F	Additive Particle Size, μm	O ₂ in Flue Gas, vol %	Ca/S Mole Ratio	SO ₂ in Flue Gas, ppm	Reduction in SO ₂ Emission, %	CaO Utiliz., %	NO in Flue Gas, ppm	Reduction in NO Emission, %
1A	1550	25	3.5	0	3780	-	-	720	-
1B			3.5	1.5	1600	58	39	600	17
1C			3.6	2.0	1250	67	33	600	17
1D			3.6	2.6	650	83	32	600	17
1E			3.8	4.2	400	89	21	~650	10
1F ^a			1.7	3.4	700	82	24	600	17
2A	1650	25	3.0	0	4400	-	-	840	-
2B			3.0	1.5	2050	54	36	580	31
2C			3.5	2.6	1150	74	28	600	28
2D			3.5	3.0	850	81	27	600	28
2E			3.5	3.7	620	86	23	640	24
3A	1650	103	3.8	0	4000	-	-	-	-
3B			3.4	2.4	1600	60	-	-	-
3C			3.4	0.8	1800	55	-	-	-
3D			3.3	0.6	2300	43	-	-	-
3E			2.9	0.8	2300	42	-	-	-
4A	1550	103	2.7	0	3400	-	-	760	-
4B			2.6	4.0	160	95	24	530	30
4C			2.6	1.7	1400	59	35	550	28
4D			2.6	0.6	2300	32	53	690	9
4E			2.6	2.4	920	73	30	530	30

^aData in this portion of the run were suspect because of changing coal and additive feed rates and low excess air.

SO₂ removals obtained at the same Ca/S mole ratios but with different additive particle sizes in the feed showed that additive particle size had essentially no effects in the range studied. This result, coupled with the fact that attainment of a specific Ca/S mole ratio in an experiment was time-consuming, indicated that the data from this statistically designed set of experiments could be analyzed by stepwise multiple-regression techniques. The results of the multiple regression analysis are discussed in Section VI.A.1.c of this report.

Fig. A.1. Schematic Diagram of Baffle Plate Installed in Combustor for Expt. BC-1

3. BC Series, AR Series

a. BC-1, Baffle Plate Installed in Reactor

A baffle (see Fig. A.1) was constructed and installed in the combustor in an effort to improve gas-solids mixing in the fluidized bed. The baffle cone was used in experiment BC-1, which is summarized in Table A.5. As shown in this table, the SO₂ removal at a Ca/S ratio of 2.0 in experiment BC-1 was 65%, essentially the same as the 65% reduction obtained in SACC-9 at a Ca/S ratio of 1.7 without the baffle.

b. BC-2 to BC-5, Tymochtee Dolomite

Experiments BC-2 to BC-5 were performed to test the

TABLE A.5. Operating Conditions and Results, Expt. BC-1

Equipment:	6-in.-dia fluidized-bed combustor with baffle plate
Starting bed:	13.2-kg alumina (30 mesh)
Coal:	-14 mesh, ~4.5 wt % sulfur (as received)
Additive:	Limestone No. 1359 (98% CaCO ₃ , 1.3 wt % MgCO ₃), 25-μm average particle size
Combustion temperature:	1600°F
Bed height:	15 in. static (~24 in. fluidized)
Superficial gas velocity:	~3 ft/sec

Expt.	Ca/S Mole Ratio	Reduction in SO ₂ Emission, %	CaO Utiliz., %	Reduction in NO Emission, %
BC-1	1.2	53	44	22
	2.0	65	32	22

effectiveness of a dolomite from the Tymochtee formation in Western Ohio for SO₂ removal in coal-combustion experiments. The operating conditions and results for these experiments are given in Table A.6. The particle-size distribution of the larger-sized dolomite used in experiments BC-2 and BC-3 is characterized in Table A.7; the finer-sized dolomite particles were all minus 325 mesh; a particle-size distribution for the latter is not available.

TABLE A.6. Operating Conditions and Results, Expts. BC-2 to BC-5

Equipment:		6-in.-dia fluidized-bed combustor						
Starting bed:		29.1 lb sintered alumina (30 mesh)						
Coal:		-14 mesh, 4.5 wt % sulfur						
Additive:		Tymochtee dolomite (49.3 wt % CaCO ₃ and 36.6 wt % MgCO ₃)						
Combustion temperature:		1600°F						
Bed height:		15 in. static (24 in. fluidized)						
Superficial gas velocity:		2.8 to 2.9 ft/sec						
Expt. BC-	Additive Avg. Particle Size, μm	O ₂ in Flue Gas, vol %	Ca/S Mole Ratio	SO ₂ in Flue Gas, ppm	Reduction in SO ₂ Emission, %	CaO Utiliz., %	NO in Flue Gas, ppm	Reduction in NO Emission %
2	-	3.7	0	3950	-	-	530	-
	650	2.8	1.6	530	87	54	~500	~6
3	-	3.5	0	3950	-	-	720	-
	650	3.0	1.5	850	78	52	550	24
4	-	3.5	-	3350	-	-	600	-
	<44	3.0	0.6	1850	45	64	350	42
	<44	3.2	1.2	1050	69	46	395	34
5	-	2.0	-	3650	-	-	510	-
	<44	2.2	1.5	1250	66	33	365	28
	<44	2.5	2.1	620	83	31	400	22

TABLE A.7. Particle-size Distribution for +60 Mesh Tymochtee Dolomite

(average particle size = 650 μm)

U.S. Mesh	wt %	U.S. Mesh	wt %
-10 +18	7.8	-35 +45	19.9
-18 +25	28.0	-45 +60	17.1
-25 +35	27.1		

c. BC-6 to BC-10 and AR-1 (Fluidized Bed of Partially Sulfated Limestone)

A series of experiments was performed using as the starting fluidized-bed material partially sulfated limestone rather than alumina. A large portion of the large-particle-size limestone used remained in the

fluidized bed (rather than being elutriated). Long-term feeding of large-particle-size additive with provision for continuous drawoff of bed material would result in displacement of the initial starting-bed material.

(1) Experiments BC-6, BC-7, and BC-8. Fresh limestone No. 1359 with an average particle size of $615\ \mu\text{m}$ was the initial fluid-bed material for experiment BC-6. This material was calcined during combustion of coal and then sulfated not only by SO_2 generated by the combustion

Fig. A.2. Calcination of a Fluidized Bed of 18 to 45 Mesh Limestone No. 1359 as Indicated by Flue-gas CO_2 Level and Bed Pressure Drop, Expt. BC-6

of coal but also by a side stream of SO_2 added from an external source. During the first part of the experiment, calcination of limestone was clearly indicated by changes in the CO_2 content of the flue gas and the pressure drop across the fluidized bed (see Fig. A.2). During calcination, the CO_2 concentration in the flue gas was 25 vol % (and included CO_2 generated by coal burned to maintain the temperature). During calcination, the pressure drop across the bed decreased markedly, owing to a lower bed density during evolution of CO_2 . The bed temperature was 1500°F while calcination

was progressing and increased to 1600°F when calcination was complete. CO_2 concentration decreased to an average of 16.2 vol % after calcination.

The operating conditions and results for experiment BC-6 are shown in Table A.8. During the initial 11.5 hr of operation, the bed was calcined and sulfated by combustion of coal. During this period of operation, the calculated sulfur pickup in the bed corresponded to a CaO utilization of 25%.

TABLE A.8. Operating Conditions and Results, Expts. BC-6 to BC-8

Equipment:		6-in.-dia fluidized-bed combustor										
Coal:		4.5 wt % sulfur (-14 mesh)										
Additive:		Limestone No. 1359, 18 to 45 mesh, 615- μ m avg. diameter										
Combustion temperature:		1600°F										
Superficial gas velocity:		2.8 ft/sec										
Expt. BC-	Starting Bed		Duration, hr	Feed Rates, lb/hr			Ca/S Mole Ratio	O ₂ in Flue Gas, vol %	SO ₂ in Flue Gas, ppm	Reduction in SO ₂ Emission, ^a %	CaO Utiliz., %	NO in Flue Gas, ppm
	Material	Wt, lb		Coal	SO ₂	Limestone No. 1359						
6	Fresh limestone No. 1359	29.0	11.5	4.4	-	-	-	3.0	130	96	(25) ^b	~600
			5.5	4.4	0.52	-	-	~3	250 to 5900	82	(47) ^b	~400
			3.5	4.4	-	1.6	2.6	3.0	960	79	30	~380
7	Bed from BC-6	27.5	1.25	4.9	-	-	-	2.5	2250	55	-	340
			19.5	5.4	-	1.8	2.3	1.0 to 3.5	930	83	36	~220
8	Bed from BC-7	18.2	1.0	4.5	-	-	-	3.1	3350	27	-	310
			23.0	4.3	-	1.6	2.5	~3.5	940	79	32	~320

^aBased on total sulfur fed to combustor.

^bCumulative CaO utilization of limestone bed material.

Starting after 12 hr of operation, sulfur input to the bed was more than doubled for a 5-hr period by adding SO₂ from an external gas cylinder to sulfate the bed more rapidly. At the start of additive injection (after 18 hr of operation), the total sulfur pickup by the bed material corresponded to a CaO utilization of 47%.

For experiment BC-7 (see Table A.8), the initial fluidized bed was the partially sulfated bed from experiment BC-6. In experiment BC-8, the starting bed consisted of 18.2 lb of the final bed from BC-7, and the observed height of the fluidized bed under operating conditions was ~24 in. The particle-size distribution of the limestone No. 1359 additive used in experiments BC-6 to BC-8 is shown in Table A.9.

TABLE A.9. Particle-size Distribution for
18 to 45 Mesh Limestone No. 1359
(average particle size = 615 μ m)

U.S. Mesh	wt %	U.S. Mesh	wt %
-16 +18	0.4	-35 +45	24.1
-18 +25	25.6	-45	3.4
-25 +35	46.5		

(2) Experiment BC-9. In experiment BC-9, limestone No. 1360 was tested as additive material. The starting bed was the final bed of calcined and sulfated limestone No. 1359 from experiment BC-8. The operating conditions and results are shown in Table A.10. The limestone No. 1360 additive had the particle-size distribution shown in Table A.11.

(3) Experiment BC-10. Dolomite No. 1337 was tested as additive material in experiment BC-10. The dolomite, screened to a nominal -14 +40 mesh, had an average diameter of 540 μ m and the particle-size distribution given in Table A.12. The combustion temperature for BC-10 was 1600°F during most of the experiment; operation was at 1480 and 1800°F at the end of the experiment. The operating conditions and results are shown in Table A.10.

TABLE A.10. Operating Conditions and Results, Expts. BC-9, BC-10, and AR-1

Equipment: 6-in.-dia fluidized-bed combustor Coal: -14 mesh, 4.5 wt % sulfur Superficial gas velocity: 2.5 to 3.1 ft/sec															
Expt.	Starting Bed			Run Period, hr	Feed Rates, lb/hr		Ca/S Mole Ratio	Combustion Temp, °F	Flue-gas Composition (dry basis)					Reduction in SO ₂ Emission, %	CaO Utiliz., %
	Material	Wt, lb	Additive		Coal	Additive			O ₂ , vol %	CO, ppm	CH ₄ , ppm	NO, ppm	SO ₂ , ppm		
BC-9	From BC-8	18.3	Limestone ^a No. 1360	21.5	4.1	1.7	2.3	1600	~3.5	NA	NA	~400	900-1250	74	32
BC-10	From BC-9	18.3	Dolomite ^b No. 1337	21	4.3	2.6	2.2	1600	~4.0	NA	NA	~440	670-1120	81	37
				3	4.3	2.6	2.2	1480	4.0	NA	NA	380	420	91	41
				1.3	4.3	2.6	2.2	1800	3.6	NA	NA	460	3650	17	8
AR-1	From BC-10	18.0	Limestone ^c No. 1359	4	4.6	1.7	2.5	1400	3.4	4570	210	250	~2600	44	18
				4	4.6	1.7	2.5	1450	3.0	3750	200	280	1480	65	26
				4	4.6	1.7	2.5	1500	3.5	1480	48	360	420	91	36
				4	4.6	1.7	2.5	1550	3.4	700	52	430	420	91	36
				4	4.6	1.7	2.5	1600	3.3	900	56	430	900	86	34
				4	4.6	1.7	2.5	1400	3.2	3930	200	270	2450	53	21

^a-14 +40 mesh, 630- μ m average size, 78 wt % CaCO₃, 22 wt % MgCO₃.

^b-14 +40 mesh, 540- μ m average size, 53.4 wt % CaCO₃, 46.5 wt % MgCO₃.

^cAs-received limestone, -14 mesh, 490- μ m average size, 98 wt % CaCO₃, 1.2 wt % MgCO₃.

NA: not available.

TABLE A.11. Particle-size Distribution for -14 +40 Mesh
Limestone No. 1360, Expt. BC-9
(average particle size = 630 μ m)

U.S. Mesh	wt %	U.S. Mesh	wt %
-14 +18	7.3	-40 +60	18.5
-18 +25	26.7	-60 +100	1.1
-25 +30	15.1	-100	2.9
-30 +40	28.8		

TABLE A.12. Particle-size Distribution for -14 +40 Mesh
Dolomite No. 1337, Expt. BC-10
(average particle size = 540 μ m)

U.S. Mesh	wt %	U.S. Mesh	wt %
-14 +25	4.8	-40 +60	20.2
-25 +30	28.5	-60	1.6
-30 +40	44.9		

TABLE A.13. Particle-size Distribution for
Limestone No. 1359 (Medium), Expt. AR-1

U.S. Mesh	wt %	U.S. Mesh	wt %
-14 +25	15.6	-80 +170	13.1
-25 +35	29.8	-170 +325	2.5
-35 +45	15.1	-325	0.8
-45 +80	22.7		

(4) Experiment AR-1. As-received limestone No. 1359 having the particle-size distribution shown in Table A.13 was the additive in experiment AR-1. The starting bed was the final bed from BC-10. The combustion temperature in AR-1 was first increased

from 1400 to 1600°F in 50°F increments; the experiment was concluded by lowering the combustion temperature to 1400°F to determine whether initial SO₂ levels would be reestablished. The results of experiment AR-1 are summarized in Table A.10.

4. NG Series--Natural-gas Fuel

An objective of fluidized-bed combustion experiments with natural gas as fuel was to study nitric oxide emission during combustion of a fuel containing no nitrogenous compounds. Additionally, natural gas provided a source of ash-free fuel, allowing study of the reaction of SO₂ and limestone in the absence of coal ash. The operating conditions and results of experiments NG-1 to NG-4 are shown in Table A.14. The results for NG-5 are summarized in Table A.15.

In all experiments with natural-gas fuel, the nitric oxide level remained in a narrow range of 60-100 ppm over a wide range of operating conditions, including flow rates for fluidizing air giving oxygen concentrations in the flue gas of 0.6 to 4.6 vol %.

TABLE A.14. Operating Conditions and Results for Experiments with Natural Gas Fuel

		Equipment: 6-in.-dia fluidized-bed combustor									
		Starting bed: ^a 29.1 lb sintered alumina (30 mesh)									
		Fuel: Natural gas									
		Additive: Limestone No. 1359 (97.8 wt % CaCO ₃), 25- μ m average particle size									
		Bed height: 15 in. static (24 in. fluidized)									
		Superficial gas velocity: 2.1 to 2.8 ft/sec									
Expt. NG-	Combustion Temp, °F	Feed Rates				Flue-gas Composition			Reduction in SO ₂ Emission, %	CaO Utiliz., %	Remarks
		Natural Gas, ^b scfm	SO ₂ , scfh ^b	Additive, lb/hr	Ca/S Mole Ratio	O ₂ , vol %	SO ₂ , ppm	NO, ppm			
1	1625	0.6	-	-	-	3.7	-	90	-	-	
2	1800	0.8	-	-	-	1.2-4.6	≤2450	65	-	-	
3	1620	0.8	1.5	c	-	~3.5	≤3780				
	1600	0.8	1.5	0.6	1.5	~3.5	160 ^d	75	99	66	SO ₂ added at preheater.
	1600-1850	0.8	-	-	-	0.6-2.0	400-4900	65	-	-	SO ₂ desorption step.
4	1600	0.8	1.5	-	-	3.6	4350	65	-	-	SO ₂ added at coal inlet.
	1600	0.8	1.5	0.85	2.1	3.5	350	60	92	44	

^aThe starting bed for NG-1 was the final bed from SA-4; the same bed was reused for Expts. NG-2 to NG-4.

^b70°F, 1 atm.

^c1.95 lb of additive slugged into the combustor in 5 min.

^dThe apparent zero point for the SO₂ IR detector was 145 ppm.

TABLE A.15. Operating Conditions and Results, Expt. NG-5

Equipment:	6-in.-dia fluidized-bed combustor							
Starting bed:	29.1 lb sintered alumina (30 mesh)							
Fuel:	Natural gas, 0.82 scfm, ^a plus SO ₂ added at 1.7 scfh ^a							
Additive:	Limestone No. 1359 (97.8 wt % CaCO ₃) 25- μ m average particle size							
Combustion temperature:	1600°F							
Bed height:	15 in. static (24 in. fluidized)							
Superficial gas velocity:	2.7 ft/sec							

Added Solids	Al ₂ O ₃ or Flyash, lb/hr	Limestone No. 1359, lb/hr	Mole Ratio, Ca/S	Flue Gas			% SO ₂ Removal	% CaO Utiliz.
				O ₂ , vol %	SO ₂ , ppm	NO, ppm		
-	-	0	0	3.7	3840	70	-	-
-	-	0.8	1.8	3.4	180	75	95	53
Fine Al ₂ O ₃	1.4	0.8	1.8	3.3	180	75	95	53
Flyash	0.9	0.8	1.6 ^b	≤3.2	~400	~100	90	56
Flyash	0.9	0.8	1.6 ^b	≤3.2	~400	~100	90	56
Flyash	1.7	0.8	1.4 ^b	≤3.2	~620	~100	84	60

^aSTP at 70°F, 1 atm.^bThe flyash contained 2.4 wt % sulfur.

As noted in Table A.14, the same bed material was used in experiments NG-1 to NG-4, and the starting bed for NG-1 was the final bed from SA-4 (a coal combustion-limestone additive experiment with an alumina bed). The starting bed contained some calcined and sulfated limestone that was further reacted during the combustion of coal at successively higher temperatures in NG-1 and NG-2.

During combustion of natural gas in NG-2, SO₂ began to desorb from the bed when the bed temperature was ~1720°F. (Any desorption of SO₂ at a lower temperature was not recorded because the SO₂ detector was off-stream.) The SO₂ desorption increased rapidly as the temperature was increased, reaching a peak value of 2450 ppm in the flue gas at a temperature of 1820°F, when the oxygen concentration in the flue gas was 1.3 vol %. Subsequently, SO₂ emission decreased substantially to 200 ppm as the oxygen level in the flue gas increased to 4.4 vol %. When oxygen in the flue gas was decreased to 1.2 vol % during the final hour of operation, the SO₂ level rose to 2200 ppm. Because moderate temperature changes also occurred during NG-2, it cannot be stated conclusively that the excess oxygen concentration was the sole factor controlling decomposition of the sulfated limestone in the bed. Desorption of SO₂ appears to depend on both oxygen level and temperature.

In experiments NG-3 and NG-4 (see Table A.14), natural gas was used as an ash-free fuel so that the reaction of SO₂ (from an external source) with limestone No. 1359 could be studied in the absence of coal ash.

Experiment NG-3 was carried out in three parts: Parts 1 and 2 consisted of reaction of SO_2 with additive at approximately 1600°F ; part 3 was an investigation of SO_2 release from partially sulfated additive in the fluidized bed (from parts 1 and 2) as the temperature was increased from 1625 to 1850°F . In experiment NG-3, sulfur dioxide was added to the fluidizing gas upstream of the preheater.

Part 3 of NG-3 (see Table A.14) was designed to elucidate the cause of SO_2 release from sulfated limestone when the temperature of the fluidized bed was increased from 1625 to about 1850°F during the combustion of natural gas. With this objective, the fluidized-bed combustor was purposely cycled through a range of combustion temperatures with 1.8 vol % oxygen in the flue gas, and subsequently, with the combustion temperature held at 1840°F , the oxygen level in the flue gas was varied between 1.8 and 0.5 vol %. The SO_2 level in the flue gas decreased from 2250 ppm at 1840°F to 800 ppm at 1790°F while the oxygen concentration was held at 1.8 vol %. Similarly, when the bed temperature was stabilized at 1850°F and the oxygen concentration was varied, the results shown in Table A.16 were obtained.

TABLE A.16. Effect of Oxygen Concentration in the Flue Gas on Desorption of SO_2 from Partially Sulfated Limestone

Elapsed Run Time, hr	O_2 in Flue Gas, vol %	Max SO_2 in Flue Gas, ppm
4.0-4.2	1.8	2700
4.2-5.5	1.5	2820
5.5-7.6	1.0	4280
7.6-8.1	0.5	4900
8.1-8.6	1.8	2050

The desorption step of experiment NG-3 demonstrated that release of SO_2 from partially sulfated limestone No. 1359 is increased by increasing the temperature and by lowering the oxygen concentration in the flue gas.

In experiments NG-3 to NG-5, the combustor was kept free of coal ash during startup by heating the system electrically to $\sim 1000^\circ\text{F}$ and then injecting and igniting liquified petroleum gas (propane). When the bed temperature increased to $\sim 1200^\circ\text{F}$, natural gas (principally methane) was injected with the propane. Subsequently, the propane flow was shut off and the bed temperature was increased to the desired operating temperature by the combustion of natural gas.

In part 1 of NG-3, sulfur dioxide was injected into the fluidizing gas at various rates until the flue gas contained 3780 ppm SO_2 . This value was within 10% of the expected SO_2 concentration calculated from the

SO₂ feed rate.* Additive injection at a Ca/S mole ratio of 1.5 in part 2 of NG-3 decreased the SO₂ concentration to 160 ppm, corresponding to an SO₂ removal of 99% and a CaO utilization of 66%. Both values are much higher than results obtained during combustion of coal, especially for Ca/S mole ratios less than 2.

In experiment NG-4, SO₂ was injected into the fluidized bed through a feed port next to the coal and additive injection ports to determine whether the location of SO₂ addition had an appreciable effect on SO₂ removal. A carrier gas (air) for the SO₂ was introduced at the same flow rate (1.5 scfm) as is used for pneumatic transport of coal. The level of SO₂ in the flue gas when no additive was being fed was 4350 ppm. With additive injection at a Ca/S mole ratio of 2.1, the SO₂ concentration decreased to 350 ppm. These results correspond to a reduction in SO₂ emission of 92% and a CaO utilization of 44%, which are not as high as for NG-3 but appreciably higher than in experiments with coal.

Experiment NG-5 was carried out with natural gas spiked with SO₂ and fine-particle (25- μ m) limestone No. 1359. With SO₂ but no additive fed to the fluidized bed, the initial SO₂ level in the flue gas was 3840 ppm. When additive was injected into the fluidized bed at a Ca/S mole ratio of 1.8, the SO₂ level dropped to 180 ppm; this corresponds to a 95% reduction in SO₂ emission and a CaO utilization of 53%. To determine whether fines and specifically flyash have physical or chemical effects on SO₂ level in the flue gas, alumina particles (-325 mesh) and then flyash were added to the fluidized bed. With fine alumina particles injected into the reactor at a rate of 1.4 lb/hr (which is approximately three times the usual rate of flyash production during coal-combustion experiments), the reaction of SO₂ with limestone was not affected.

In three separate flyash addition periods of NG-5, the initial introduction of flyash caused sharp maximum peaks of SO₂ and NO emissions and sharp minima for oxygen in the flue gas. This initial response may have been caused by slugging of quantities of flyash when ash feeding was started. Since no slugging was observed during the initial minutes of the second and third flyash feeding periods, the rapid changes in SO₂, NO, and oxygen levels remain unexplained.

During the first and second flyash injection periods, flyash was injected at approximately twice the rate of flyash production during combustion of coal; during period 3, the introduction rate was approximately 3.5 times

*The SO₂ was injected into the preheater which was at 1000°F. At this temperature, the $\text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3$ equilibrium favors the formation of SO₃. However, at 1600°F, which is the gas temperature at the inlet of the fluid bed, the maximum SO₃ concentration predicted by equilibrium considerations is about 10% of the SO₂ concentration. Therefore, any contribution to the reactivity of the gas phase by the presence of SO₃ is not considered significant.

the normal ash-production rates. The SO_2 removal decreased from 95% (initially) to 90% in periods 1 and 2 and 84% in period 3. The release of SO_2 from partially sulfated additive at 1600°F was thus shown to be fairly independent of the presence of flyash (NG-5, Table A.15) and hence may be attributable to localized reducing conditions (the presence of CO) in the fluidized bed.

The NO concentration in the flue gas increased from 75 to ~100 ppm upon the addition of flyash (see Table A.15).

APPENDIX B

Laboratory-scale Sulfations of Elutriated Solids

Both SO₂ removal and limestone utilization might be improved by recycling elutriated fines to the fluidized-bed combustor for further reaction, since these fines contain an appreciable quantity of incompletely sulfated limestone. However, SO₂ level in the flue gas was not decreased nor limestone utilization improved by recycling fines collected in the primary cyclone to the fluidized-bed combustor.

In an attempt to discover the reason for the failure of recycled fines to react, a series of laboratory-scale experiments was designed and performed. These experiments were of two general types: (1) experiments designed to determine if reactivity of the recycled fines could be improved by changing the physical condition of the limestone (e.g., by grinding to produce a finer, more reactive particle, or by a hydration-dehydration cycle, which might result in a more porous and reactive structure) and (2) tests to compare the reactivities of elutriated material and fresh unreacted limestone.

The flyash-limestone mixture tested for further reactivity with SO₂ was material collected in the primary cyclone during the final hour of bench-scale experiment SACC-9 and had the following composition: calcium, 28.4 wt %; sulfur, 3.73 wt %; CO₂, 10.7 wt %; and carbon, 11 wt %. The Ca/S ratio for the mixture averaged 6.08, corresponding to a CaO utilization of 16.4%.

The sulfating-gas mixture for these experiments, consisting of SO₂, oxygen, and nitrogen, was produced by metering the individual components or by adding oxygen to a premixed SO₂-nitrogen mixture. The gas mixture contained 4000-4300 ppm SO₂ and 2-3 vol % oxygen, the remainder being nitrogen. Limestone No. 1359 identical to that used as feed in bench-scale experiment SACC-9 was used in a series of laboratory tests to determine the relative reactivities of fresh limestone and partially sulfated limestone. This limestone was shown by analysis to contain 97.8 wt % CaCO₃ and 1.3 wt % MgCO₃ and had a nominal particle size of 25 μ m.

The major equipment item used in these experiments was a 2-in.-dia stainless steel horizontal boat reactor. The reactor was about 18 in. long; about 12 in. of this was inside a heating furnace. The solid samples to be sulfated were contained in stainless steel sample boats. Associated with the reactor was a gas-handling manifold through which the sulfating gas entered the reactor, and a vent through which spent gas flowed to gas-analysis instruments. The gas-analysis instruments included IR detectors for SO₂, NO, CH₄, and CO, a paramagnetic detector for oxygen, a Mast coulometric NO₂ analyzer, and a gas chromatograph for CO₂.

An experiment was conducted in the following manner. A sample boat containing a limestone or flyash-limestone sample was placed in the 2-in.-dia reactor and then heated to the reaction temperature of 1600°F while a stream of air passed through the reactor. During this heat-up period, probably any carbonates in the sample were calcined and carbon was converted to CO₂. When the reactor reached the selected reaction temperature of 1600°F, the flow of sulfating gas was started. The degree of sulfation achieved in these tests was determined by two methods:

- (1) by analysis for sulfur in the solid at the end of an experiment and
- (2) by integration of the SO₂ IR trace obtained by continuous monitoring of SO₂ concentration of the off-gas with the Beckman IR detector.

Fig. B.1. Off-gas Composition during Sulfation of Limestone No. 1359 at 1600°F, Expt. LST-22

Figure B.1 represents a typical IR trace of the SO₂ concentration in the gas phase leaving the sulfation reactor. The shaded area represents the quantity of SO₂ absorbed by the solid reactant.

To allow comparison of the two methods of estimating quantity of SO₂ reacted, Table B.1 presents analytical data for other experiments.

The data indicate good agreement between the two methods for experiments in which large quantities of SO₂ were absorbed. However, for experiments in which smaller quantities were absorbed, the IR method resulted in values as much as 40% greater than those obtained by wet chemical means. Therefore, the relative rate data obtained from the IR traces are considered qualitative.

TABLE B.1. Quantity of Sulfur Dioxide Reacted--Comparison of Determinations by Wet Chemical Analysis of Solids and by Instrumental Analysis of Off-gas

Expt.	Total Weight of SO ₂ Reacted, g		Ratio, Gas Analysis/ Solids Analysis
	Analysis of Solids	Analysis of Off-gas	
LST-15	0.62	0.88	1.42
FAST-19	0.41	0.58	1.42
FAST-20	0.94	1.08	1.15
LST-16/17	1.13	1.12	0.99
FAST-21	0.35	0.51	1.46

Seven experiments (FAST-1 to FAST-7) were performed to show the effects of physical and/or chemical modification of the flyash-limestone mixture on the capacity for further sulfation. In these experiments, the flyash-limestone mixture was used (1) as received, (2) after grinding, or (3) following a hydration procedure. Hydration was accomplished by the

slow dropwise addition of about 5 cc of distilled water (about an eightfold excess for the 5-g sample). The hydrated sample was, of course, converted back to CaO when heated in the reactor. Operating conditions for these FAST experiments were 60 min at 1600°F using a sulfating-gas mixture containing 4000 ppm SO₂ and 2.1 vol % oxygen in nitrogen at a gas flow rate of 2.8 liters/min. Sulfation was continued for a fixed time interval, followed by analysis of the solid to determine the extent of sulfation.

Three experiments were performed using the as-received material, and two experiments each for the ground and hydrated material. The degree of CaO utilization, originally 16.4%, increased as a result of sulfation to average values of 45.5, 51.5, and 41% for the as-received, ground, and hydrated materials, respectively (see Table B.2). Significant additional sulfation was obtained in these experiments; on the average, the final extent of sulfation was nearly three times the original extent of sulfation. The data also indicate that grinding the flyash-limestone mixture increased sulfation only slightly if at all and that hydration of the sample did not improve sulfation. These preliminary experiments indicate that there is no barrier to further reaction with SO₂ of the CaO in the flyash-limestone material elutriated from the fluidized bed.

TABLE B.2. Further Sulfation of Mixture of Flyash and Partially Sulfated Limestone

Equipment:	2-in.-dia laboratory-scale horizontal boat reactor					
Reaction temperature:	1600°F					
Sulfation time:	60 min					
Gas flow rate:	2.8 liters/min					
Gas composition:	4000 ppm SO ₂ , 2.1 vol % O ₂ , and the balance nitrogen					
	Ca, wt %	S, wt %	CO ₂ , wt %	C, wt %	Ca/S Mole Ratio	CaO Utiliz., %
Composition of Original Material	28.4	3.73	10.7	11.0	6.08	16.4
FAST-1 (no pretreatment)	23.9	8.3	0.14	0.7	2.30	44.5
FAST-2 (no pretreatment)	27.3	11.2	a	a	1.95	51
FAST-3 (no pretreatment)	28.28	9.3	a	a	2.43	41.2
FAST-4 (ground)	28.77	11.5	a	a	2.0	50.0
FAST-5 (ground)	27.86	11.8	a	a	1.89	53.0
FAST-6 (hydrated)	28.4	8.8	a	a	2.58	39.5
FAST-7 (hydrated)	28.53	12.1	a	a	2.36	42.5

^aAnalysis not performed.

The second series of experiments was performed to obtain comparative rather than absolute reaction-rate data for the flyash-limestone mixture and for limestone No. 1359. Reaction-rate data were obtained as a function of reaction time by integrating the IR trace of SO₂ concentration in the reactor off-gas. Since these data were produced only for comparison,

Fig. B.2. Reaction Rates of Flyash-Limestone No. 1359 Mixtures and Limestone No. 1359 as a Function of Reaction Time at 1600°F

it is not important whether they deviated from ultimate extents of reaction that could be determined by wet chemical analysis (noted above). The initial experiments were performed at 1600°F using a sulfating gas containing 4200 ppm SO₂ and 3 vol % oxygen in nitrogen at a flow rate of 2.7 liters/min. Data obtained for limestone No. 1359 and for the flyash-limestone No. 1359 mixture are shown in Fig. B.2 as plots of the reaction rate in mg SO₂/(g CaO)(min) versus reaction time in minutes.

Examination of data for experiments FAST-21 and FAST-19 indicated that at the ~50% level of CaO utilization, the molar quantity of SO₂ absorbed was approximately equivalent to, and possibly related to, the molar quantity of CO₂ evolved by calcination. However, the degree of CaO utilization appears to be related to the time of the experiment

rather than the quantity of CO₂ evolved, as was shown by longer-term experiments (2 hr) in which a higher degree (86%) of utilization was obtained.

An additional experiment was performed to show that the apparent relationship between the extent of additional sulfation and the degree of calcination of the limestone-flyash mixture was fortuitous. This experiment, FAST-21, was performed in such a manner as to decrease further calcination of the mixture by minimizing the time the sample was in the reactor before sulfation started. To accomplish this, the sample was placed in the preheated reactor rather than in the cold reactor, since the latter procedure would result in the solid sample being heated for several hours before sulfation started. During the long heatup period of the original procedure, calcination probably was completed before sulfation was started; with a short heatup before sulfation, calcination and sulfation reactions probably occurred simultaneously. The reaction-rate data show that the reaction rate of limestone No. 1359 differed little from that of flyash-limestone No. 1359 mixtures, and that the reaction rates for the two samples of flyash-limestone No. 1359 sulfated by different procedures were similar, indicating that calcination does not affect the sulfation reaction. This result does not explain the lack of reactivity of recycled flyash-limestone material in bench-scale experiments.

The partial pressure of SO_2 in the fluidized-bed combustor, about 0.4 mm, was one-tenth that in the laboratory experiments. This could be the reason for the evidently slower reaction of flyash-limestone mixture with SO_2 in the fluidized-bed combustor. Additional laboratory experiments were performed to test the effect of a low partial pressure of SO_2 . Both limestone No. 1359 and a flyash-limestone No. 1359 mixture were tested at

Fig. B.3. Reaction Rates for Limestone No. 1359 and Flyash-Limestone No. 1359 Mixtures with SO_2 at SO_2 Concentrations of 4200 and 570 ppm. Temp: 1600°F; Gas flow rate: 350 ml/min.

ture is possible and that the reactivity of the limestone in flyash-limestone material is essentially the same as for fresh limestone. The lack of further reaction of recycled material may be a result of insufficient gas-solids contact in the combustor.

1600°F, using a gas phase containing either 4200 ppm SO_2 (3.2 mm) or 570 ppm SO_2 (0.4 mm) at a gas flow rate of 350 ml/min. The lower flow rate was used so that low SO_2 concentrations could be maintained. The reaction rates for limestone and flyash-limestone mixture were similar at each SO_2 partial pressure (see Fig. B.3). This indicates that the apparently low reactivity in the fluid-bed combustor of recycled flyash-limestone mixture is not caused by a difference in reaction rate as a function of SO_2 partial pressure.

In conclusion, these results indicate that the ineffectiveness of recycle operation in reducing SO_2 levels in the combustor flue gas cannot be accounted for by a reason intrinsic to the rate of reaction of flyash-limestone material with SO_2 . The results do show that high utilization of the limestone in the mix-

APPENDIX C

Mathematical Modeling1. A Model for Predicting the Extent of Reaction of Limestone and SO₂ during Fluidized-bed Combustion of Coal (L. Koppel*)

The heterogeneous reaction of SO₂ with additive limestone particles in a fluidized-bed coal combustor is complex physically and hence mathematically. The objective of this study is to devise a mathematical model that is convenient to use, yet yields reasonably accurate predictions of SO₂ removal and determines how SO₂ removal is affected by typical operating variables. To achieve this, several assumptions regarding the process are made.

a. Model and Assumptions

With respect to Fig. C.1, it is assumed that the gas flow through the bed is plug flow, so that no gradients of SO₂ concentration exist trans-

Fig. C.1. Schematic Diagram of Fluidized-bed Combustor

verse to the direction of flow. Particle mixing in the bed is assumed to be perfect; hence the bed temperature is taken to be uniform. The combustion and consequent SO₂ generation occur throughout the bed with a pattern described by a generation function $G(x)$. Here $G(x)$ is the rate of generation of SO₂ per unit length of bed height, at a distance x from the bed entrance. The SO₂ is assumed to react with additive particles according to a first-order rate law.

Kinetic data have been obtained by NAPCA (National Air Pollution Control Administration) for precalcined limestone particles. These ex-

periments involved exposing an additive particle to SO₂ at a concentration C_0 equivalent to the SO₂ concentration that would result from combustion with no additive at the anticipated combustion temperature. The results were of the form illustrated in Fig. C.2, which is a plot of y , the mass of SO₂ reacted with a particle per original mass of CaO in the additive particle, versus time, t . The actual mechanisms responsible for the exact shape of such curves are complex, involving intraparticle diffusion. To simplify these, a first-order rate constant k is defined from this data curve by the equation

$$\frac{dy}{dt} = kC_0. \quad (C.1)$$

*L. Koppel, Purdue University, consultant to the Chemical Engineering Division, Argonne National Laboratory.

Fig. C.2. Typical Particle Kinetic Data

The rate constant k at the given temperature is assumed to depend only on the value of loading y ; thus, $k = k(y)$. The value of k decreases with increasing y because of consumption of additive, pore blockage, etc. The simplifying assumption that any two (identically sized) particles with the same SO_2 loading have the same reactivity removes the need for analyzing the complex intraparticle mechanisms. At any other SO_2 concentration, C , the reaction rate would be kC . Although, on a stoichiometric basis, the particle would ultimately be expected to reach the stoichiometric loading y_s , in actuality pore blockage can cause an ultimate loading y_e , that is lower than y_s .

b. Material Balances

With the above assumptions, a material balance on the gas phase can be written for each differential length dx of bed height. The result is

$$F \frac{dC}{dx} = G(x) - \bar{k}aC. \quad (\text{C.2})$$

Here, F is the mass flow rate of gas and $\bar{k}$ is the rate constant obtained by averaging $k(y)$ over the various SO_2 loadings of the additive particles (assumed to be perfectly mixed) in the bed;

$$\bar{k} = \int_0^{y_e} k(y)\phi(y) dy, \quad (\text{C.3})$$

where $\phi(y) dy$ is the fraction of the bed particles with loadings between y and $(y + dy)$. The constant, a , is the concentration of additive particles in the bed, expressed as (mass of original CaO)/(bed height). At the bed entrance, $x = 0$; it follows that $C = 0$, since no SO_2 has yet been generated. The solution of Eq. C.2, with this entrance condition, for the exit SO_2 concentration C_L is

$$C_L = \frac{1}{F} \int_0^L G(x) \exp\left[-\frac{\bar{k}a}{F}(L-x)\right] dx. \quad (\text{C.4})$$

To obtain the SO_2 concentration C_0 , which would occur at the exit if there were no additive, set $\bar{k} = 0$ in Eq. C.4 to obtain

$$C_0 = \frac{1}{F} \int_0^L G(x) dx. \quad (\text{C.5})$$

The SO_2 removal, R , is defined as

$$R = \frac{C_0 - C_L}{C_0}, \quad (\text{C.6})$$

which with Eqs. C.4 and C.5 leads to

$$R = \frac{\int_0^L G(x) \left\{ 1 - \exp \left[-\frac{\bar{k}_a}{F} (L - x) \right] \right\} dx}{\int_0^L G(x) dx}. \quad (\text{C.7})$$

A material balance for the particle phase is obtained by equating SO_2 removal from the gas phase with SO_2 consumed by the additive

$$F(C_0 - C_L) = w\bar{y}, \quad (\text{C.8})$$

where w is the feed rate of additive to the bed in (mass of CaO)/(time) and $\bar{y}$ is the average loading of the additive leaving the bed. Since the bed particles are perfectly mixed, this is the same as the average loading of the bed particles; hence,

$$\bar{y} = \int_0^{y_e} y\phi(y) dy. \quad (\text{C.9})$$

Also, combining Eqs. C.6 and C.8 yields

$$R = \frac{w\bar{y}}{FC_0} \quad (\text{C.10})$$

for SO_2 removal.

Thus, there are four equations to be satisfied: Eqs. C.7, C.10, C.3, and C.9. When these are satisfied, removal R is known.

c. Specific Patterns for Calculation

To perform calculations, specific forms are required for the functions $G(x)$, $k(y)$, and $\phi(y)$. Primary considerations in selecting these

functions are (1) reasonable correspondence with physical reality and (2) ease of calculation. The following forms were selected:

$$G(x) = \frac{FC_0\alpha}{L} \frac{e^{-\alpha x/L}}{1 - e^{-\alpha}} \quad (C.11)$$

$$k(y) = \frac{y_e}{C_0 t_{0.63}} \left(1 - \frac{y}{y_e}\right), \quad (C.12)$$

and

$$\phi(y) = \frac{\beta e^{-\beta y/y_e}}{y_e(1 - e^{-\beta})}. \quad (C.13)$$

The reasons for these selections are discussed next.

Fig. C.3. Normalized Generation Rate of SO_2 as a Function of Fractional Bed Height

$$y = y_e \left(1 - e^{-t/t_{0.63}}\right).$$

The generation patterns $G(x)$ resulting from Eq. C.11 are shown in Fig. C.3 for typical values of the arbitrary shape parameter α . As α is decreased, more of the SO_2 is generated near the bed exit. For $\alpha = \infty$, all SO_2 is generated at the entrance; for $\alpha = 0$, the SO_2 is generated uniformly throughout the bed; and for $\alpha = -\infty$, all SO_2 is generated at the exit. Note that Eq. C.11 satisfies

$$\int_0^L G(x) dx = FC_0,$$

so that the total generation rate is FC_0 , as it must be. Cumulative SO_2 generation patterns are sketched in Fig. C.4. Thus, a single parameter produces a wide range of generation patterns.

Equation C.12 follows if it is assumed that the data curve of Fig. C.2 can be fit to the equation

$$(C.14)$$

Use of Eq. C.14 with Eq. C.1 immediately leads to Eq. C.12.

Fig. C.4

Fraction of SO_2 Generated as a Function of Distance From Bed Entrance for Various Generation Patterns

*These values also represent the normalized SO_2 concentrations (C/C_0) when the additive feed rate is zero ($r = 0$).

Equation C.13 is selected because experimental distributions are typical for perfectly mixed systems. The shapes for $\phi(y)$ are obviously similar to those for $G(x)$, and hence are not sketched. However, it is important to emphasize that here the shape parameter is not arbitrary. There are two equations to be satisfied by $\phi(y)$: Eqs. C.3 and C.9. This fixes the value of β . Note that

$$\int_0^1 \phi(y) dy = 1,$$

as it must be.

With these forms, evaluation of the various integrals in Eqs. C.3, C.7, and C.9, elimination of β , and combination of Eqs. C.3, C.7, C.9, and C.10 lead to the following implicit equation for SO_2 removal, R :

$$R = \frac{1}{1 - e^{-\alpha}} \left[1 - \frac{\alpha \exp \left[- \left(1 - \frac{R}{r} \right) H \right] - \left(1 - \frac{R}{r} \right) \text{He}^{-\alpha}}{\alpha - \left(1 - \frac{R}{r} \right) H} \right] \quad (\text{C.15})$$

where

$$r = \frac{wy_e}{FC_0} \quad (\text{C.16})$$

is the effective ratio of additive feed to SO_2 feed, and where

$$H = \frac{aLy_e}{FC_0t_{0.63}} \quad (C.17)$$

is a normalized bed height.

Thus, given the data w , y_e , FC_0 (the total rate of generation of SO_2 in mass/time), a , L , $t_{0.63}$, and a selected shape parameter α for the SO_2 generation pattern, trial-and-error solution of Eq. C.15 yields the predicted SO_2 removal, R .

A quantity called particle consumption, C , can be defined to measure the efficiency of the process from the standpoint of the particles:

$$C = \frac{\bar{y}}{y_e} \quad (C.18)$$

Clearly, C is related to the usually defined particle utilization, U , by

$$U = \frac{y_e}{y_s} C, \quad (C.19)$$

where y_s is the stoichiometric particle loading. For different particles, the correction factor y_e/y_s between U and C varies. However, U is always less than C . From Eqs. C.16 and C.18 and the definition of r , it follows that

$$C = \frac{R(\bar{r})}{r} \quad (C.20)$$

d. Illustrative Results

Figures C.5, C.6, and C.7 present values (calculated as described in the preceding section) of SO_2 removal and particle consumption for various values of r , α , and H . In each figure, the normalized bed-height variable H is constant. Removal R and consumption C are plotted against additive-to- SO_2 feed ratio r at various values of α , the shape parameter for the SO_2 generation pattern.

As r is increased beyond approximately 10, SO_2 removal does not significantly increase with further increases in r . This is because the bed height is constant. At $r = 10$, the bed essentially contains only highly reactive, unconsumed particles. This represents the maximum possible bed reactivity, and further increases in r would not be expected to improve SO_2 removal. Obviously, CaO consumption is so low at these values of r that even the asymptotic value cannot be economically attained.

Fig. C.5. Calculated SO₂ Removal and Particle Consumption, $H = 10$

Fig. C.6. Calculated SO₂ Removal and Particle Consumption, $H = 30$

Fig. C.7. Calculated SO₂ Removal and Particle Consumption, $H = 100$

For a shallow bed, $H = 10$, the effect of SO_2 generation pattern, α , is quite strong. However, as the bed height is increased, α becomes less important.

Also shown in each of Figs. C.5-C.7 are two curves, one representing maximum possible values of particle consumption and the other maximum possible SO_2 removal. Since r is the effective additive-to- SO_2 feed ratio, maximum possible removal occurs at complete consumption ($C = 1$) if the value of r is less than unity, and maximum possible removal is unity if r exceeds unity. Similarly, maximum possible consumption occurs at complete removal ($R = 1$) at values of r greater than unity, and is unity for values of r less than unity. Thus,

$$R_{\max} = r \text{ and } C_{\max} = 1 \text{ if } r \leq 1;$$

$$R_{\max} = 1 \text{ and } C_{\max} = \frac{1}{r} \text{ if } r \geq 1.$$

The curves in Figs. C.5-C.7 show how closely ideal conditions are approached at different values of α .

Figure C.8 shows the effect of bed height on SO_2 removal and particle consumption. The additive-to- SO_2 feed ratio r is held fixed at

Fig. C.8. Calculated SO_2 Removal and Particle Consumption, $r = 1$

unity, and R and C (which are equal when $r = 1$) are plotted against H for various values of α . Clearly, deep beds are desirable, and a bed as deep as $H = 1000$ (or an equivalent series of shallow beds) should give virtually complete SO_2 removal and particle consumption, regardless of the SO_2 generation pattern. This statement would not apply in case of gas bypassing, an effect not included in this model, or if segregated combustion occurred at the top of the bed, producing an effective α value much lower than -5.

e. Application to Fluidized-bed Combustion Data

The major requirement for application of Eq. C.15 to predict SO_2 removal is knowledge of the two parameters y_e and $t_{0.63}$ from kinetic data. In general, curves such as Fig. C.2 are not available for the particles that have been used in ANL fluidized-bed combustion tests. The kinetic parameters y_e and $t_{0.63}$ must be estimated from data for other related particle systems. Furthermore, even if data such as Fig. C.2 were available for the relevant particles, there is no

guarantee that the course of reaction in the fluidized bed, in which a particle is exposed to varying conditions, will be the same as that in the laboratory test conducted at constant conditions.

With these reservations in mind, a sample calculation will be given to illustrate use of the model. Kinetic data are taken from NAPCA¹⁵ tests with the same additive material but having a different particle size from that in the ANL fluidized bed.

Run BCR-8 Conditions

Coal feed rate: 4.4 lb/hr.

Additive (limestone No. 1359) feed rate: 1.6 lb/hr.

Bed weight: 18 lb of 30 mol % CaSO_4 - CaO .

Estimated Data

$$y_e = 0.8 \frac{\text{lb SO}_2}{\text{lb CaO}};$$

$$t_{0.63} = 1050 \text{ sec};$$

$$aL = 15.1 \text{ lb CaO};$$

$$w = 0.8 \frac{\text{lb CaO}}{\text{hr}};$$

$$FC_0 = 0.38 \frac{\text{lb SO}_2}{\text{hr}}.$$

Then from Eq. C.16,

$$r = \frac{y_e w}{FC_0} = 1.7,$$

and from Eq. C.17,

$$H = \frac{aLy_e}{t_{0.63}FC_0} = 110.$$

From Fig. C.7, the expected removal is between 90% for $\alpha = -5$ and 99% for $\alpha = \infty$.

The observed removal is only 80%. This discrepancy is believed to occur because the assumed kinetic data do not rigorously apply, as discussed above.

(1) Fluidized-bed Estimation of Kinetic Data. To avoid the problem of estimation of kinetic parameters, the following type of experiment can be conducted in a fluidized-bed situation. The original bed should

contain fresh additive, but no fresh additive should be fed during SO_2 generation. Bed samples taken at intervals can be analyzed to obtain curves of the type in Fig. C.4, from which the parameters y_e and $t_{0.63}$ can be estimated. The experiment should continue until SO_2 removal falls essentially to zero.

It must be recognized that this procedure is not ideal. The bed additive particles will be exposed, on the average, to a steadily rising SO_2 concentration level. Since the history of the SO_2 concentration at the particle surface can affect pore blockage, a somewhat different y_e behavior may result from that which would be observed at constant SO_2 concentration. A model that includes diffusion inside the particles could be constructed, but this would become very complicated. Hopefully, the error introduced by ignoring the effect of concentration history on y_e will be small. The effect of SO_2 concentration on instantaneous values of y versus t cannot be ignored, since the reaction rate is assumed to be first order. Hence, the observed SO_2 concentration C in the exit gas must be used at each instant to correct the y versus t curve and obtain $k(y)$.

2. Modeling Studies of Coal Feeding for a Large-bed Combustor (J. D. Gabor*)

Studies were initiated on modeling a large fluidized-bed combustor (20 ft wide, 80 ft long, 2 ft high) to predict the distribution of coal particles in the combustor and to help resolve the technical uncertainties involved in fluidized-bed combustion and its application to pollution control. This work is directed toward estimating the effects of nonuniform feeding of coal on localized reducing or oxidizing conditions (i.e., gas compositions) at points within and above the bed and its potential effects on efficiency of combustion.

To determine the gas compositions from point to point within the bed, a model of the concentration gradients of coal within the bed is needed. Our initial work on modeling the mixing of coal particles is based on the use of a diffusion coefficient to describe particle mixing. Highley, Rogers, and Dryburgh¹⁶ concluded from their studies that a simple diffusion model provides an adequate description of particle mixing in a wide, shallow fluidized bed.

a. Models for Concentration Gradients of Coal--Base-point Feed Injection

For modeling purposes, the large fluidized-bed combustor is considered to consist of 16 identical modules, each of 10-ft width, 10-ft length, and 2-ft bed depth, each module having a centrally located coal feed point at the base. By approximating each 10- by 10-ft square module by a module of circular cross section with a diameter of 10 ft, the model can readily be solved analytically with the following assumptions:

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1. There is no concentration gradient in the vertical direction. Vertical mixing is very rapid.

2. A first-order reaction rate describes the coal combustion.

3. A diffusion coefficient can adequately describe mixing in the horizontal direction.

The equation of continuity is

$$\frac{v_0 r_0}{r} \frac{dC}{dr} = D \left(\frac{d^2 C}{dr^2} + \frac{1}{r} \frac{dC}{dr} \right) - kC, \quad (C.21)$$

where

v_0 = radial velocity of bed material at the point of injection because of material displacement by coal feed, ft/hr,

r_0 = radius of injector tube, ft,

r = radial position, ft,

C = coal concentration within the fluidized bed, lb/ft³,

C_0 = coal concentration at feed point, lb/ft³,

D = diffusion coefficient, ft²/hr,

and

k = reaction rate constant, hr⁻¹.

The boundary conditions are

$$\text{at } r = r_0, C = C_0, \quad (C.22)$$

and

$$\text{at } r = R, \frac{dC}{dr} = 0, \quad (C.23)$$

where R is the radius of the module.

The solution for Eqs. C.21-C.23 is

$$C = r^\nu \left[AI_\nu \left(r \sqrt{\frac{k}{D}} \right) + BK_\nu \left(r \sqrt{\frac{k}{D}} \right) \right], \quad (C.24)$$

where

$$\nu = \frac{v_0 r_0}{2D}$$

and

$$K_\nu \left(r \sqrt{\frac{k}{D}} \right) \text{ and } I_\nu \left(r \sqrt{\frac{k}{D}} \right)$$

are modified Bessel functions of order ν and argument x .

By letting

$$\beta = \sqrt{\frac{k}{D}},$$

$$x = R \sqrt{\frac{k}{D}},$$

$$F_A = R^\nu \left[\frac{\nu}{R} I_\nu(x) + \beta I_{\nu+1}(x) \right] + \nu R^{\nu-1} I_\nu(x),$$

and

$$F_B = R^\nu \left[\beta K_{\nu+1}(x) - \frac{\nu}{R} K_\nu(x) \right] - \nu R^{\nu-1} K_\nu(x),$$

we obtain

$$A = \frac{C_0}{r_0 \nu \left[I_\nu(r_0 \beta) + \frac{F_A}{F_B} K_\nu(r_0 \beta) \right]} \quad (C.25)$$

and

$$B = \frac{C_0}{r_0 \nu \left[\frac{F_B}{F_A} I_\nu(r_0 \beta) + K_\nu(r_0 \beta) \right]} \quad (C.26)$$

For the operating conditions currently under consideration for the coal combustor with v_0 varied over a range of two orders of magnitude, ν was found to be effectively 0. For $\nu = 0$, the solution is simplified further:

$$C = A I_0 \left(r \sqrt{\frac{k}{D}} \right) + B K_0 \left(r \sqrt{\frac{k}{D}} \right), \quad (C.27)$$

where

$$A = \frac{C_0}{I_0(\beta r_0) + \frac{I_1(\beta R)}{K_1(\beta R)} K_0(\beta r_0)} \quad (C.28)$$

and

$$B = \frac{C_0}{\frac{K_1(\beta R)}{I_1(\beta R)} I_0(\beta r_0) + K_0(\beta r_0)} \quad (C.29)$$

The above equations have fewer terms, and the Bessel functions are of integer order and can be found readily from existing tables.

The coal concentration can be related to the feed rate, W (lb/hr), and bed height, H , by the following equation:

$$\frac{W}{H} = -D2\pi r \left. \frac{dC}{dr} \right|_{r=r} = -2\pi r D \beta [A I_1(\beta r) - B K_1(\beta r)]. \quad (C.30)$$

Figures C.9 and C.10 are plots of $C/(W/2\pi DH)$ versus r/R for various values of kR^2/D . These plots are in terms of dimensionless numbers and will allow prediction of concentration gradients in terms of feed rate over a wide range of conditions. Some typical concentration profiles for anticipated normal operating conditions are discussed later in this appendix.

Fig. C.9. Dimensionless Concentration Profile for Coal Feeding at Base Point; Low Values of kR^2/D

Fig. C.10. Dimensionless Concentration Profile for Coal Feeding at Base Point; High Values of kR^2/D

b. Models for Concentration Gradients in Coal--Horizontal-jet Feed Injection

The case of horizontal-jet feed injection has also been considered. For this case, it is assumed that the velocity of the feed jet is very high and that penetration by the feed into the bed is deep. Since it is also assumed that particle mixing in the vertical direction is instantaneous, the particles will diffuse from a plane of height equivalent to the bed height and of width equal to the depth of feed penetration. Particle diffusion occurring in a 2-ft-high module of 10- by 10-ft square cross section is next considered.

For this case, the equation of continuity is

$$D \frac{d^2 C}{dx^2} = kC. \quad (C.31)$$

The boundary conditions are

$$\text{at } x = 0, C = C_0, \quad (C.32)$$

and

$$\text{at } x = R, \frac{dC}{dx} = 0, \quad (C.33)$$

where R in this case is one-half the length of the module.

The solution to the above equations is

$$\frac{C}{C_0} = \frac{\cosh \left[R\beta \left(1 - \frac{x}{R} \right) \right]}{\cosh (R\beta)} \quad (C.34)$$

where β again is $\sqrt{\frac{k}{D}}$.

C/C_0 is plotted as a function of x/R for various values of $R\beta$ in Fig. C.11. This plot for diffusion and reaction for a horizontal-jet feed is in dimensionless units and will permit prediction of concentration gradients over a wide range of operating conditions. Some specific concentration profiles for anticipated operating conditions are presented later.

Fig. C.11. Dimensionless Concentration Profile for Horizontal-jet Coal Feeding

The flux at the feed plane is

$$W/LH = -D \frac{dC}{dx} \Big|_{x=0} = DC_0\beta \tanh(R\beta), \quad (C.35)$$

where

W = coal feed rate, lb/hr,

H = height of fluidized bed,

and

L = depth of feed penetration.

Equation C.35 gives the relationship of C_0 to coal feed rate.

The average coal concentration in the bed, C_{ave} , is found by integration:

$$\frac{C_{ave}}{C_0} = \frac{\int_0^R (C/C_0) dx}{\int_0^R dx} = \frac{1}{R\beta} \tanh(R\beta). \quad (C.36)$$

c. Application of Models to Anticipated Operating Conditions

The models are next applied to the anticipated operating conditions in a large combustor, 20 by 80 ft, divided into sixteen 10- by 10-ft modules. The anticipated operating conditions are

Combustor temperature: 1600°F;

Superficial gas velocity: 3ft/sec;

Coal burning rate: 20 lb/(hr)(ft²);

Bed height: 2 ft;

Particle size of coal feed: <1/16 in.;

Particle size of inert bed material: -10 mesh;

Ratio of air feed to coal feed: 10 lb air/lb of coal.

On the basis of a report by Highley, Rogers, and Dryburgh,¹⁶ a diffusion coefficient, D , of 300 ft²/hr is estimated for the rate of coal mixing in the large-scale reactor.

The reaction-rate constant, k , can be estimated from bench-scale data at Argonne by assuming that the data are from a backmix reactor.¹⁷ For a 2-ft-high bed, $-r_d$ (the rate of coal depletion) is calculated as follows:

$$-r_d = [20 \text{ lb}/(\text{hr})(\text{ft}^2)]/2 \text{ ft} = 10 \text{ lb}/(\text{hr})(\text{ft}^3).$$

For the Argonne bench-scale experiments, the average coal concentration in the bed is 0.05 wt %. The bed density at operating conditions is estimated to be 55 lb/ft³. Therefore, for a backmix reactor and a first-order reaction,

$$k = \frac{-r_d}{C_{\text{ave}}} = \frac{10}{(0.0005)(55)} = 365 \text{ hr}^{-1}.$$

Fig. C.12. Coal Concentration for Base-point Feeding into a 10- by 10-ft Module

For feeding at a base point, Fig. C.12 shows the coal concentration in terms of C/C_0 at various radial distances from a feed point in the center of a 10- by 10-ft module. The effect of varying the magnitude of the reaction-rate constant k between 100 and 2000 hr⁻¹ is shown by the series of curves in Fig. C.12. For a k of 365 hr⁻¹ and a combustion rate of 20 lb/(hr)(ft²), the feed rate, W , is 2000 lb/hr and C_0 is 1.35 lb/ft³.

In Figs. C.13 and C.14 are plotted coal concentrations at various radial distances from the feed point for the cases of feed points at the center of 6- by 6-ft and 3- by 3-ft modules. The coal concentration is much more uniform for the small modules (greater number of coal feed points). Near the coal feed point, the coal concentration is high and the efficiency of oxygen utilization and the tendency of CO to form are high. This effect will be given further consideration in the modeling studies.

In Figs. C.15-C.17, coal concentrations for horizontal-jet feed injection into 10- by 10-ft, 6- by 6-ft, and 3- by 3-ft modules are plotted. For the 10- by 10-ft module with a k of 365 hr⁻¹ and a feed rate of 2000 lb/hr, C_0 is 0.151 lb/ft³. The value of C_0 for horizontal-jet feed injection is about a factor of 10 less than that for base-point feed injection ($C_0 = 1.35 \text{ lb/ft}^3$). Horizontal-jet feed injection results in a more uniform distribution of coal throughout the bed than the base-point feed system does. The concentration ratio C/C_0 for horizontal-jet feeding decreases from

Fig. C.13. Coal Concentration for Base-point Feeding into a 6- by 6-ft Module

Fig. C.14. Coal Concentration for Base-point Feeding into a 3- by 3-ft Module

Fig. C.15. Coal Concentration for Horizontal-jet Feeding into a 10- by 10-ft Module

Fig. C.16. Coal Concentration for Horizontal-jet Feeding into a 6- by 6-ft Module

Fig. C.17. Coal Concentration for Horizontal-jet Feeding into a 3- by 3-ft Module

form if coal is injected horizontally in a jet with deep penetration into the bed than if coal is injected vertically from a point at the base of the bed.

1.0 to 0.01 at a k value of 365 hr^{-1} as x increases from 0 to 5 ft; in contrast, C/C_0 for base-point feeding decreases from 1.0 to essentially zero as r increases from 0 to 5 ft. It appears, therefore, that feeding the coal as a horizontal jet would decrease CO formation.

Complete coal combustion involves burning of both volatile and nonvolatile components. If it is desired to consider the combustion of these two types of components separately, the appropriate model (horizontal-jet or base-point feed injection) can be used. For this case, the reaction-rate constant appropriate for the combustion of one type of component (volatile or nonvolatile) would be used in predicting the concentration profile of that component.

It can be concluded from these initial studies that coal concentration in the bed is more uni-

APPENDIX D

Combustion Efficiency

1. Combustion of Coal

The combustion efficiency for various experiments performed in the combustor was determined and is expressed as percentage of completely burned carbon (see Table D.1). The efficiency is calculated by determining unburnt carbon which leaves the system in three ways: (1) carbon associated with the elutriated solids, (2) incompletely burned gases, i.e., carbon monoxide and hydrocarbons, and (3) carbon associated with fluidized-bed material taken from the system. In all experiments with alumina fluidized beds, carbon losses in the bed material were negligible. Only about 10-20% of the carbon loss has been due to formation of carbon monoxide and hydrocarbons. The major carbon loss (80-90%) has occurred by elutriation of fine particles in the exhaust gases before combustion was complete. Combustion efficiency can be increased by recycling the elutriated ash-carbon mixture to the fluidized bed or to a carbon burnup cell.

TABLE D.1. Combustion Efficiency of
6-in.-dia Fluidized-bed Reactor

Starting bed:	Alumina (30 mesh)
Coal:	4.5 wt % S (- 14 mesh)
Combustion temperature:	1600°F
Superficial gas velocity:	3 ft/sec
Excess air:	10 to 20%

Percentage of Carbon Loss, %			
Expt.	In Elutriated Solids	In Flue Gas	Combustion Efficiency, %
SACC-9	87	13	93.4
SA-1	81	19	94.6
SA-2	90	10	94.4
SA-3	86	14	95.6
SA-4	88	12	94.7
BC-1 ^a	82	18	97.2
BC-2	80	20	95.1
BC-3	83	17	94.7
BC-4	80	20	95.7
DC-5	84	16	95.1

^aBaffle plate in combustor during this run.

The efficiencies in Table D.1 were calculated for a steady-state operating period in each experiment. The calculated carbon losses for the flue gas are based on analyses of one or two grab samples of gas for CO and total hydrocarbons. Carbon losses attributed to elutriated solids were calculated from carbon analyses of material collected in the primary and secondary cyclones; these carbon loss values were adjusted for known carbonate contents and total solids on the final filter. Combustion efficiency was 93.4-95.7% in the absence of a baffle plate and 97.2% with a baffle plate installed.

2. Combustion of Natural Gas

During the combustion of natural gas, the elutriation of carbon-bearing fine particles is negligible and the major loss of unburnt carbon is attributed to carbon monoxide and total hydrocarbons in the flue gas. Combustion efficiencies, calculated from analyses of grab samples of the flue gas, ranged from 94.1 to 99.2% at 1600°F. At 1800°F, combustion efficiencies of 94.1-98.8% were observed. These results are similar to data reported by the U.S.S.R.¹⁸ on combustion of gas in a fluidized bed. Although the U.S.S.R. data indicated that combustion efficiency is principally affected by bed temperature, combustion efficiency is also likely to be a function of bed depth, gas velocity, and excess oxygen concentration. For example, in experiment NG-3 at 1800°F, combustion efficiency was decreased to 91% when the combustion was intentionally forced toward more reducing conditions, i.e., 1.5 vol % O₂ rather than 1.8-4.5 vol % O₂ in the flue gas.

Essentially complete combustion has been demonstrated in experiments with natural gas under certain operating conditions. Although optimum combustion efficiency is highly desirable in an industrial facility, this was not the main purpose of these experiments. The natural-gas injection system used on the Argonne coal combustor would have to be re-designed to optimize combustion of the gas under all operating conditions.

The extreme simplicity of the fluidized-bed combustion concept for a fluid fuel such as natural gas is noteworthy. Because ash is absent and because the fuel can be readily distributed throughout the fluidized bed, scale-up would be much simpler than for coal. Only small-scale experimentation would be needed to optimize the operating conditions for high combustion efficiency. Hence, if a market exists for this concept, it could represent a means for the early demonstration of fluidized-bed combustion on a prototype scale.

APPENDIX E

Material Balances

The material balances for sulfur, carbon, and calcium in experiments SACC-9 and SA-1 to SA-4 are shown in Table E.1. For the coal and additive input streams, weights were measured with scales, and these weights were checked against measured inputs and outputs of material in the feed hoppers. The solids output streams were collected for analysis. The flue gas was monitored continuously for SO₂ concentration, and the curves for each experiment were integrated to determine total sulfur in the flue gas. Carbon in the flue gas was obtained by analyzing (and averaging) 16-20 grab samples of gas per run for CO₂ and two grab samples of gas per run for CH₄ and hydrocarbon (HC) content.

TABLE E.1. Material Balances for Sulfur, Carbon, and Calcium; Expts. SACC-9 and SA-1 through SA-4

	SACC-9			SA-1			SA-2			SA-3			SA-4		
	S, lb	C, lb	Ca, lb	S, lb	C, lb	Ca, lb	S, lb	C, lb	Ca, lb	S, lb	C, lb	Ca, lb	S, lb	C, lb	Ca, lb
<u>Material in^a</u>															
Coal	2.10	31.0	0.30	1.79	25.0	0.20	2.02	28.3	0.22	1.65	23.2	0.18	1.86	26.0	0.20
Additive	-	1.2	3.90	-	1.5	4.94	-	1.6	5.32	-	0.8	2.72	-	0.86	2.84
	2.10	32.2	4.2	1.8	26.5	5.1	2.0	29.9	5.5	1.6	24.0	2.9	1.9	26.9	3.0
<u>Material out^a</u>															
Flue gas	0.99	23.8 ^b	-	0.56	21.5 ^b	-	0.88	23.9 ^b	-	0.90	20.3 ^b	-	1.07	23.9 ^b	-
	-	0.29 ^c	-	-	0.26 ^c	-	-	0.17 ^c	-	-	0.38 ^c	-	-	0.42 ^c	-
Primary cyclone	0.37	2.10	2.29	0.43	2.90	2.8	0.43	2.50	3.39	0.34	1.61	1.90	0.23	1.64	2.22
Secondary cyclone	0.20	0.31	0.69	0.18	0.14	0.76	0.15	0.15	0.53	0.03	0.08	0.17	0.04	0.15	0.12
Final filter	0.05	0.02	0.08	0.13	0.03	0.20	0.18	0.05	0.36	0.06	0.04	0.06	-	d	-
Fluid bed and samples	0.35	<0.01	0.63	0.41	<0.01	0.85	0.39	<0.01	0.68	0.31	<0.01	0.60	0.29	<0.01	0.47
Σ	2.0	26.5	3.7	1.7	24.8	4.6	2.0	26.8	5.0	1.6	22.4	2.7	1.6	26.1	2.8
% Balance	95	83	88	94	94	90	100	90	90	100	93	93	84	97	93

^aThe time basis for different elements may differ within an experiment.

^bAs CO₂ (avg. conc.), vol %

^cAs CO + HC (avg. conc.), ppm

^dNot enough solids collected for a sample.

In general, the material balances for sulfur, carbon, and calcium are in the range 90-100%. In one experiment, SA-4, the sulfur balance was 84%, but in this case one source of sulfur, the final filter, did not contain enough solids for analytical purposes. The sulfur balance for SA-4 would improve if additional sulfur could be assigned to the final filter, as was the case in experiments SA-1 to SA-3. In experiment SACC-9, the carbon balance of 83% was low compared with 90-97% determined in SA-1 to SA-4. The reason for a low carbon balance in SACC-9 may be non-representative sampling of the primary cyclone solids, which appeared to contain less carbon than did the primary cyclone samples from the other experiments.

APPENDIX F

Alternative Methods for Calculating SO₂ Removal (Percent of Sulfur
in the Feed or Percent Reduction in Flue Gas Emissions)

Percentage of SO₂ removal, such as that reported in this work and in the literature, can be calculated on either of two bases: (1) the total sulfur fed to the system and SO₂ found in the flue gas after the introduction of additive, or (2) the sulfur found in the flue gas as SO₂ before and after the introduction of additive. In some cases, sulfur in the flue gas before the introduction of additive may be less than the total sulfur in the feed. The relationship between the two methods of calculation has been derived to determine whether values of SO₂ removal determined by the two methods differ significantly.

Let

R_1 = percentage SO₂ removal, based on sulfur in the feed,

R_2 = percentage SO₂ removal, based on sulfur in the flue gas prior to additive injection,

r_1 = fraction SO₂ removal, based on sulfur in the feed,

r_2 = fraction SO₂ removal, based on sulfur in the flue gas,

C_{01} = sulfur in feed, mass/unit time,

C_{02} = sulfur initially in flue gas, mass/unit time,

and

C = sulfur in flue gas during limestone injection for SO₂ control, mass/unit time, $n = 1, 2$.

Then

$$R_1 = \frac{C_{01} - C}{C_{01}} 100, \quad R_2 = \frac{C_{02} - C}{C_{02}} 100; \quad (\text{F.1})$$

$$r_1 = 1 - \frac{C_1}{C_{01}}, \quad r_2 = 1 - \frac{C_2}{C_{02}}; \quad (\text{F.2})$$

and

$$C_1 = (1 - r_1) C_{01}, \quad C_2 = (1 - r_2) C_{02}. \quad (\text{F.3})$$

At the same level of SO₂ concentration in the flue gas

$$C_1 = C_2$$

and

$$(1 - r_1) C_{O_1} = (1 - r_2) C_{O_2} \quad (F.4)$$

Now let C_{O_2} be some fraction, f , of C_{O_1} ($f \leq 1$),

$$(1 - r_1) C_{O_1} = (1 - r_2) f C_{O_1}, \quad (F.5)$$

from which

$$r_1 = 1 - f + f r_2. \quad (F.6)$$

Equation F.6 can be used to determine the difference between the two bases of calculation; e.g., if 90% of the total sulfur in the feed is observed initially in the flue gas and if SO_2 removal is 85% ($r_2 = 0.85$) based on SO_2 in the flue gas before additive injection, then at the same SO_2 concentration in the flue gas after additive injection, the reported SO_2 reduction based on sulfur in the feed would be 86.5%. Figure F.1 shows several cases for f of 1.0, 0.9, and 0.8. For any value of $f < 1$, the percentage of SO_2 removal based on sulfur initially in the flue gas is more conservative; however, at high levels of SO_2 removal, $>80\%$, the difference between the two methods of calculation appears to be minimal and less than the experimental error.

Fig. F.1. SO_2 Removal as Percent of Sulfur in Feed vs Percent Reduction in Flue Gas

APPENDIX G

Calculated Waste Burden from Limestone and Dolomite Additives

The use of limestone additive to reduce the emissions of SO_2 during the combustion of coal would increase the quantity of waste solids to be disposed of (over and above the quantity of ash). The magnitude of the increase has been calculated as a function of the sulfur content of the coal, the rate of additive feeding, and the type of additive material used.

Figure G.1 shows, for coals containing 4 and 2 wt % sulfur, the required feed rates of limestone additive and the waste burden at various Ca/S mole ratios for the limestone additive and coal in the feed. Figure G.2 presents similar information for a dolomite additive (50 mol % CaCO_3 , 50 mol % MgCO_3).

Fig. G.1. Effect of Calcium/Sulfur Mole Ratio on Waste Burden due to Limestone Additive

Fig. G.2. Effect of Calcium/Sulfur Mole Ratio on Waste Burden due to Dolomite Additive

The magnitude of the additional waste burden has been compared with the quantities of ash burdens for systems that do not employ limestone additives. Although the ash and sulfur contents of coals vary considerably (see Table G.1),¹⁹ it was assumed in this comparison that an average coal contains 10 wt % ash (10 lb ash/100 lb coal). As shown in Fig. G.1, the use of limestone (100% CaCO_3) at a rate equivalent to 150% of

the stoichiometric requirement (Ca/S mole ratio of 1.5) would result in an increase in the quantity of waste solids for a 2 wt % sulfur coal of 10 lb/100 lb coal and an increase for a 4 wt % sulfur coal of 20 lb/100 lb coal. Hence, the total waste solids (including ash) to be disposed of, if limestone were added, would be two to three times the quantities due to the ash burden alone. The use of a dolomite additive (50 mol % CaCO_3 , 50 mol % MgCO_3) would result in even greater increases in the total waste solids burden, as seen from Fig. G.2. These large waste burdens indicate that unless the desired levels of SO_2 removal can be achieved at a low additive feed rate, regenerable systems should be considered in order to avoid excessive waste burdens, particularly for high-sulfur coals.

TABLE G.1. Ash and Sulfur Contents¹⁹ of Coals Selected for Fluidized-bed Combustion Research Program

Type of Coal	Ash Content, wt %	Sulfur Content, wt %
Anthracite	9.0	0.7
Low volatile bituminous	22.5	2.3
Medium volatile bituminous	6.0	5.0
Two high volatile "A" bituminous	7.6 10.6	2.5 4.3
High volatile "B" bituminous	7.9	3.1
High volatile "C" bituminous	15.7	4.5
Lignite	10.7	1.2

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