.28
6-5-81

②

R4840

MASTER

ORNL/MIT-322

ornl

OAK
RIDGE
NATIONAL
LABORATORY

UNION
CARBIDE

Sulfur Capture in an Atmospheric Fludized-Bed Combustor

D. M. Baars
C. A. Hunter
E. N. Keitelman

OPERATED BY
UNION CARBIDE CORPORATION
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A04 Microfiche A01

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. *Neither* the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, *recommendation*, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/MIT-322

Contract No. W-7405-eng-26*

ENGINEERING TECHNOLOGY DIVISION

SULFUR CAPTURE IN AN ATMOSPHERIC FLUIDIZED-BED COMBUSTOR

D.M. Baars
C.A. Hunter
E.N. Keitelman

Consultants:
G.P. Zimmerman, R.H. Guymon, and R.S. Holcomb

Date Published - June 1981

950 0153

Oak Ridge Station
School of Chemical Engineering Practice
Massachusetts Institute of Technology
C.H. Byers, Director

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830
Operated by
Union Carbide Corporation
for the
Department of Energy

483 2000

*Research sponsored under Interagency Agreement between TVA, DOE, and ORNL (TV-48296A, Subagreement 5)

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ABSTRACT

Sulfur capture in an atmospheric fluidized-bed combustor (AFBC) both with and without recycle of fines elutriated from the bed was studied. Two empirical correlations, one by Babcock and Wilcox and the other by Westinghouse, correlate sulfur capture as a function of the calcium-to-sulfur mole ratio and gas residence time. Both correlations fit the experimental no-recycle results quite well. Of the limestones tested with no recycle, Vulcan Materials exhibits the best sulfur-capture performance.

Data collected with Reed limestone indicates that recycle improves sulfur-capture compared with once-through performance. However, there is a decreasing effect on sulfur capture as the recycle rate is increased to large values. At 90% sulfur capture, the fractional reduction of fresh limestone feed attributable to recycle is 24-35% over a gas-residence time range of 0.7-0.4 s.

Contents

Page

1. Summary 1
2. Introduction 2
3. Experimental Apparatus and Procedure 3
   3.1 Experimental Apparatus 3
   3.2 Experimental Procedure 5
   3.3 Operating Parameters 6
   3.4 Raw-Data Analysis 9
4. Correlation of Sulfur-Capture Data 10
   4.1 Babcock and Wilcox Correlation 10
   4.2 Westinghouse Correlation 12
   4.3 Comparison of Models 13
5. Results and Discussion 13
   5.1 Correlation of Sulfur-Capture Data Taken with No Recycle . 13
   5.2 Analysis and Correlation of Reed Limestone Sulfur-Capture Data with Recycle ... 18
   5.3 Improvement in Reed Limestone Sulfur-Capture Performance with Recycle ... 22
6. Conclusions 24
7. Recommendations 26
8. Acknowledgments 26
9. Appendix 27
   9.1 EPA Sulfur Dioxide Emission Standards 27
   9.2 Sample Raw-Data-Analysis Calculations 27
   9.3 Curve-Fitting Routines: Sample Calculations 31
   9.4 Calculation of Fractional Reduction in Reed Limestone Feed with Recycle at 90% Sulfur Capture ... 38
   9.5 Location of Data 41
   9.6 Nomenclature 41
   9.7 Literature References 43

1. SUMMARY

The imposition of stringent emission standards and the need for high-efficiency coal-burning processes have made atmospheric fluidized-bed combustors (AFBC) an economically more attractive alternative than conventional coal combustors. One of the many advantages of the AFBC is that SO_2 can be captured by limestone in the bed, eliminating the need for a flue-gas scrubber.

The Tennessee Valley Authority (TVA) is planning to begin operation of a 20-MW AFBC pilot plant by mid-1982. TVA has contracted Oak Ridge National Laboratory (ORNL) to study the sulfur-capture characteristics of five candidate limestones (Three Rivers, Vulcan Materials, Fredonia Valley Upper Ledge, Reed, and Fredonia Valley Lower Ledge) for use in the pilot plant. ORNL experiments indicate that with once-through feeding, approximately 0.4 to 0.6 kg limestone/kg coal is required to meet the EPA standard of 90% sulfur capture. Studies at Babcock and Wilcox (B&W) indicate that the limestone feed requirement could be substantially reduced by recycling elutriated bed material. Reed and Fredonia Valley limestones have been selected for recycle tests since high carryover of calcium was observed during the no-recycle tests on these limestones.

A bench-scale AFBC located in Bldg. 9201-3 is being used to obtain the sulfur-capture data. The combustor has a 25.4-cm diameter with an active bed region approximately 1 m high and a freeboard region approximately 2 m high. The bed is operated at fluidizing velocities of 1.2 to 1.8 m/s and maintained at nearly 845°C, corresponding to a range of gas residence time in the bed of 0.5 to 0.8 s.

Simplified sulfur-capture models, developed at B&W and Westinghouse, were used to correlate the sulfur-capture data. Both models express sulfur capture as a function of calcium-to-sulfur mole ratio and gas residence time. Both models correlated the no-recycle data to within a standard deviation of 7%. Vulcan Materials limestone was found to exhibit the best sulfur-capture performance of the five limestones tested with no-recycle, especially at low residence times.

Recycle data for Reed limestone was taken at three different recycle screw-feeder settings (4, 14, and 25 rpm). The sulfur-capture performance predicted by the B&W correlation indicated that the screw-feeder setting has only a small effect on the amount of active calcium recycled.

At 90% sulfur capture, the fractional reduction in the fresh limestone feed requirement,attributable to recycle predicted from the B&W correlations of the Reed limestone recycle and no recycle data, was found to range from 24 to 38% at gas residence times of 0.7 to 0.4 s, respectively.

2. INTRODUCTION

The current international oil situation dictates that the dependence on foreign oil as an energy source be reduced. The abundance of coal reserves in the U.S. has stimulated a new interest in the use of coal for the generation of steam, electricity, and process heat. Due to stringent emission control and the need for high-efficiency coal processes, atmospheric fluidized-bed combustors (AFBC) have become an economically attractive alternative to conventional coal combustors with flue-gas desulfurization.

One advantage of the AFBC over the conventional combustor is the temperature of operation required, typically 750 to 950°C for the AFBC (1, 6) compared with 1370 to 1650°C for the conventional combustor (3). The lower temperature range reduces the corrosion of heat-transfer surfaces since operation is below the temperature at which ash (mostly silica) melts and forms hard, glassy particles with sharp edges when it cools (1, 2, 18).

A second advantage of the AFBC is the excellent mixing characteristics inherent in fluidized beds, resulting in a uniform bed temperature. The heat-transfer coefficients are very high since conductive as well as convective heat transfer occurs through coils immersed in the well-mixed bed, as opposed to convective heat transfer through coils in the flue-gas stream in conventional combustors. The high heat transfer and the uniform bed temperature result in better control of the bed temperature in the AFBC.

Carbon burnup in the AFBC may be as high as 99% (3). Virtually any type of combustible material can be burned by properly adjusting factors such as type and particle size of bed material, fluidizing velocity, feed methods, and rate of feed. Fine grinding is not required since crushed coal can be burned. Low-grade coals with high ash and/or sulfur content can be utilized. This increased flexibility results in reduced fuel costs.

Improved environmental control is another advantage of using the AFBC for the combustion of coal. The formation of nitrogen oxides is less than in conventional combustors because combustion temperatures are below those at which atmospheric nitrogen fixation occurs (18). The sulfur dioxide produced during combustion is captured by limestone, which is fluidized with the coal in the bed, thereby eliminating the need for expensive flue-gas scrubbing systems.

However, AFBC is not without disadvantages. There are uncertainties associated with scaleup. The use of high-sulfur coals may result in a corrosive environment. AFBC is very promising for new plants, but the retrofitting of existing plants is difficult.

The Tennessee Valley Authority (TVA) is building a 20-MW AFBC pilot plant in Paducah, Kentucky, to be operational in mid-1982. TVA plans to burn a high-sulfur coal which would require that 90% of the sulfur in the coal be captured in the process and to reduce SO_2 emissions. Oak Ridge National Laboratory (ORNL) has been contracted to investigate the sulfur-capture characteristics of five candidate limestones (Three Rivers, Vulcan Materials, Fredonia Valley Upper Ledge, Reed, and Fredonia Valley Lower Ledge) for the pilot plant. A bench-scale AFBC has been constructed in Bldg. 9201-3 at the Y-12 Plant for performing these studies.

Experiments at ORNL indicate that with once-through feeding, an average weight ratio of 0.45 kg limestone/kg coal is required to achieve 90% sulfur capture for Vulcan Materials, Reed, and Fredonia Valley limestones. Higher weight ratios (approximately 0.6 kg/kg) are required for Three Rivers limestone (7).

Tests conducted by B&W on a 6x6-ft AFBC with Lowellville limestone indicated that sulfur capture can be improved by recycling elutriated fines, which consist mainly of unreacted CaO. With fines recycle, up to 27% reduction in the amount of fresh limestone feed rate needed to achieve 90% sulfur capture was possible (7).

Sulfur-capture tests at ORNL have been completed for the five candidate limestones and Lowellville limestone (used as a reference) with no recycle. Reed and Fredonia Valley limestones were selected for recycle tests. Currently, recycle tests are being run on Reed limestone, and future plans include recycle testing of Fredonia Valley and Lowellville limestones.

The specific objectives of this study were: (1) to correlate the sulfur-capture data collected for the five candidate limestones with no recycle, (2) to collect and correlate sulfur-capture data for Reed limestone with recycle, and (3) to quantify the effects of recycle on Reed limestone sulfur-capture performance.

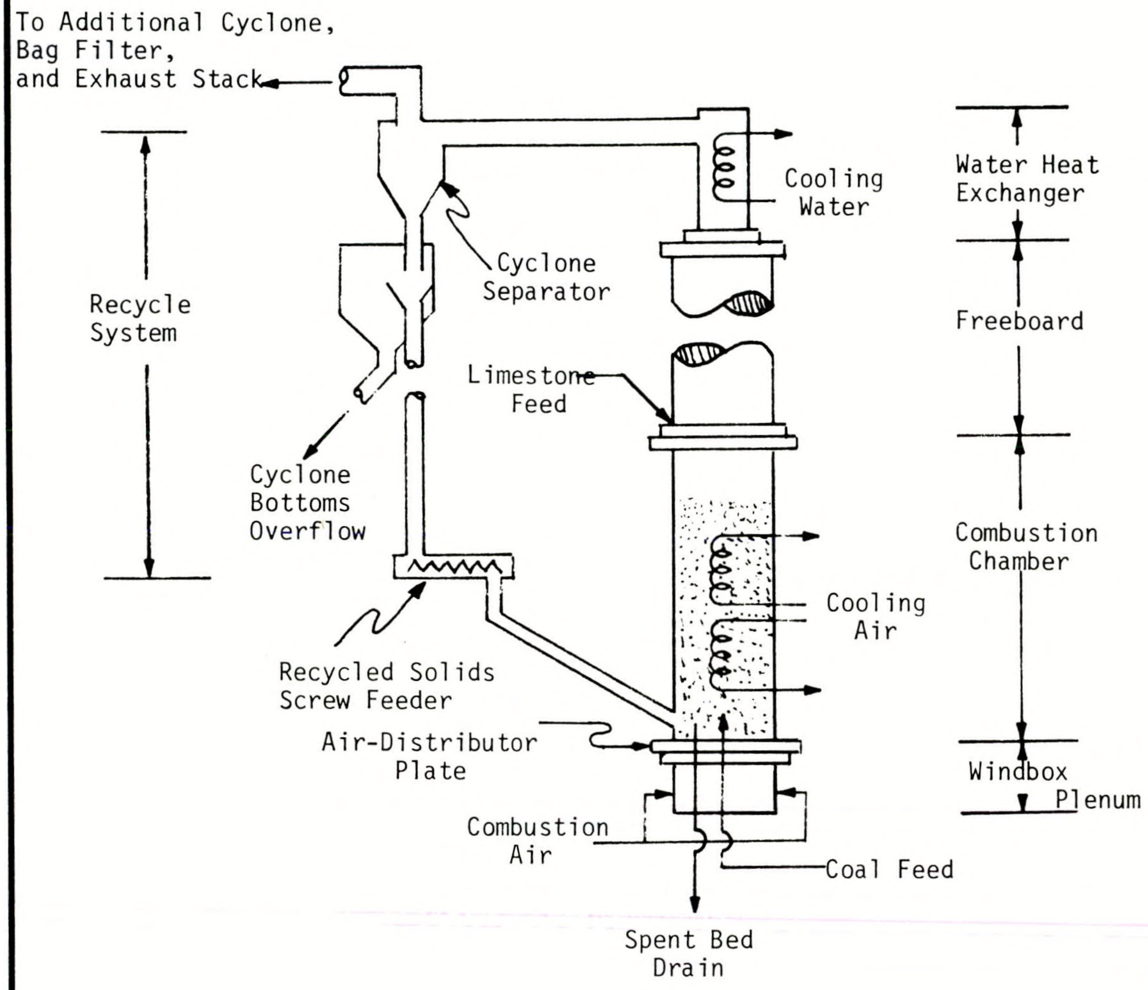
3. EXPERIMENTAL APPARATUS AND PROCEDURE

3.1 Experimental Apparatus

The ORNL bench-scale coal combustor, located in Bldg. 9201-3 at the Y-12 Plant is a 25.4-cm diameter atmospheric fluidized bed (see Fig. 1). The combustor has an active bed region approximately 1 m high (exact height depends on the amount of material in the bed and the fluidizing-air velocity) and a freeboard region approximately 2 m high. The bed consists of limestone, coal ash, and small amounts (less than 1 wt %) of unburned coal or carbon (1, 18).

Coal stored in a double-lock hopper is metered into a pneumatic transport line by a screw feeder and injected into the combustor at the base of the bed. The coal feed rate is variable between 4.5 and 13 kg/h

Limestone enters the top of the bed at feed rates ranging from 3.3 to 9.1 kg/h. The limestone, stored in a hopper near the top of the column,



MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

AFBC BENCH-SCALE COMBUSTOR
WITH RECYCLE CAPABILITY

DATE	DRAWN BY	FILE NO.	FIG.
10-22-80	ENK	CEPS-X-322	1

enters a screw feeder which regulates the flow into a 2.5-cm-diam gravity feed line.

Air flow enters the column in three places. Seventy-five to 85% of the total air is introduced at the bottom of the bed through the distributor plate. The remaining 15 to 25% enters as the transport medium for coal and as a recycle assist.

The bed temperature is held at roughly 845°C by the flow of compressed air through two heat-transfer coils submerged in the active bed region of the combustor. Each coil consists of nine C-shaped tubes, 29.5-cm long, which have a 9-mm ID and 13-mm OD. In the TVA pilot-plant operation, the heat transfer medium would be water rather than air so that steam would be generated.

The flue gas and elutriated particles leave the combustor at about 870°C. A water-cooled heat exchanger above the freeboard has the potential to cool the flue gas and elutriated particles to 120°C.

The exhaust gas stream passes through a cyclone separator, where most of the elutriated particles are separated from the flue gas. The flue gas enters a second cyclone separator followed by a bag filter for removing any remaining solids before discharge through the exhaust stack. The solids removed in the first cyclone separator are either recycled to the bottom of the bed or sent to a waste drum.

The recycle system collects a fraction of the solids from the first cyclone separator in a 2.2-m-tall standpipe which provides constant head to the recycle screw feeder. A screw feeder meters the flow of the recycled solids to a pipe inclined at 45°, from which the solids flow by gravity into the bed near the bottom. The solids from the cyclone separator, which are not recycled to the bed, overflow the standpipe and are routed to a waste drum.

The concentrations of SO_2, CO, oxides of nitrogen (NO_x), and O_2 in the flue gas are continuously monitored by a Beckman flue-gas analyzer. Thermocouples measure temperatures throughout the system. The pressure drop across the bed is monitored continuously. Combustion air flow rates are continuously measured by rotameters and orifice meters.

3.2 Experimental Procedure

Each new limestone is prepared by drying and sizing it to 6 x 100 mesh (150 to 3350 μm). The empty combustor is then charged with the new limestone. The limestone bed is fluidized at approximately 1.5 m/s at room temperature for 2 to 3 h to elutriate the fines smaller than 200 μm. The minimum fluidization velocity is determined by observing the change in the pressure drop across the bed with decreasing fluidizing velocity.

Each new limestone bed is brought to a well-sulfated state with 30 to 40 h of coal combustion at 845°C (A well-sulfated state is achieved when the SO_2 concentration in the flue gas reaches a constant value.). At this point, sulfur-capture testing can be started.

In daily operation, the bed temperature is brought to 425°C by electrically preheating the fluidizing air. The coal feed is then begun and the bed temperature rises as the coal burns. The limestone feed is not begun until the bed temperature reaches 800°C since the limestone reacts inefficiently with SO_2 below 800°C. The bed temperature is controlled at 845°C during sulfur-capture testing.

For a desired fluidizing velocity, the coal feed is varied to keep the excess combustion air at 20%. The time required for the system to achieve steady state is minimized by starting at a low limestone feed rate and increasing it as the day proceeds.

Approximately every 15 min the SO_2 and O_2 concentrations measured by the Beckman flue-gas analyzer are recorded. The coal and the limestone hopper levels are also recorded so that the feed rates may be determined by the change in the hopper levels with time.

Steady state is achieved when the SO_2 and O_2 concentrations in the flue gas and the bed temperature remain relatively constant. For no-recycle operation, steady state is achieved approximately 1 to 1.5 h after a change is made in any of the operating parameters. When operating with recycle, steady state is reached approximately 2 to 2.5 h after any changes in the operating conditions.

The following information is recorded at steady state: (1) SO_2, NO_x, CO, and O_2 concentrations in the flue gas, which are monitored continuously by a Beckman flue-gas analyzer; (2) temperatures in the bed, the outside walls of the heat transfer coils, the fluidizing air inlet, and the cooling air inlet and outlet; (3) pressure drop across the bed; (4) combustion air flow rates measured by rotameters and orifice meters; and (5) coal and limestone hopper levels as measured with a meterstick and the settings of the respective screw feeders.

At the end of the day the limestone and coal feeds are shut off, and the coal in the fluidized bed is allowed to burn completely before the remainder of the system is shut down.

3.3 Operating Paramters

The various operating parameters are as follows:

1. Kentucky #9 coal is used for all tests. A typical analysis is given in Table 1. This coal was selected since it is the coal type that will be burned in the TVA pilot plant.

Table 1. Typical Analysis of Kentucky #9 Coal (10)

64.07%	C
5.47%	H_2
4.10%	S
6.00%	O_2
1.63%	N_2
2.90%	H_2O
16.73%	Ash

heating value = 5.70 MJ/kg (11,909 Btu/lb)

2. Six different limestones were used in the tests. The five candidate limestones include Three Rivers, Vulcan Materials, Fredonia Valley upper ledge, Reed, and Fredonia Valley lower ledge. Lowellville limestone is being used as a reference for comparison with results obtained by B&W using this limestone. The six limestones have different $CaCO_3$ contents, particle size distributions, and minimum fluidization velocities, as shown in Table 2.

3. The bed temperature is kept at about 845°C. The optimum temperature for sulfur capture indicated in the literature (5, 19) lies between 800 and 870°C. The combustion stability limit imposes a lower limit of 750°C on the bed temperature (1). The upper limit for this specific system is imposed by the material used in the heat transfer coils in the bed and in the heat exchanger at the top of the bed. The material must be kept below 790°C to reduce or eliminate the risk of fatigue and ultimate failure. It was found that temperatures in the coils could be kept below 790°C if the temperature of the bed was below 855°C.

4. The total air flow is regulated so that the superficial velocity is 2 to 5 times the minimum fluidization velocity, U_{mf}, of the bed. Velocities below $2U_{mf}$ do not totally fluidize the bed which results in poor solids circulation and poor combustion. Velocities greater than $5U_{mf}$ increase elutriation of particles to unacceptable amounts. These limits result in a superficial velocity range of 1.2 to 3.0 m/s for the limestones being studied. Testing to date has been conducted at superficial velocities of 1.2 and 1.8 m/s.

5. The actual operating bed depth was not readily accessible because the visual inspection of the bed was limited to a single viewing port. However, the static bed depth could be determined by measuring the pressure drop across the bed since the pressure drop across the fluidized bed is equivalent to the weight of the static bed material. The need to achieve sufficient carbon burnup and acceptable sulfur capture imposes a lower limit on the bed depth. For no-recycle operation the upper limit on the

Table 2. Limestone Characteristics

	Three Rivers	Vulcan Materials	Fredonia Valley Upper Ledge	Lowellville	Reed	Fredonia Valley Lower Ledge
$CaCO_3$ content (wt %)	81.82 (10)	82.30 (22)	93.29 (22)	93.27 (22)	92.63 (15)	94.25 (16)
Mean particle size (after elutriation of fines)	724 μm (10)	700 μm (11)	not available	1200 μm (13)	480 μm (22)	410 μm (22)
Minimum fluidization velocity (after elutriation of fines)	0.55 m/s (10)	0.57 m/s (11)	0.43 m/s (12)	0.73 m/s (13)	0.66 m/s (22)	0.32 m/s (16)
Origin	Smithland KY (10)	Clarksville, TN (11)	Fredonia, KY (12)	Lowellville, OH (13)	Gilbertsville, KY (15)	Fredonia, KY (16)
Date of Testing	Oct., Nov., Dec. 1979	Jan. 1980	Feb. 1980	March, April 1980	May 1980 (no recycle) Sept, Oct 1980 (recycle)	June 1980

bed depth is determined by the fact that there are no heat-exchanger coils near the top of the deeper beds. Hence the combustor wall temperatures tended toward overheating. During operation with recycle, the gravity feed of the recycle stream to the bottom of the bed imposes an upper static-bed depth limit of approximately 0.9 m. The typical operating range of the static-bed depth was 0.5 to 1.0 m.

6. The calcium-to-sulfur mole ratio was varied from 2.0 to 5.5 to achieve different levels of sulfur capture. This mole ratio is defined as the ratio of the number of moles of calcium in the limestone feed to the number of moles of sulfur in the coal feed. Ideally, one mole of calcium is required to capture one mole of sulfur. However, more than one mole of calcium must be fed for every mole of sulfur fed since the utilization of the limestone in the bed is below 100%.

7. Three recycle screw feeder settings were used in collecting recycle data: (1) low rate (4 rpm), (2) medium rate (14 rpm), and (3) high rate (25 rpm). These correspond to recycle ratios of 1.5 to 5 times the coal feed rate.

3.4 Raw-Data Analysis

The raw data is analyzed for each of the steady-state data points as follows:

1. Combustion air flow is calculated as the recycle air flow plus the coal-transport air flow plus the fluidizing air flow.

2. The superficial velocity is calculated from the combustion air flow and the bed temperature.

3. The static-bed depth is calculated from the pressure drop across the fluidized bed.

4. The gas residence time is defined as the static-bed depth divided by the superficial velocity.

5. The calcium-to-sulfur mole ratio is calculated from the limestone and coal feed rates and their respective chemical analyses.

6. The sulfur capture is calculated from the flue gas composition, sulfur content of coal, coal feed rate, limestone feed rate, and percent excess combustion air.

Sample raw-data analysis calculations are given in Sect. 9.2.

4. CORRELATION OF SULFUR-CAPTURE DATA

It is necessary to correlate the effects of variables which influence sulfur capture so that the performances of the various limestones can be compared, and the effect of recycle can be accurately quantified. Two correlations of sulfur capture as a function of the calcium-to-sulfur mole ratio and gas residence time are available in the literature. They are derived from data correlation models developed by groups at B&W (3) and Westinghouse (20).

4.1 Babcock and Wilcox Correlation

The B&W correlation is derived from a theoretical model of the sulfur-capture reaction process in a fluidized bed (3). The model is based on the following assumptions:

1. Reaction of CaO with SO_2 is the rate-limiting step.

2. Saturation limit occurs as a result of pore-plugging. The molecular volume of $CaSO_4$ is substantially larger than that of CaO and $CaCO_3$; therefore, the limestone structure becomes more tightly packed.

3. Plug flow of gas.

4. Perfect mixing of solids.

5. Rate of sulfation is first-order in both available moles of CaO and the concentration of SO_2.

The rate of SO_2 removal from the gaseous phase is assumed to be proportional to the SO_2 concentration and to a factor which accounts for the availability of calcium for reaction with the SO_2. Because of the plugging of pores calcium is not completely usable. This inefficiency is accounted for by a factor, m, so that the product of m and the calcium-to-sulfur feed ratio is a measure of the total calcium initially available for sulfate formation. Of course, the total calcium sites in the bed must be reduced by those which are used for sulfur capture (E') to give the available concentration of calcium sites. Therefore, the rate expression for sulfation is given by:

$$\frac{dp}{dt} = -k'(mC - E')p \qquad (1)$$

where

p = SO_2 concentration

E' = sulfur capture, as-combusted basis

C = calcium-to-sulfur mole ratio, as-fed basis

t = gas residence time, s

m = constant related to amount of calcium available for sulfation

k' = reaction rate constant, s^{-1}

Equation (1) solved and rearranged gives the following expression for sulfur capture:

$$C = \frac{E'}{m} - \frac{\ln(1 - E')}{kt} \tag{2}$$

where

k = product of reaction rate constant, fraction of bed not elutriated, and m

E' is the sulfur capture based on sulfur which is released by combustion. The desired basis of sulfur capture is the total sulfur present in the coal since the EPA regulations specify a 90% reduction based on total sulfur not to exceed 1.2 lb/10^6 Btu. Sulfur capture will be observed in the absence of limestone feed since coal contains both organic and pyritic sulfur. Sulfur capture on an as-combusted basis is related to sulfur capture on an as-fed basis as follows (see Sect. 9.3.2 for derivation):

$$E' = \frac{E - E_o}{1 - E_o} \tag{3}$$

where

E' = sulfur capture, as-combusted basis

E = sulfur capture, as-fed basis

E_o = sulfur capture in the absence of limestone feed, as-fed basis

Previous experimental observation indicates that E_o is approximately 0.35 over a wide range of gas residence times (22) for Kentucky #9 coal.

4.2 Westinghouse Correlation

The Westinghouse correlation is also derived from a theoretical model of the sulfur-capture reaction process in a fluidized bed (20). The following assumptions are made:

1. The diffusion of SO_2 through the limestone particle pores is the controlling resistance in transporting released SO_2 to active limestone reaction sites.

2. Plug flow of gas.

3. Perfect mixing of solids.

4. Sulfation rate is first-order in SO_2 concentration.

5. SO_2 is generated uniformly throughout the bed.

6. Steady state is achieved.

A general material balance on SO_2 in the fluidized bed is given by:

$$\frac{dp}{dt} = G - kp \tag{4}$$

where

p = SO_2 concentration

G = SO_2 generation rate

t = gas residence time, s

k = reaction rate constant, s^{-1}

The reaction rate constant is dependent on the available moles of Ca,which is related to the Ca/S mole ratio. Solution of Eq. (4) for sulfur capture gives:

$$E = 1 - \frac{1}{kt}[1 - \exp(-kt)] \tag{5}$$

where

E = sulfur capture (as-fed basis) which is directly related to the exit SO_2 concentration

4.3 Comparison of Models

The main difference between the two models is that the B&W model assumes that all SO_2 is formed instantaneously on contact of coal with air; whereas, the Westinghouse model assumes that SO_2 is generated uniformly throughout the bed. The actual behavior is expected to lie between the two extremes. The rate of SO_2 generation should be greater at the bottom of the bed than at the top. However, the exact rates have not been quantified. Neither model can be said to be preferable to the other on a theoretical basis. The determining factor for deciding which correlation to use is the degree to which each correlation predicts the observed experimental data.

5. RESULTS AND DISCUSSION

5.1 Correlation of Sulfur-Capture Data Taken with No recycle

Three different correlations were applied to the sulfur-capture data collected with no recycle. Correlations, based on models derived by B&W (3) and Westinghouse (20), involve two parameters: the calcium-to-sulfur mole ratio and the gas residence time. The Reed limestone data were used to compare the ability of each correlation to accurately predict the experimentally observed sulfur-capture data for the following reasons: (1) 30 data points had been obtained for Reed limestone, which is more than was obtained for any of the other limestones, and (2) Reed limestone was the first limestone to be tested with recycle.

The B&W correlation assumes that E is a function of both C and the gas residence time t (see Sect. 4.1). Linear regression of the data to determine the constants m and k used in the B&W correlation (see Sect. 9.3.2) yields the following for sulfur capture:

$$C = 1.01\,E' - \frac{\ln(1 - E')}{1.10\,t} \tag{6}$$

where

$$E' = \frac{E - E_o}{1 - E_o} = \frac{E - 0.35}{0.65} \tag{7}$$

The sulfur-capture values predicted by this correlation are shown in Fig. 2 for various values of t. The family of curves appears to improve the fit of the data over the simple single-parameter fit. All the curves are forced through 35% sulfur capture at zero limestone feed due to the boundary condition ($E_0 = 0.35$) imposed on the correlation.

The Westinghouse correlation also assumes that E is a function of C and t (see Sect. 4.2). Linear regression of the experimental data to determine the functional dependence of the reaction rate constant k on C resulted in the following expression for sulfur capture:

$$E = 1 - \frac{1}{kt}[1 - \exp(-kt)] \qquad (8)$$

where

$$k = \exp(0.49C + 0.97) \qquad (9)$$

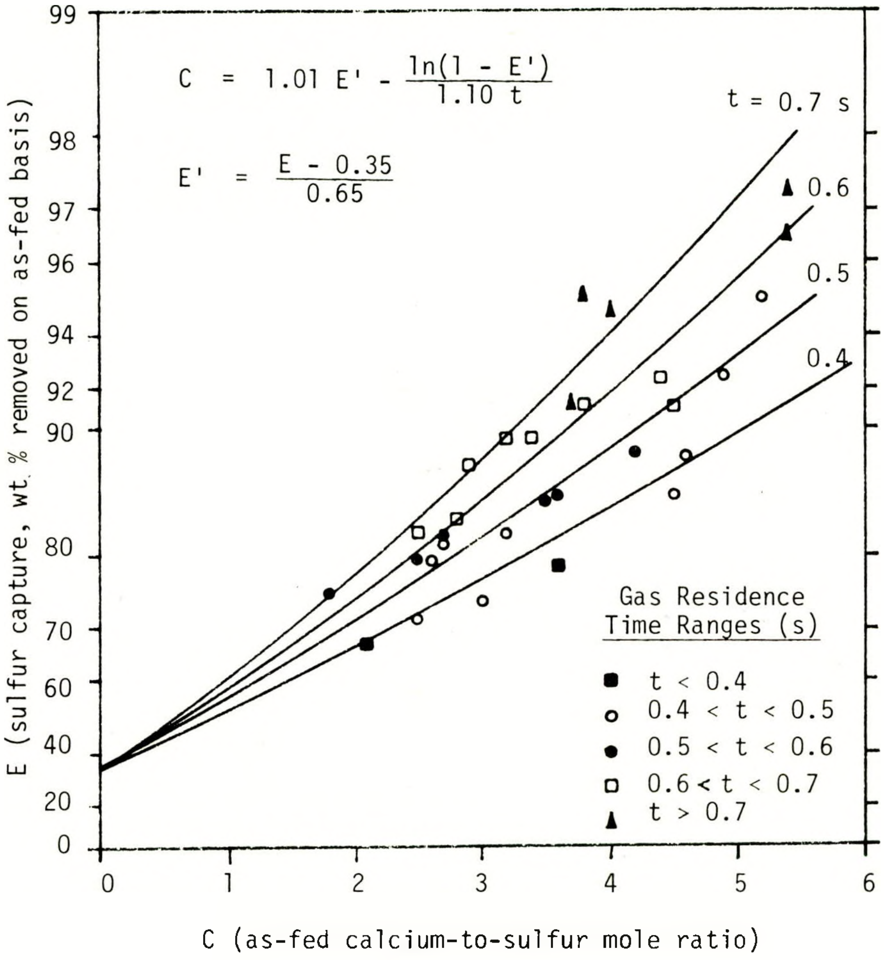
The sulfur-capture values predicted by this correlation are shown in Fig. 3 for various values of t. Again, the family of curves appears to fit the data better than the single-parameter model. The curves are not forced to any particular sulfur capture at zero limestone feed. The correlation inherently predicts sulfur captures at zero limestone feed ranging from 38% at t = 0.4 s to 54% at t = 0.7 s. This appears to be a deficiency of the correlation.

The abilities of each correlation to accurately predict the experimentally observed sulfur-capture data can be determined by comparing experimental values of E to values predicted by the correlations. In a plot of the predicted values of E versus the experimental values of E, the points would fall on a 45° line for a perfect correlation. The accuracy of each correlation can be measured quantitatively by calculating the standard deviation of the points from the 45° line as follows:

$$\sigma = \sqrt{\frac{\Sigma(E_{exp} - E_{pred})^2}{N - 1}} \qquad (10)$$

where

σ = standard deviation



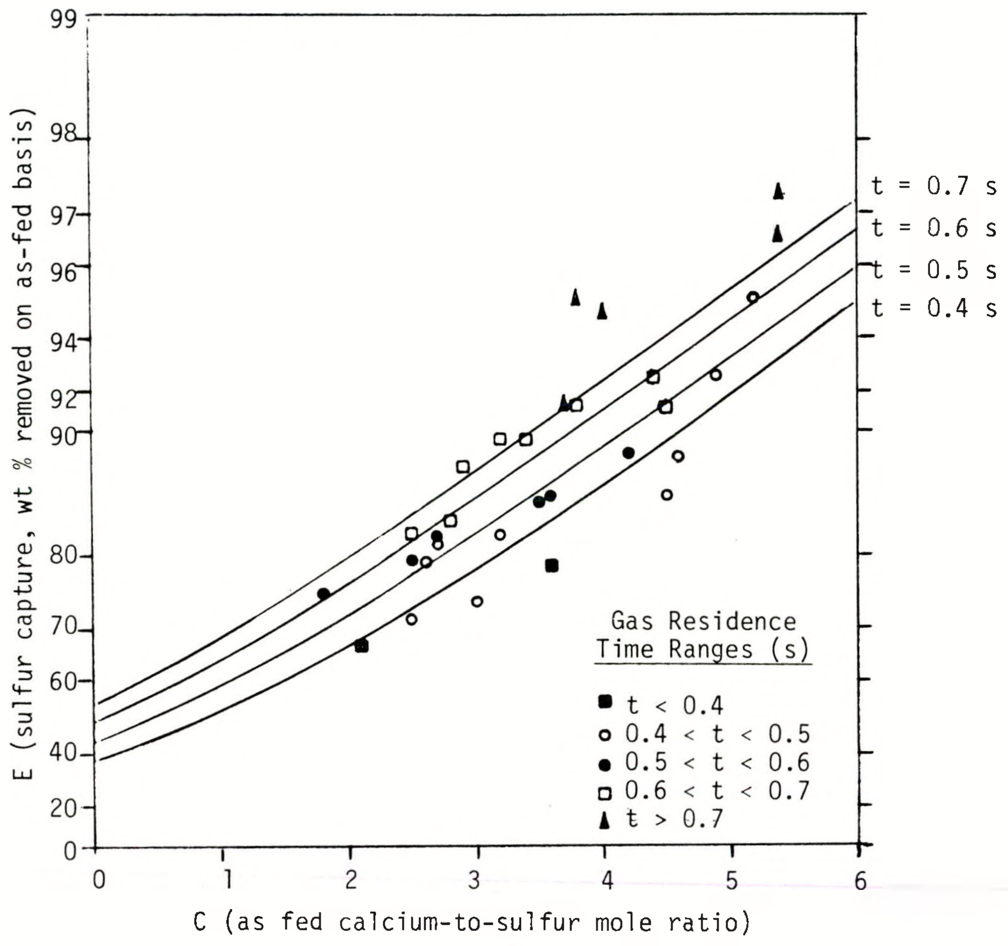
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

B&W CORRELATION OF REED LIMESTONE
SULFUR-CAPTURE DATA WITH NO RECYCLE

DATE	DRAWN BY	FILE NO.	FIG.
10-22-80	ENK	CEPS-X-322	2

$$E = 1 - \frac{1}{kt}[1 - \exp(-kt)]$$

$$k = \exp(0.49\ C + 0.97)$$



MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

WESTINGHOUSE CORRELATION OF REED LIMESTONE SULFUR-CAPTURE DATA WITH NO RECYCLE

DATE	DRAWN BY	FILE NO.	FIG.
10-22-80	ENK	CEPS-X-322	3

E_{exp} = experimentally measured sulfur capture

E_{pred} = predicted sulfur capture

N = number of data points

The standard deviations of the B&W and the Westinghouse correlations are 1.97 and 2.03%, respectively, for Reed limestone (see Sects. 9.3.1 through 9.3.3). There appears to be essentially no difference between the B&W and Westinghouse correlations with respect to the approach taken. However, the B&W correlation is possibly preferable to the Westinghouse correlation because of the ease with which it is applied. The sulfur capture E is expressed explicitly as a function of the calcium-to-sulfur mole ratio C.

Results of correlating the sulfur capture data for Vulcan Materials, Three Rivers, and Fredonia Valley limestones using the B&W correlation are summarized in Table 3. The correlation for Fredonia Valley limestone includes data taken for limestone from both the upper ledge and the lower ledge of the Fredonia Valley quarry. Significantly poorer correlations were obtained for Three Rivers limestone (σ = 5.7%) and Vulcan Materials limestone (σ = 6.8%) than with Reed limestone (σ = 2.0%) and Fredonia Valley limestone (σ = 3.0%). This can be explained partly because fewer data points were available for Three Rivers and Vulcan Materials limestone than for Reed and Fredonia Valley limestones. There was also wide variation in the analysis of the sulfur content of the coal used during the tests of Three Rivers and Vulcan Materials limestones (22).

Table 3. Results of Babcock and Wilcox Correlation for No-Recycle Sulfur-Capture Data

	Correlation Constants			
Limestone	m	k	Number of Data Points, N	Standard Deviation, σ
Three Rivers	0.30	4.14	15	5.70%
Vulcan	0.36	4.17	17	6.83%
Fredonia Valley	0.53	1.62	29	3.02%
Reed	0.99	1.10	30	1.97%

The sulfur-capture performances of the various limestones with no recycle are compared in Table 4. The calcium-to-sulfur mole ratios

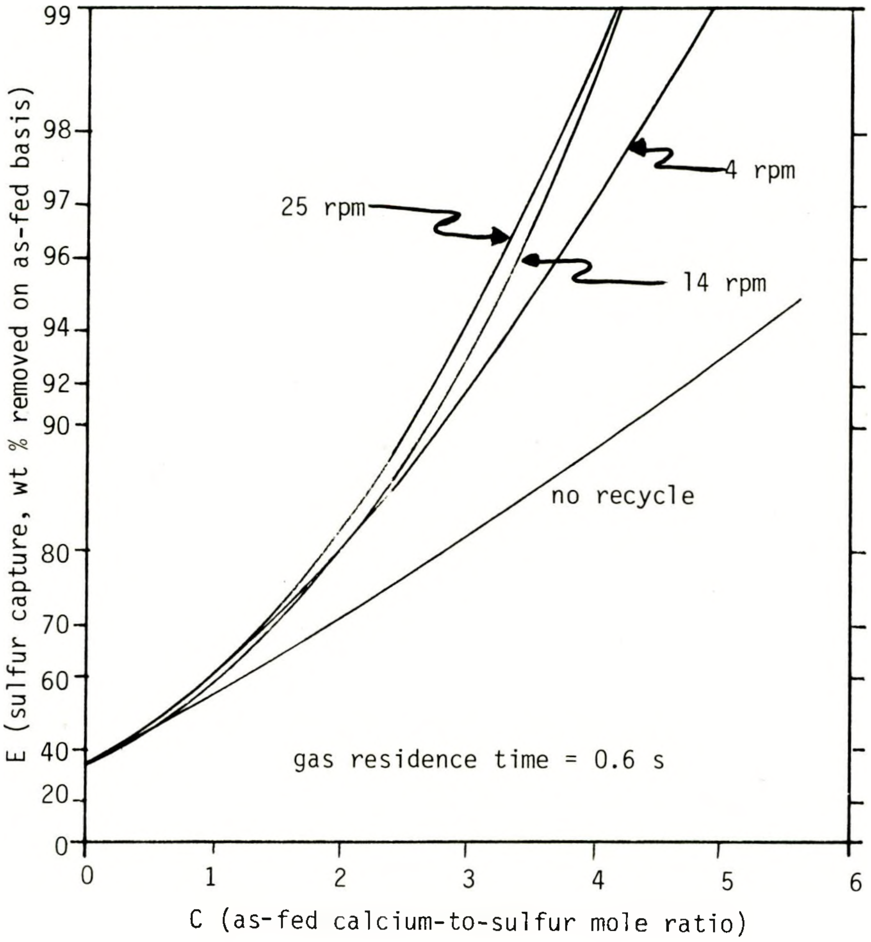
Table 4. Calcium-to-Sulfur Mole Ratios Needed for 90% Sulfur Capture (No Recycle)

Limestone	C(t = 0.4 s)	C (t = 0.6 s)
Three Rivers	4.0	3.6
Vulcan	3.5	3.1
Fredonia Valley	4.5	3.7
Reed	5.1	3.7

required to achieve 90% sulfur capture at gas residence times of 0.4 and 0.6 s are predicted by the B&W correlation. The Vulcan Materials limestone appears to have the best performance, requiring only 69 to 87% as much calcium as the other limestones at t = 0.4 s and 84 to 86% as much calcium at t = 0.6 s. However, it should be noted that the limestones contain different percentages of $CaCO_3$. When this is taken into account, it is still found that less Vulcan Materials limestone is required than the others, but not by as great a margin. The results in Table 4 also show the importance of residence time on sulfur capture performance. This is especially true for the Reed and Fredonia Valley limestones, which require 1.4 and 1.2 times as much limestone feed, respectively, at t = 0.4 s than they do at t = 0.6 s to achieve 90% sulfur capture.

5.2 Analysis and Correlation of Reed Limestone Sulfur-Capture Data with Recycle

Reed limestone sulfur-capture data was collected at three different recycle screw feeder settings (4, 14, and 25 rpm). Six data points were taken at the low screw feeder setting, 15 points at the medium setting, and 8 points at the high setting. The B&W correlation was applied to all three sets of data. The results indicate that recycle has a significant effect on the sulfur-capture performance of Reed limestone. However, preliminary analysis indicated that there is only a small difference between the predicted sulfur-capture performances for the three screw-feeder settings tested. The trend observed was a large increase from the no-recycle case to the low recycle rate, and then a diminished effect as the recycle rate was increased further. This is shown in Fig. 4 for a gas residence time of 0.6 s. The values of C predicted by the three curves at t = 0.6 s lie within 15% of each other for values of E less than 0.94. Larger deviations exist at sulfur captures above 94%, probably because of the small number of data points (only 4) taken at these high sulfur captures. Obviously the results at very high sulfur capture is of less interest than those in the 90% range.



MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

B&W CORRELATION OF REED LIMESTONE
SULFUR-CAPTURE DATA WITH RECYCLE AT
VARIOUS SCREW FEEDER RPM

DATE	DRAWN BY	FILE NO.	FIG.
10-22-80	ENK	CEPS-X-322	4

The validity of the assumption that there are only small differences between the predicted sulfur-capture performances for the three screw-feeder settings was tested by applying the B&W correlation to all of the recycle data as a group. This yielded the following expression:

$$C = 1.93 E' - \frac{\ln(1 - E')}{3.06 t} \qquad (11)$$

where

$$E' = \frac{E - 0.35}{0.65} \qquad (12)$$

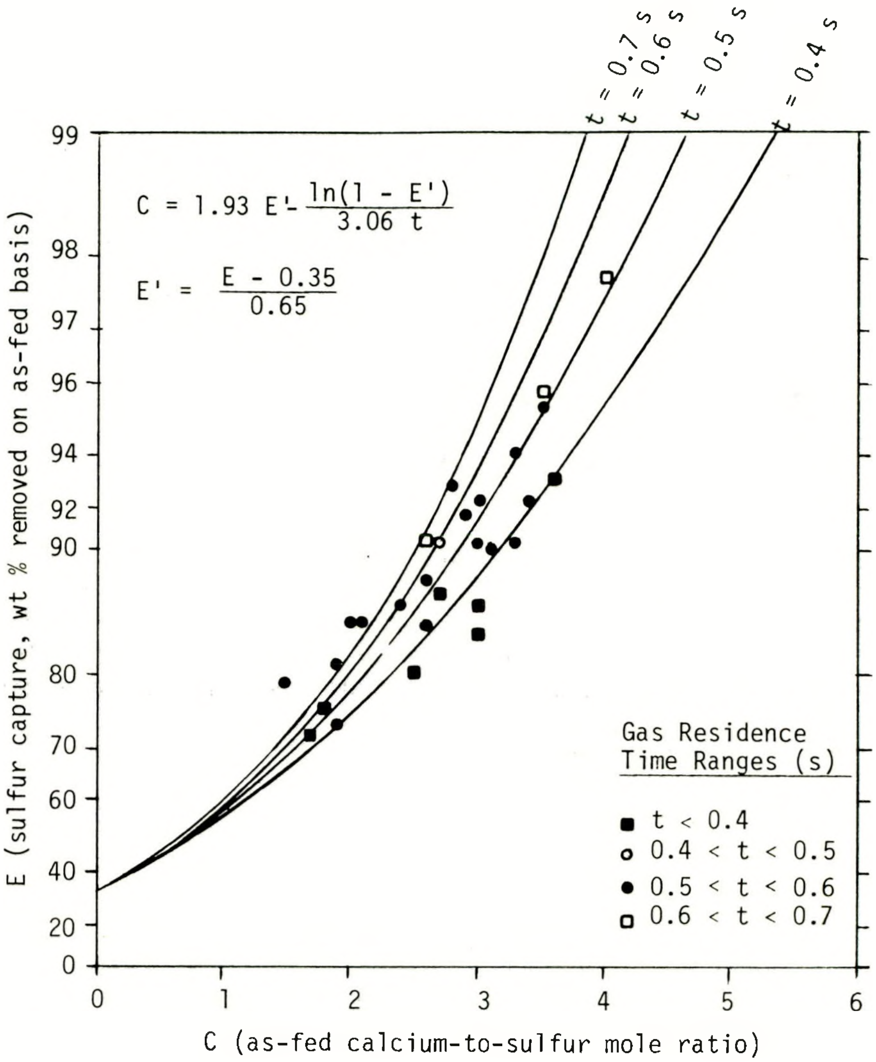
The predictions of this correlation are shown graphically in Fig. 5.

A summary of the results obtained by correlating all the recycle data together and by correlating the data for each screw-feeder setting individually is given in Table 5. The standard deviations indicate that correlating all the recycle data together predicts the experimental data as well as correlating the data separately for each setting. This implies that the differences from varying the recycle screw-feeder setting from 4 to 25 are indeed small.

Table 5. Correlation of Reed Limestone Recycle Data with B&W Correlation for Various Recycle Screw-Feeder Settings

Screw-Feeder Setting (rpm)	B&W Constants		Number of Data Points	Standard Deviation, σ (%)
	m	k		
4	0.71	1.98	6	2.28
14	0.52	3.04	15	3.14
25	0.60	2.79	8	4.79
all data	0.52	3.06	29	3.32

One possible explanation for this behavior is that the setting may not indicate the actual recycle rate due to the varying resistance to recycle at different bed heights. Another possibility is the difference in physical handling which the materials undergo at different feeder rates. Recycle material is presumably considerably deactivated by the fact that sulfate cakes the particle surface. If there were more abrasion at lower rates (longer exposure to the screw feeder), it might cause more exposure of fresh CaO per unit weight of material passing through the recycle tube, and thus provide more active recycle material.



MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

B&W CORRELATION OF REED
LIMESTONE SULFUR-CAPTURE
DATA WITH RECYCLE

DATE	DRAWN BY	FILE NO.	FIG.
10-22-80	ENK	CEPS-X-322	5

The Westinghouse correlation was used to provide an alternative analysis of the Reed limestone recycle data. It has an advantage over the B&W correlation in that it does not require an estimation of the sulfur capture in the absence of limestone feed, since the correlation inherently predicts a value. Application of the Westinghouse correlation yields the following expression for the recycle case:

$$E = 1 - \frac{1}{kt}[1 - \exp(-kt)] \tag{13}$$

where

$$k = \exp(0.78C + 0.77) \tag{14}$$

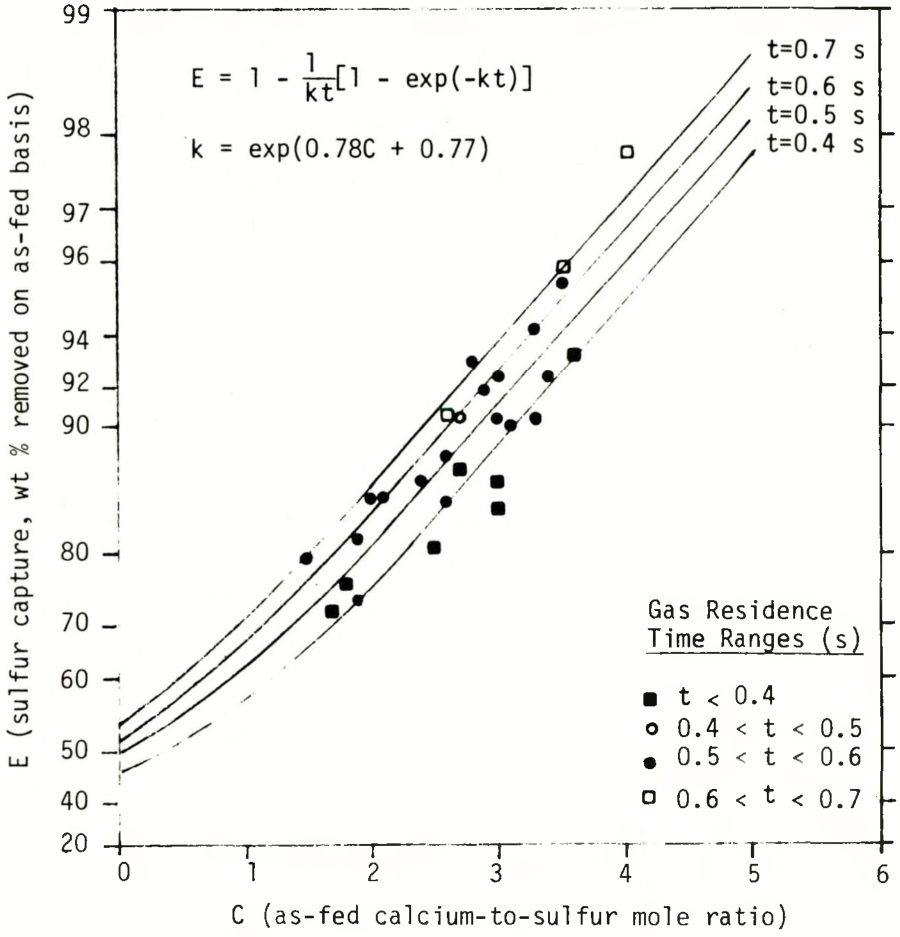
The predictions of this correlation are shown in Fig. 6. The standard deviation between predicted and experimentally observed sulfur capture is 2.74%, which is slightly smaller than the 3.32% that was calculated for the B&W correlation.

The B&W and Westinghouse correlations predict significantly different sulfur capture performance for recycle at calcium-to-sulfur mole ratios less than 2 and greater than 3 as was shown in Figs. 5 and 6. However, in the region of 90% sulfur capture, the two correlations predict almost the same behavior. This is to be expected because most of the data and indeed the interest are in this region. The values of C predicted by the two correlations for 90% sulfur capture are within 3% over the range of residence times from 0.4 to 0.7 s.

5.3 Improvement in Reed Limestone Sulfur-Capture Performance with Recycle

The improvement in the sulfur-capture performance of Reed limestone as a result of recycling elutriated bed material can be measured in terms of the fractional reduction in fresh limestone feed needed to achieve a particular sulfur capture. The fractional reduction in fresh limestone feed is defined by:

$$R = \frac{C_o - C_R}{C_o} \tag{15}$$



MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

WESTINGHOUSE CORRELATION OF REED
LIMESTONE SULFUR-CAPTURE
DATA WITH RECYCLE

DATE	DRAWN BY	FILE NO.	FIG.
10-22-80	ENK	CEPS-X-322	6

where

R = fractional reduction in fresh limestone feed

C_o = calcium-to-sulfur mole ratio (as-fed basis) needed for no recycle at a particular gas residence time and sulfur capture

C_R = calcium-to-sulfur mole ratio (as-fed basis) needed with recycle at the same gas residence time and sulfur capture

The fractional reduction in fresh limestone feed attained at 90% sulfur capture is of the greatest interest since this is the sulfur capture that the TVA pilot plant will have to achieve during operation. Using the expressions for C_o and C_R predicted by B&W correlations for Reed limestone [Eqs. (6) and (11)], the fractional reduction in fresh limestone feed attained at 90% sulfur capture is given by (see Sect. 9.4 for derivation):

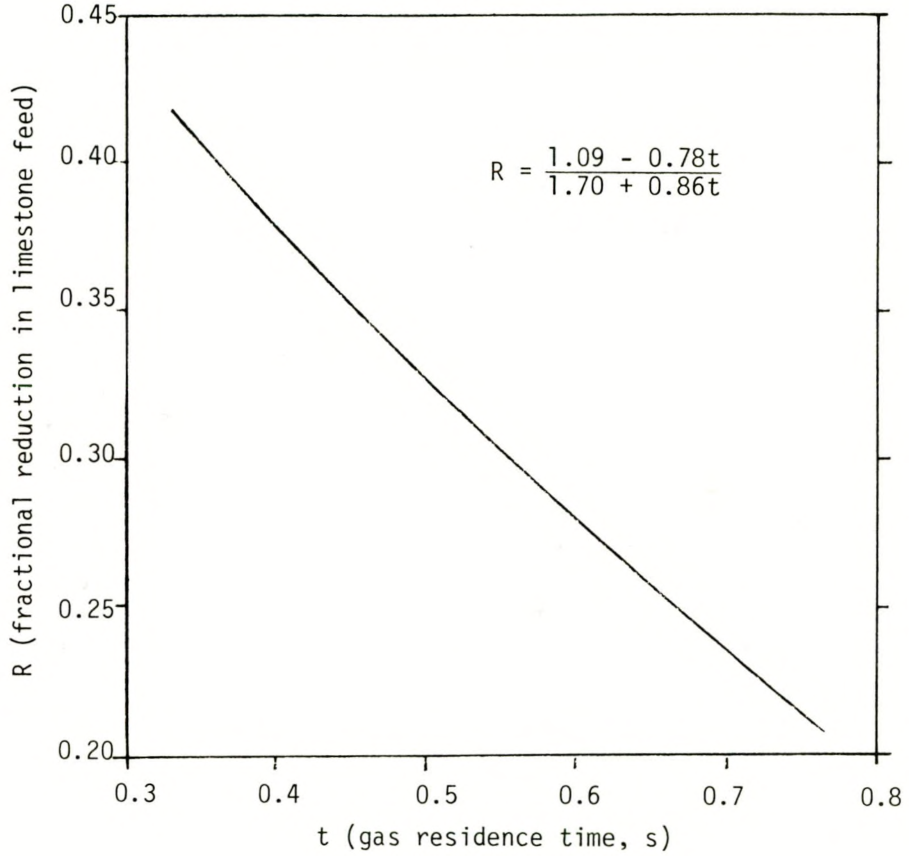
$$R = \frac{1.09 - 0.78\ t}{1.70 + 0.86\ t} \tag{16}$$

The B&W correlations are simpler to use in Eq. (15) than the Westinghouse correlations since C_o and C_R are expressed explicitly as functions of E and t.

The functionality of Eq. (16) is shown in Fig. 7. The fractional reduction in fresh limestone feed obtained by recycle for achieving 90% sulfur capture varies from 38 to 24% for residence times of 0.4 and 0.7 s, respectively. These fractional reductions are comparable to the 27% reduction in fresh limestone feed obtained in the B&W 6 x 6-ft AFBC test unit with Lowellville limestone (7). The reduction in limestone feed is greater at low gas residence times (e.g., high superficial velocities). This occurs because there is more elutriation of bed materials at high superficial velocities. Thus, there is a greater potential for improvement by recycling at low gas residence times.

6. CONCLUSIONS

1. Gas residence time has an important effect on sulfur capture in the bench-scale AFBC. The B&W and Westinghouse correlations, which take into account the gas residence time as well as the calcium-to-sulfur mole ratio, appear to perform equally well in correlating sulfur-capture data. They represent an improvement over a one-parameter correlation which accounts only for the calcium-to-sulfur mole ratio.



MASSACHUSETTS INSTITUTE OF TECHNOLOGY SCHOOL OF CHEMICAL ENGINEERING PRACTICE AT OAK RIDGE NATIONAL LABORATORY			
FRACTIONAL REDUCTION IN LIMESTONE FEED WITH RECYCLE AS A FUNCTION OF GAS RESIDENCE TIME FOR REED LIMESTONE			
DATE 10-22-80	DRAWN BY ENK	FILE NO. CEPS-X-322	FIG. 7

2. Vulcan Materials limestone requires the lowest Ca/s mole ratio of the five TVA candidate limestones tested without recycle to attain 90% sulfur capture.

3. From the results in the bench-scale test unit, recycling elutriated bed material results in a limestone savings ranging from 24% at a gas residence time of 0.7 s to 38% at a gas residence time of 0.4 s to achieve 90% sulfur capture using Reed limestone.

7. RECOMMENDATIONS

1. Experimentally determine E_o (sulfur capture at zero fresh limestone feed) as a function of the recycle rate for the limestones to be tested with recycle. This value can then be used with the B&W model to correlate recycle data.

2. Investigate modifications of the recycle system so that the rate of recycle can be measured and so that the recycle stream entering the bed will have the same composition as the material leaving the cyclone separator.

3. Investigate methods other than recycle for improving calcium usage by breaking apart the sulfated limestone particles to expose more active calcium. This could be done either by a physical grinding process or by addition of water (as steam, for instance), which has been shown to crack open sulfated particles through reaction to form calcium hydroxide.

8. ACKNOWLEDGMENTS

We thank Greg Zimmerman for giving freely of his time to help guide us in this project. We also thank Ralph Guymon, Fred Lynch, and Bob Holcomb for sharing their vast knowledge of fluidized-bed coal combustion with us.

9. APPENDIX

9.1 EPA Sulfur Dioxide Emission Standards

The current EPA sulfur dioxide emission standards for new sources (21) are:

> "SO_2 emissions to the atmosphere are limited to 520 ng/J (1.20 lb/million Btu) heat input, and a 90 percent reduction in potential SO_2 emissions is required at all times except when emissions to the atmosphere are less than 260 ng/J (0.60 lb/million Btu) heat input. When SO_2 emissions are less than 260 ng/J (0.60 lb/million Btu) heat input, a 70 percent reduction in potential emissions is required."

The term "new sources refers to electric utility steam-generating units capable of firing more than 73 MW (250 million Btu/h) heat input. The term "heat input" refers to the heating value of the fuel. Reduction is based on total sulfur present in fuel. A 90% reduction means that 90% of all the sulfur entering an electric utility steam-generating unit (e.g., AFBC) must be prevented from exiting in the flue gases.

TVA plans to use Kentucky #9 coal, which has a sulfur content of about 4% and a heating value of nearly 28 J/mg (11,909 Btu/lb). A 90% reduction would result in an SO_2 emission of about 285 ng/J (0.66 lb/million Btu) heat input. Thus TVA is concerned with achieving 90% reduction (e.g., 90% sulfur capture) since the 520 ng/J emission standard would be simultaneously satisfied.

9.2 Sample Raw-Data-Analysis Calculations

The raw data include the following: six thermocouple readings for the bed, flow meter readings and pressures, pressure drop across bed, coal feed and limestone feed-hopper levels, and flue-gas composition (percent oxygen, percent sulfur, ppm nitrogen oxides, and percent carbon monoxide). The procedure used for analyzing the raw data will be illustrated for the data point taken at 1:40 pm on October 1, 1980 for Reed limestone with recycle (22).

1. The bed temperature was assumed to be the arithmetic average of the six thermocouple readings for the bed:

$$\begin{aligned} T_{bed} &= \frac{1}{6}(1498 + 1518 + 1502 + 1519 + 1517 + 1517)^\circ F \\ &= 1512^\circ F = 822^\circ C \end{aligned} \tag{17}$$

2. The atmospheric pressure was determined from a barometer located in Rm 228, Bldg. 9201-3 as follows:

$$P_{atm} = (\text{barometric reading, in. Hg})\left(\frac{13.6 \text{ in. } H_2O}{1 \text{ in. Hg}}\right)\left(\frac{0.03613 \text{ psi}}{1 \text{ in. } H_2O}\right)$$

$$= 14.29 \text{ psia} = 98.5 \text{ kPa} \qquad (18)$$

3. The recycle assist air flow rate was measured by a rotameter and given by:

$$\dot{m}_R = \frac{FI111A}{14}(PI111A + P_{atm})^{0.5} = 10.5 \text{ lb/h} = 1.32 \text{ g/s} \qquad (19)$$

where

$\dot{m}_R$ = recycle assist air flow rate, lb/hr

FI111A = rotameter reading, % of scale = 20

PI111A = rotameter pressure, psig = 40

14 = constant for reference gas and rotameter

4. The coal-transport air-flow rate was measured by a rotameter and given by:

$$\dot{m}_C = \frac{FI73}{5.84}(PI73 + P_{atm})^{0.5} = 26.1 \text{ lb/h} = 3.29 \text{ g/s} \qquad (20)$$

where

$\dot{m}_C$ = coal-transport air-flow rate, lb/h

FI73 = rotameter reading, % of scale = 37

PI73 = rotameter pressure, psig = 2.7

5.84 = constant for reference gas and rotameter

5. The fluidizing air-flow rate was measured by an orifice meter and given by:

$$\dot{m}_F = 1198.1\left[\frac{(P_{orifice})(\Delta P_{orifice})}{TE11A + 460}\right]^{0.491825} = 116.6 \text{ lb/h} \qquad (21)$$

$$= 14.69 \text{ g/s}$$

where

$\dot{m}_F$ = fluidizing-air-flow rate, lb/h

$P_{orifice}$ = orifice-meter pressure, psia = 20.97

$\Delta P_{orifice}$ = pressure drop across orifice meter, psia = 0.23

TE11A = orifice-meter temperature, °F = 85

The orifice-meter pressure is given by:

$$P_{orifice} = (PI11)\left(\frac{13.6\text{ in. }H_2O}{1\text{ in. Hg}}\right)\left(\frac{0.03613\text{ psi}}{1\text{ in. }H_2O}\right) + P_{atm}$$
$$= 20.97\text{ psi} = 144.6\text{ kPa} \quad (22)$$

where

PI11 = orifice-meter pressure = 13.6 in. Hg

The orifice-meter pressure drop is given by:

$$\Delta P_{orifice} = (FI11)\left(\frac{0.03613\text{ psi}}{1\text{ in. }H_2O}\right) = 0.23\text{ psig} = 1.6\text{ kPa} \quad (23)$$

where

FI11 = orifice-meter pressure drop, in. H_2O = 6.3

6. The combustion air flow is given by:

$$\dot{m} = \dot{m}_R + \dot{m}_C + \dot{m}_F = 153.2\text{ lb/h} = 19.3\text{ g/s} \quad (24)$$

7. The superficial velocity is given by:

$$U = \frac{(\dot{m}_R + \dot{m}_C + \dot{m}_F)(T_{bed} + 460)}{(5330.5)(P_{atm})}\left(\frac{0.3048\text{ m}}{\text{ft}}\right) = 1.22\text{ m/s} \quad (25)$$

where

U = superficial velocity, m/s

8. The static bed depth is given by:

$$h = \frac{\text{PdIX-C}}{\rho}\left(\frac{62.4\ \text{lb}\ H_2O}{\text{ft}^3}\right) = 28\ \text{in.} = 0.71\ \text{m} \qquad (26)$$

where

h = static bed depth, in.

PdIX-C = pressure drop across bed, in. H_2O = 31.5

ρ = bulk density of unfluidized limestone, lb/ft^3 = 70

9. The gas residence time is given by:

$$t = \frac{h}{U} = 0.58\ \text{s} \qquad (27)$$

10. The coal feed rate was determined by plotting the coal feed hopper level vs time and then calculating the slope of the line. The slope must be multiplied by the density of the coal, which is determined from daily calibration:

$$\text{coal feed} = \left(\frac{6.10\ \text{in. hopper}}{\text{h}}\right)\left(\frac{2.80\ \text{lb coal}}{\text{in. hopper}}\right)\left(\frac{0.454\ \text{kg}}{\text{lb}}\right) = 7.8\ \text{kg/h} \qquad (28)$$

11. The limestone feed rate was determined by plotting the limestone feed-hopper level vs time and then calculating the slope of the line. The slope must be multiplied by the density of the limestone, which is determined from daily calibration:

$$\text{limestone feed} = \left(\frac{6.77\ \text{in. hopper}}{\text{h}}\right)\left(\frac{0.72\ \text{lb limestone}}{\text{in. hopper}}\right)\left(\frac{0.454\ \text{kg}}{\text{lb}}\right) = 2.2\ \text{kg/h} \qquad (29)$$

12. The calcium-to-sulfur mole ratio on an as-fed basis is given by:

$$C = \left(\frac{\text{limestone feed}}{\text{coal feed}}\right)\left(\frac{L}{S}\right)\left(\frac{1\ \text{mole Ca}}{100.09\ \text{g}\ CaCO_3}\right)\left(\frac{32.064\ \text{g S}}{1\ \text{mole S}}\right) = 1.9 \qquad (30)$$

where

L = percentage calcium carbonate in limestone = 92.63

S = percentage sulfur in coal = 4.40

13. The limestone feed-to-coal feed weight ratio is given by:

$$X = \frac{\text{limestone feed}}{\text{coal feed}} = 0.287 \qquad (31)$$

14. The sulfur capture is determined by the following expression:

$$E = \frac{\left(\frac{\%\ O_2}{\%\ SO_2}\right)\left[6.741 - 32.087\left(\frac{\%\ O_2}{100}\right)\right] - \left(\frac{6.741}{0.138}\right)\left(\frac{\%\ O_2}{100}\right)\left[31.087 + X\right]}{\left[\left(\frac{\%\ O_2}{\%\ SO_2}\right) - \frac{1}{2}\right]\left[6.741 - 32.08\left(\frac{\%\ O_2}{100}\right)\right] + 6.741\left[\frac{1}{2} - \frac{3}{2}\left(\frac{\%\ O_2}{100}\right)\right]} = 0.816 \qquad (32)$$

where

E = sulfur capture, as-fed basis

$\%\ O_2$ = percentage O_2 in flue gas, dry basis

$\%\ SO_2$ = percentage SO_2 in flue gas, dry basis

The above expression was derived assuming complete combustion of coal and complete calcination of limestone (see calculation file for complete derivation). The sulfur capture as a function of sulfur dioxide concentration and oxygen concentration in the flue gas for a typical sample of Kentucky #9 coal is shown in Fig. 8.

9.3 Curve Fitting Routines: Sample Calculations

9.3.1 One-Parameter Correlation

The form of the one-parameter correlation is:

$$\ln(1 - E) = a + bC \qquad (33)$$

where

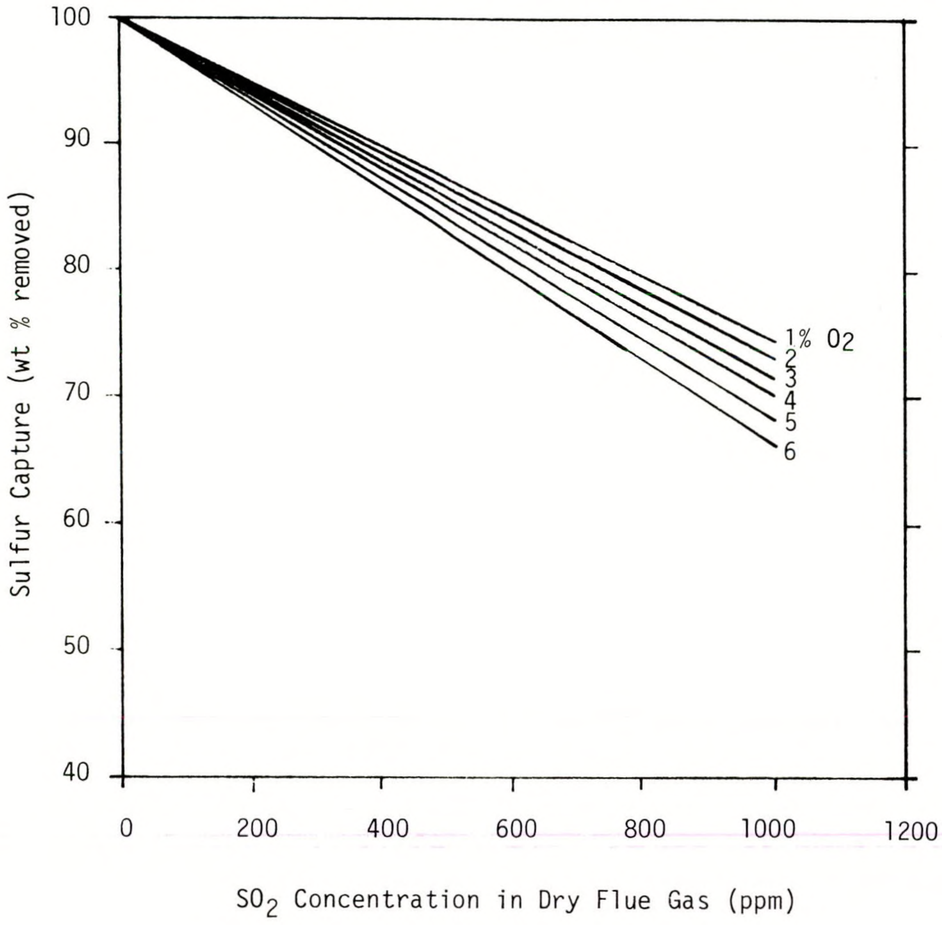
E = sulfur capture, as-fed basis

C = calcium-to-sulfur mole ratio, as-fed basis

a, b = constants

A least-squares fit of all the experimental no-recycle data for Reed limestone (15) using a TI58C calculator, yields the following constants:

$a = -0.2101$



MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

SULFUR CAPTURE AS A FUNCTION OF SO_2 AND O_2 CONCENTRATION IN FLUE GAS FOR KENTUCKY #9 COAL (4.1% SULFUR)

DATE	DRAWN BY	FILE NO.	FIG.
10-22-80	ENK	CEPS-X-318	8

$b = -0.5374$

correlation coefficient = 0.836

Thus for Reed limestone, the one-parameter correlation for no recycle is:

$$E = 1 - 0.8105 \exp(-0.5374\ C) \tag{34}$$

The accuracy of the one-parameter correlation is determined by comparing experimental values of E to values predicted by the correlation for a given C. The predicted values of sulfur capture are plotted against the experimental values for Reed limestone with no recycle in Fig. 9. The standard deviation of the predicted sulfur capture from the experimental sulfur capture is calculated as follows:

$$\sigma = \sqrt{\frac{\Sigma(E_{exp} - E_{pred})^2}{N - 1}} = 0.0434 \tag{35}$$

where

σ = standard deviation

E_{exp} = experimental sulfur capture, as-fed basis

E_{pred} = predicted sulfur capture, as-fed basis

N = number of data points

9.3.2 Babcock and Wilcox Correlation

The form of the Babcock and Wilcox correlation (4) is:

$$C = \frac{E'}{m} - \frac{\ln(1 - E')}{kt} \tag{36}$$

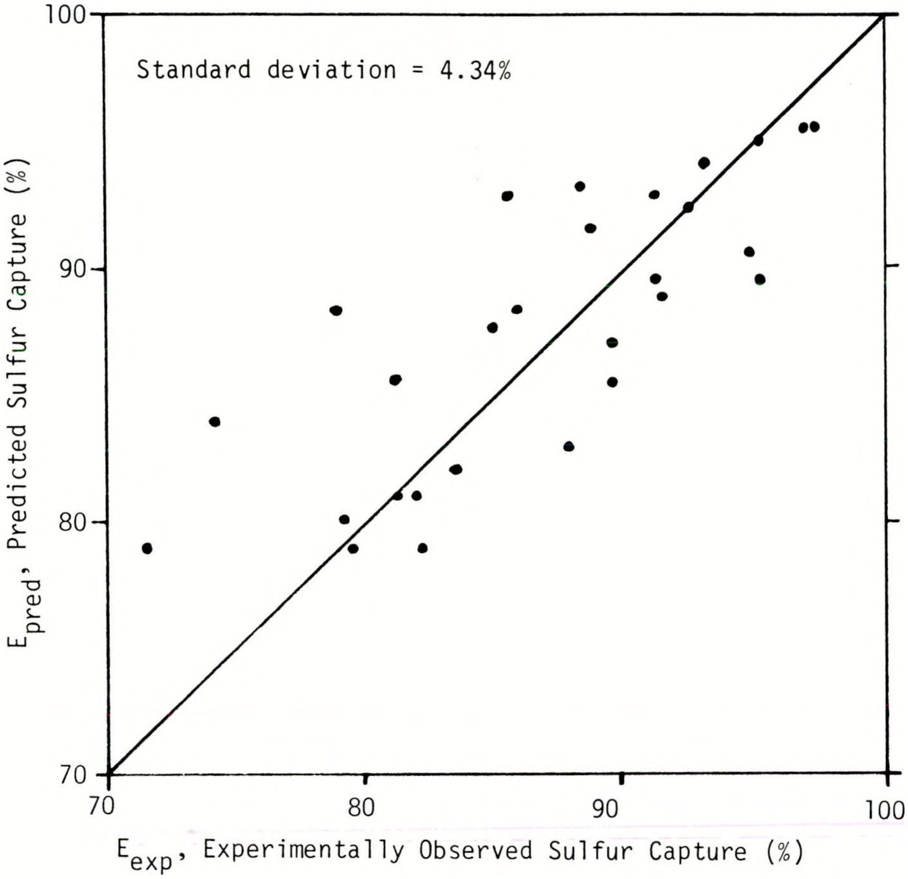
where

C = calcium-to-sulfur mole ratio, as-fed basis

E' = sulfur capture, as-combusted basis

t = gas residence time, s

m = constant related to fractional amount of Ca available for reaction



MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

PREDICTED VS EXPERIMENTAL SULFUR CAPTURES WITH ONE-PARAMETER CORRELATION FOR REED LIMESTONE DATA WITH NO RECYCLE

DATE	DRAWN BY	FILE NO.	FIG.
10-22-80	ENK	CEPS-X-318	9

k = constant related to reaction rate constant, bed material not elutriated, and the constant m

The sulfur capture on a combusted basis is defined by:

$$E' \equiv 1 - \frac{S_\ell}{S_b} \tag{37}$$

where

S_ℓ = sulfur captured by limestone

S_b = sulfur released by coal burnup

The desired basis of sulfur capture is the total sulfur present in the coal since the EPA regulations specify a 90% reduction based on total sulfur. Coal contains both burnable and nonburnable (pyritic) sulfur. Thus some sulfur capture will be observed in the absence of limestone feed due to the presence of unburned sulfur.

The sulfur capture on an as-fed basis is defined by:

$$E \equiv 1 - \frac{S_\ell}{S_b + S_p} \tag{38}$$

where

E = sulfur capture , as-fed basis

S_p = pyritic sulfur (non-burnable)

The sulfur capture on an as-combusted basis is related to the sulfur capture on an as-fed basis as follows:

$$E' = \frac{E - E_o}{1 - E_o} \tag{39}$$

where

E_o = sulfur capture in the absence of limestone feed , as-fed basis

Previous experimental observation indicates that E_o is approximately 0.35 over a wide range of gas residence times (22).

The form of the B&W correlation can be rearranged to resemble an equation for a line. The values of m and k can be determined using linear regression if Eq. (33) is rearranged as follows:

$$\frac{C}{E'} = -\frac{1}{k}\frac{\ln(1 - E')}{E't} + \frac{1}{m} \qquad (40)$$

A least-squares fit based on the experimental no-recycle data for Reed limesone (15), using a TI58C calculator, yields the following constants:

$$\frac{1}{m} = 1.011$$

$$\frac{1}{k} = 0.909$$

correlation coefficient = 0.87

Thus for Reed limestone, the B&W correlation for no recycle is given by:

$$C = 1.555(E - 0.35) - \frac{\ln\left(\frac{1 - E}{0.65}\right)}{1.1\ t} \qquad (41)$$

The accuracy of the B&W correlation is determined by comparing experimental values of E to values predicted by the correlation for a given C and t. The predicted values of sulfur capture are plotted against the experimental values for Reed limestone with no recycle in Fig. 10. The standard deviation of the predicted sulfur capture from the experimental sulfur capture is calculated as follows:

$$\sigma = \sqrt{\frac{\Sigma(E_{exp} - E_{pred})^2}{N - 1}} = 0.0197 \qquad (42)$$

9.3.3 Westinghouse Correlation

The form of the Westinghouse Correlation (10) is:

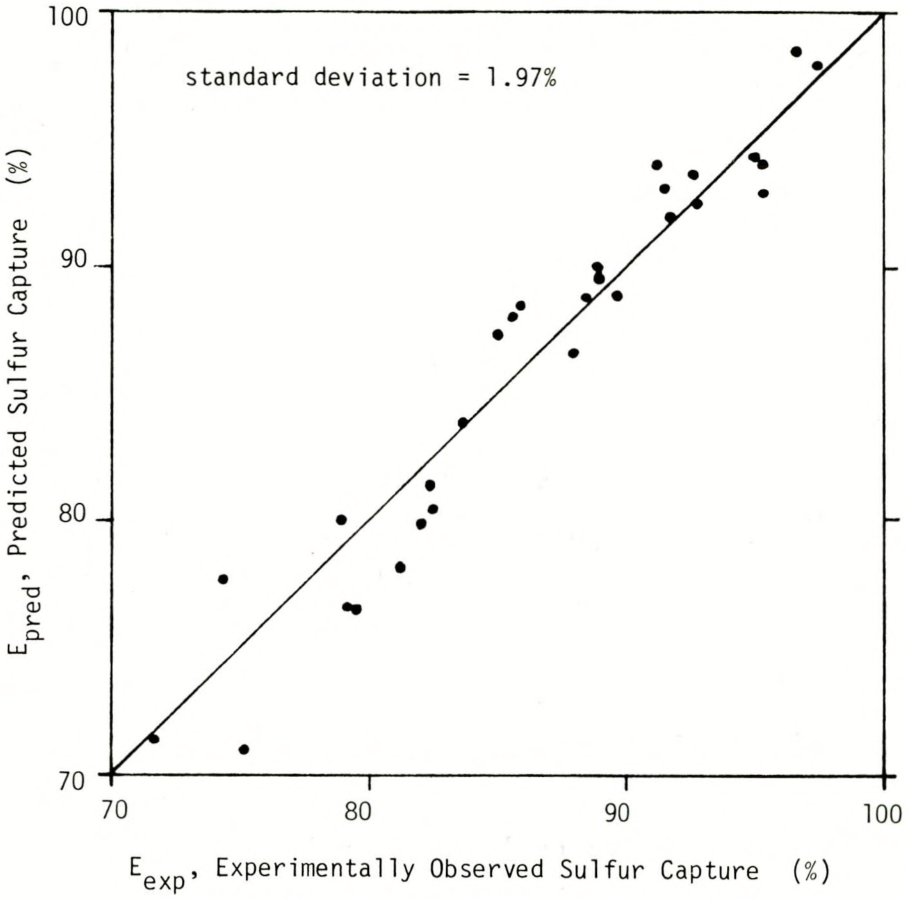
$$E = 1 - \frac{1}{kt}[1 - \exp(-kt)] \qquad (43)$$

where

E = sulfur capture, as-fed basis

t = gas residence time, s

k = reaction rate constant, s^{-1}



MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

PREDICTED VS EXPERIMENTAL SULFUR CAPTURE WITH BABCOCK AND WILCOX CORRELATION FOR REED LIMESTONE NO-RECYCLE DATA

DATE	DRAWN BY	FILE NO.	FIG.
10-22-80	ENK	CEPS-X-322	10

Rearranging the equation gives:

$$kt = \left(\frac{1}{1 - E}\right)[1 - \exp(-kt)] \tag{44}$$

For a particular value of E, the value of kt can be determined by iteration (this is easily done using the zero-function program on a TI58C calculator). Since t is known, the value of k can be determined. The predicted values of k for the experimental no-recycle data for Reed limestone (15) lie on a straight line when plotted on semi-log graph paper as a function of C, the calcium-to-sulfur mole ratio (as-fed basis), as shown in Fig. 11. The least-squares fit of these data, using a TI58C calculator, yields the following expression for k:

$$\ln k = 0.4926C + 0.9666 \tag{45}$$

where

correlation coefficient = 0.931

The accuracy of the Westinghouse correlation is determined by comparing experimental values of E to values predicted by the correlation for a given C and t. The predicted values of sulfur capture are plotted against the experimental values for Reed limestone with no recycle in Fig. 12. The standard deviation of the predicted sulfur capture from the experimental sulfur capture is calculated as follows:

$$\sigma = \sqrt{\frac{\Sigma(E_{exp} - E_{pred})^2}{N - 1}} = 0.0203 \tag{46}$$

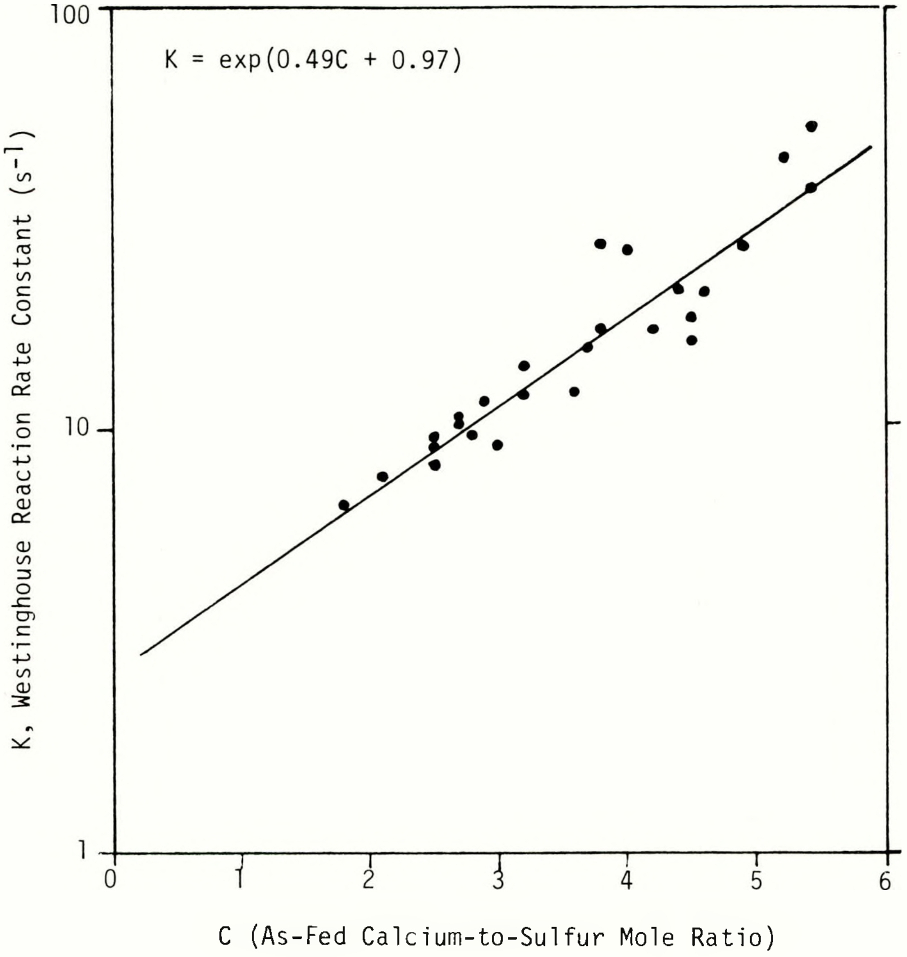
9.4 Calculation of Fractional Reduction in Reed Limestone Feed with Recycle at 90% Sulfur Capture

The fractional reduction in limestone feed is defined as:

$$R = 1 - \frac{C_R}{C_o} = \frac{C_o - C_R}{C_o} \tag{47}$$

From the B&W correlation of the Reed limestone, no-recycle data [Eqs. (7) and (8)],

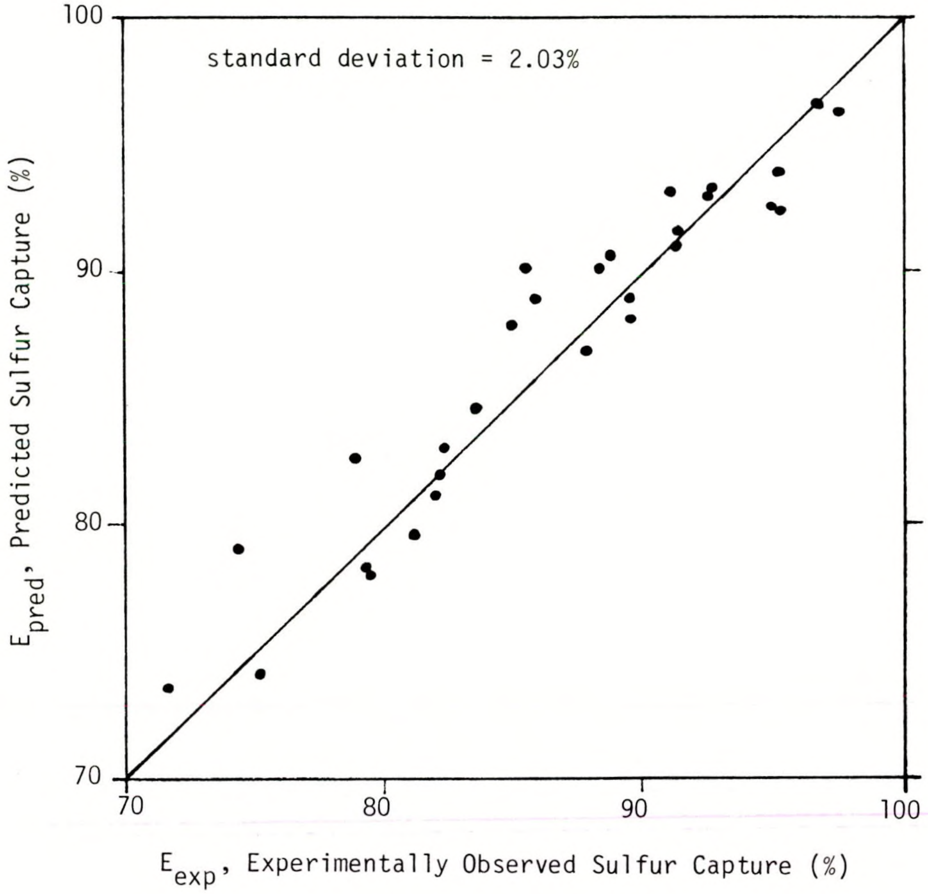
$$C_o = 1.56(E - 0.35) - \frac{\ln\left(\frac{1 - E}{0.65}\right)}{1.10\ t} \tag{48}$$



MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

WESTINGHOUSE-MODEL REACTION-RATE CONSTANT AS A FUNCTION OF CALCIUM-TO-SULFUR MOLE RATIO FOR REED LIMESTONE WITH NO RECYCLE

DATE	DRAWN BY	FILE NO.	FIG.
10-22-80	ENK	CEPS-X-322	11



MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY

PREDICTED VS EXPERIMENTAL SULFUR CAPTURE WITH WESTINGHOUSE CORRELATION FOR REED LIMESTONE DATA WITH NO RECYCLE

DATE	DRAWN BY	FILE NO.	FIG.
10-22-80	ENK	CEPS-X-322	12

From the B&W correlation of the Reed limestone recycle data [Eqs. (11) and (12)]:

$$C_R = 2.97(E - 0.35) - \frac{\ln\left(\frac{1 - E}{0.65}\right)}{3.06\ t} \qquad (49)$$

At E = 0.9, C_o and C_R are given by:

$$C_o = 0.86 + \frac{1.70}{t} \qquad (50)$$

and

$$C_R = 1.64 + \frac{0.61}{t} \qquad (51)$$

Substituting these expressions into Eq. (47) and rearranging yields:

$$R = \frac{1.09 - 0.78\ t}{1.70 + 0.86\ t} \qquad (52)$$

9.5 Location of Data

The data for this investigation are located in Calculation File 322 at the MIT School of Chemical Engineering Practice, ORNL, Bldg. 1505.

9.6 Nomenclature

a	constant
b	constant
C	calcium-to-sulfur mole ratio, as-fed basis
C_o	calcium-to-sulfur mole ratio with no recycle, as-fed basis
C_R	calcium-to-sulfur mole ratio with recycle, as-fed basis
E	sulfur capture, as-fed basis
E'	sulfur capture, as-combusted basis
E_o	sulfur capture in the absence of limestone feed, as-fed basis

E_{exp}	experimentally measured sulfur capture, as-fed basis
E_{pred}	predicted sulfur capture, as-fed basis
FI	rotameter reading, % of scale
G	SO_2 generation rate
h	static bed depth, m
k	Babcock and Wilcox constant related to k', bed material not elutriated and m, s^{-1} Westinghouse reaction rate constant, s^{-1}
k'	Babcock and Wilcox reaction rate constant, s^{-1}
L	percent calcium carbonate in limestone
m	constant related to fractional amount of Ca available for reaction
$\dot{m}$	combustion air flow, g/s
$\dot{m}_C$	coal transport air flow rate, g/s
$\dot{m}_F$	fluidizing air flow rate, g/s
$\dot{m}_R$	recycle assist air flow rate, g/s
N	number of data points
p	SO_2 concentration
P	pressure, kPa
P_{atm}	atmospheric pressure, kPa
P_{dIX-C}	pressure drop across bed, in. H_2O
PI	rotameter pressure, kPa
R	fractional reduction in fresh limestone feed
S	percent sulfur in coal
S_b	sulfur released by coal burnup
S_ℓ	sulfur captured by limestone
S_p	pyritic sulfur
t	gas residence time, s

T	temperature. °C
U	superficial velocity, m/s
U_{mf}	minimum fluidization velocity, m/s
X	limestone-to-coal feed weight ratio
ρ	bulk density of unfluidized limestone, lb/ft^3
σ	standard deviation

9.7 Literature References

1. Beér, J.M., "The Fluidized Combustion of Coal," *16th International Symposium on Combustion*, MIT, Cambridge, MA (1976).

2. Beér, J.M., and A.F. Sarofim, "Fluidized Combustion-Research Needs," *NSF Workshop: Fluidization and Fluid-Particle System-Research Needs and Priorities*, Rensselaer Polytechnic Institute, Troy, NY, Oct. 17-19, 1979.

3. Berman, I.M., "Fluidized Bed Combustion Systems: Progress and Outlook," *Power Eng.*, 46 (Nov. 1979).

4. Hansen, W.A., "Conceptual Studies and Preliminary Design of a Fluid Bed Fired Boiler for Service in an Electric Utility," TV-45715A, CRD-1006, p. 3-43, Babcock and Wilcox, Alliance, OH (April 28, 1978).

5. Highley, J., "Fluidized Combustion as a Means of Firing Gas Turbines and Reducing Atmospheric Pollution," *Institute of Fuel Symposium Series No. 1: Fluidized Combustion*, London (Sept. 1975).

6. Hoke, R.C., L.A. Ruth, and H. Shaw, "Combustion and Desulfurization of Coal in a Fluidized Bed of Limestone," *Combustion*, p. 6 (Jan. 1979).

7. Holcomb, R.S., "Comparison of Sulfur Capture Performance of Four Candidate Limestones for TVA Pilot Plant," personal correspondence to A.M. Manaker (TVA), ORNL (June 4, 1980).

8. Holcomb, R.S., R.H. Guymon, and G.P. Zimmerman, "AFBC Bench-Scale Facility - Task 5," *Fossil Energy Program Progress Report*, L.E. McNeese, editor, p. 47, ORNL-TM-7144 (Monthly Report, Oct. 1979).

9. *Ibid.*, p. 40, ORNL-TM-7171 (Monthly Report, Nov. 1979).

10. *Ibid.*, p. 253, ORNL-5630 (Quarterly Report, Dec. 31, 1979).

11. *Ibid.*, p. 60, ORNL-TM-7251 (Monthly Report, Jan. 1980).

12. *Ibid.*, p. 61, ORNL-TM-7285 (Monthly Report, Feb. 1980).

13. *Ibid.*, p. 84, ORNL-TM-7322 (Monthly Report, March 1980).

14. *Ibid.*, p. 76, ORNL-TM-7375 (Monthly Report, April 1980).

15. *Ibid.*, p. 92, ORNL-TM-7414 (Monthly Report, May 1980).

16. *Ibid.*, p. 80, ORNL-TM-7444 (Monthly Report, June 1980).

17. *Ibid.*, (Quarterly Report, June 30, 1980), in press.

18. Keairns, D.L., "Fluidized Bed Combustion," Third Annual International Conference on Coal Gasification and Liquifaction, University of Pittsburgh, Pittsburgh, PA (Aug. 3-5, 1976).

19. "Multicell Fluidized-Bed Boiler Design, Construction and Test Program," EX-76-C-01-1237, p. 175, Pope, Evans and Robbins, Inc., New York, NY (Nov. 1978).

20. Newby, R.A., N.H. Ulerich, and D.L. Keairns, "A Technique to Project the Sulfur Removal Performance of Fluidized-Bed Combustors," 6th International Conference on Fluidized Bed Combustion, Atlanta, GA (April 1980).

21. "Standards for Performance for New Stationary Sources for Electric Utility Steam Generating Units," Fed. Register, 45(26), 8210 (Feb. 6, 1980).

22. Zimmerman, G.P., data files, ORNL (1979-80).

23. Zimmerman, G.P., personal communication, ORNL (October 1980).

ORNL/MIT-322

INTERNAL DISTRIBUTION

1.	D.A. Canonico
2.	C.S. Daw
3.	E.C. Fox
4.	R.H. Guymon
5-19.	R.S. Holcomb
20.	M.E. Lackey
21.	G.E. Moore
22.	J.W. Wells
23.	R.G. Wymer
24-28.	G.P. Zimmerman
29-30.	Central Research Library
31.	Document Reference Section
32-34.	Laboratory Records
35.	Laboratory Records, ORNL R.C.
36.	ORNL Patent Office
37-51.	MIT Practice School

EXTERNAL DISTRIBUTION

52.	W.C. Rousseau, MIT, Cambridge, MA 02139
53.	J.W. Tester, MIT, Cambridge, MA 02139
54.	J.E. Vivian, MIT, Cambridge, MA 02139
55.	P. Walsh, MIT, Cambridge, MA 02139
56.	H.M. Wood, MIT, GE, Selkirk, NY 12158
57.	Morgantown Energy Technology Center P.O. Box 880, Morgantown, WV 25404
58.	Office Asst. Mgr., Energy R&D, DOE
59-85.	Technical Information Center