TECHNICAL REPORT
September 1 through November 30, 1993

Project Title: **SULFUR REMOVAL IN ADVANCED TWO-STAGED
PRESSURIZED FLUIDIZED-BED COMBUSTION**

DOE Grant Number: DE-FC22-92PC92521 (Year 2)
ICCI Project Number: 93-1/2.1A-1M
Principal Investigator: Javad Abbasian, Institute of Gas
Technology
Other Investigators: Andy H. Hill, James R. Wangerow,
and David M. Rue, Institute of Gas
Technology
Project Manager: Franklin I. Honea, Illinois Clean
Coal Institute

ABSTRACT

The objective of this study is to obtain data on the rates of reaction between hydrogen sulfide (H_2S) and uncalcined calcium-based sorbents under operating conditions relevant to first stage (carbonizer) of Advanced Two-Stage Pressurized Fluidized-Bed Combustors (PFBC). In these systems the CO_2 partial pressure in the first stage generally exceeds the equilibrium value for calcium carbonate decomposition. Therefore, removal of sulfur compounds takes place through the reaction between H_2S and calcium carbonate.

To achieve this objective, the rates of reaction between hydrogen sulfide and uncalcined calcium-based sorbents will be determined by conducting tests in pressurized thermogravimetric analyzer (TGA) and high-pressure/high-temperature fluidized-bed reactor (HPTR) units. The effects of sorbent type, sorbent particle size, reactor temperature and pressure, and CO_2 and H_2S partial pressures on the sulfidation reaction rate will be determined.

During this quarter, a pressurized TGA unit has been purchased by IGT for use in this project. Installation of the unit is expected to be completed during the second quarter of this project. Therefore, no experimental data was obtained during this quarter.

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EXECUTIVE SUMMARY

Second generation staged combustion processes for power generation systems such as Advanced Two Stage Fluidized-Bed Combustion (PFBC) combined cycle plants can achieve higher thermal efficiencies and a lower cost of electricity than a conventional pulverized coal-fired (PC fired) plant equipped with flue gas desulfurization. Because two-stage PFBC plants incorporate coal gasification and combustion and can use high sulfur coals in an environmentally acceptable manner, they have the potential to expand the marketability of high sulfur Illinois coals. Projected costs for two-stage PFBC plants are substantially lower than comparable pulverized-coal (PC) combustion plants, especially if air emission regulations were to require much lower SO₂ emissions.

In the two-stage PFBC processes supported by the United States Department of Energy, calcium-based sorbents such as limestone and dolomite are added to the first stage reactor to capture hydrogen sulfide as calcium sulfide (CaS) in the reducing atmosphere of the carbonizer. The partially sulfided calcium-based sorbent is transferred to the second stage where the unreacted calcium oxide is reacted with SO₂ and oxygen in the oxidizing atmosphere of the combustor to produce calcium sulfate. The calcium sulfide is also expected to react with oxygen and convert to calcium sulfate.

The partial pressure of CO₂ in the carbonizer usually exceeds the equilibrium value for calcination of calcium carbonate. Under such conditions, the removal of sulfur compounds takes place through the reaction of hydrogen sulfide and calcium carbonate (direct sulfidation reaction). However, the kinetics of the direct sulfidation reaction at the carbonizer operating condition is not available. This information is one of the key factors in determination of the optimum sorbent needs in two-stage PFBC processes.

A systematic study of the direct sulfidation reaction occurring in the first stage of the two-stage PFBC is necessary in order to improve the economic and environmental advantages of two-stage PFBC processes by maximizing the utilization of calcium-based sorbents and minimizing the production of solid waste materials by such processes.

The objective of this investigation is to obtain data on the rates of reaction between hydrogen sulfide (H₂S) and uncalcined calcium-based sorbents under operating conditions expected in the first stage of the two-stage PFBC (carbonizer), where because of generally high CO₂ partial pressure, sulfur capture takes place through the direct reaction between H₂S and calcium carbonate.

This project will focus on the determination of the rates of reaction between uncalcined sorbents and hydrogen sulfide at the operating conditions that are expected to prevail in the carbonizer. This systematic study will include determination of the effects of sorbent type (i.e. limestone or dolomite), sorbent particle size, CO_2 and H_2S partial pressures, as well as reactor temperature and pressure on the direct sulfidation reaction. The rate of reaction with fully calcined sorbents at near equilibrium CO_2 partial pressure will also be measured to determine the relative rates of sulfidation reactions involving calcined and uncalcined sorbents.

The results of this study will allow a more accurate estimation to be made of the amount of sorbent needed in two-stage PFBC processes, thereby maximizing the sulfur capture efficiency while minimizing disposal of solid wastes and reducing the cost of electricity produced by these types of plants.

During this quarter, a pressurized TGA unit has been purchased by IGT for use in this project. Installation of the unit is expected to be completed during the second quarter of this project. Therefore, no experimental data was obtained during this quarter.

OBJECTIVES

The overall objective of this project is to obtain data on the rates of reaction between hydrogen sulfide (H_2S) and uncalcined calcium carbonate in limestone and dolomite under operating conditions expected in the first stage of two-stage PFBC (carbonizer), where in general, because of high CO_2 partial pressure, sulfur capture takes place through the direct reaction between H_2S and calcium carbonate.

The program goal is especially directed toward combustion, research priority Section 2.1A: Studies that would lead to improved performance or solve problems, related to advanced CFBC or PFBC and other innovative combustors.

The specific objectives of this project are to -

1. Obtain experimental data on the rates of reaction between selected uncalcined (and calcined) calcium-based sorbents and hydrogen sulfide at operating conditions expected in the carbonizer or gasifier.
2. Determine the effects of operating variables such as reactor temperature and pressure, sorbent type and particle size; and CO_2 and H_2S partial pressures on the sulfidation reaction rates.
3. Provide a direct comparison between the rates of sulfidation reactions involving calcium-based sorbent under CO_2 partial pressure in the vicinity of the equilibrium value for calcination of calcium carbonate.
4. Estimate the extent of desulfurization in the first stage (carbonizer) of the Advanced Two Stage Pressurized Fluidized-Bed Combustors.
5. Establish a guideline for selection of the operating variables in the two-stage PFBC process for optimum removal of H_2S in the carbonizer stage.

INTRODUCTION AND BACKGROUND

Illinois has large reserves of high-sulfur, caking coals. These coals cannot be used directly for power generation due to emissions regulations of SO_2 , unless scrubbers are used which decrease thermal efficiency and increase the cost of electricity (COE). Two technologies⁽¹⁻⁴⁾, Advanced Two Stage Fluidized Bed Combustion (PFBC), and Integrated Gasification Combined Cycle (IGCC), are being developed that can use high sulfur coals in an economical and environmentally sound manner.⁽⁵⁻⁶⁾ Two-stage PFBC involves the use of a

pressurized fluid bed combustor integrated with a fluid bed "partial" gasifier in a combined cycle plant to generate power. Depending on the design selected, two-stage PFBC can achieve 45% efficiency and a COE at least 20% lower than that of a pulverized coal-fired (PC-fired) plant equipped with flue gas desulfurization.^(1,2) IGCC is another attractive option for power generation. In this concept, pressurized fluidized bed gasification of coal is integrated into a power and steam generating combined cycle.⁽⁴⁻⁵⁾ With either option, sulfur removal efficiencies of at least 90% are expected by using calcium-based sorbents as in-situ capture agents.

In the two-stage PFBC processes supported by the United States Department of Energy, such as those proposed by Foster Wheeler⁽¹⁾, Kellogg⁽²⁾, and British Coal⁽³⁾, calcium-based sorbents such as limestone and dolomite are added to the first stage reactor to capture hydrogen sulfide as calcium sulfide (CaS) in the reducing atmosphere of the carbonizer. The partially sulfided calcium-based sorbent is transferred to the second stage where the unreacted calcium oxide is reacted with SO₂ in the oxidizing atmosphere of the combustor to produce calcium sulfate. The calcium sulfide is also expected to react with oxygen and convert to calcium sulfate.

Depending on the partial pressure of CO₂ in the carbonizer, the CaCO₃ in the sorbent will either exist as CaCO₃ or calcine to CaO. Calcination of CaCO₃ proceeds by the following reaction:

H₂S is either removed in the carbonizer/gasifier by reaction with uncalcined limestone, as in Reaction (2):

or by reaction with calcined limestone, as in Reaction (3):

The extent to which Reaction (1) proceeds is determined by the bed temperature and the partial pressure of CO₂ in the carbonizer. The following correlation was used to estimate the equilibrium CO₂ partial pressure for the decomposition of CaCO₃.⁽⁷⁾

$$P_{\text{CO}_2} = 10^{\left[\frac{-8799.7}{T} + 7.521 \right]} \quad (i)$$

In Equation (i), P_{CO_2} is the equilibrium partial pressure of CO_2 in atmospheres, and T is temperature in degrees Kelvin. If the partial pressure of CO_2 in the gasifier is less than the equilibrium CO_2 pressure determined by Reaction (1). H_2S removal will take place by Reaction (3). If the CO_2 partial pressure exceeds that equilibrium pressure, H_2S will be removed by Reaction (2). It should be noted that the $MgCO_3$ present in the feed limestone or dolomite always calcines to MgO under typical fluidized-bed gasifier operating conditions. Furthermore MgO does not remove H_2S from the system to any significant extent.

Experimental data on the reactivity of calcium-based sorbents toward H_2S in the direct sulfidation reaction (Reaction 2) at the carbonizer operating conditions are not available. This information is one of the key factors in determination of the optimum calcium to sulfur ratio in the two-stage PFBC processes.

Experimental data of the sulfidation under operating conditions in the vicinity of the equilibrium condition for calcium carbonate decomposition are needed to determine the relative rate of the sulfidation reaction [Reactions (2) and (3)] to optimize the operating conditions for successful desulfurization in the carbonizer.

The other key factor for determination of the optimum utilization of calcium-based sorbent in two-stage PFBC is sulfation of the partially sulfided sorbent in the second stage of the process (pressurized combustor) --

Experimental data of this direct sulfation reaction involving partially sulfided sorbent are also not available. The calcium sulfide present in the sorbent can also react with oxygen in the combustor to produce calcium sulfate

The calcium sulfate produced through Reaction (5) may plug the pores of the sorbent (especially when limestone is used) and prevent diffusion of SO_2 and oxygen into the unreacted core resulting in inability of the sorbent to capture sulfur dioxide. Fresh sorbent may be added to the

second stage (pressurized combustor) to overcome such a problem.

A systematic study of the complex desulfurization reactions occurring in the both stages of the two-stage PFBC is necessary in order to improve the economic and environmental advantages of two-stage PFBC processes by maximizing the utilization of calcium-based sorbents and minimizing the production of solid waste materials by such processes.

This research program will focus on the determination of the mechanism and the rate of sulfur capture through the direct sulfidation reaction (Reaction 2) that is expected to prevail in the gasifier. Sulfidation tests with calcined sorbents will also be conducted to determine the relative rates of Reactions (2) and (3). This is the first step toward the determination of the optimum desulfurization technique in two-stage PFBC processes. Determination of the mechanism and the rate of sulfur capture through the reactions prevailing in the combustor should follow upon completion of this program.

The experimental tests in this program will be conducted in a pressurized batch, fluidized-bed reactor currently available at IGT and a state-of-the-art pressurized Thermogravimetric Analyzer (TGA) unit that has been purchased by IGT for use in this program. The proposed study will specifically focus on the determination of the effects of various operating variables on the sulfidation reaction [Reactions (2) and (3)] at carbonizer operating conditions.

The information that will be generated in this program is very important in the development of Advanced Two-Stage Fluidized Bed Processes (PFBC) that are especially suitable for utilization of high sulfur Illinois coals.

EXPERIMENTAL PROCEDURE

The project is divided into the following four tasks:

- Task 1. Sorbent Preparation and Characterization
- Task 2. Direct Sulfidation Reaction Tests in the Pressurized TGA
- Task 3. Pressurized Fluidized-Bed Tests
- Task 4. Analyses of Reaction Rate Data

Because the equilibrium partial pressure of CO_2 at carbonizer temperatures exceeds one atmosphere, the tests must

be conducted in pressurized reactors. The tests in this program will be conducted in a pressurized Thermogravimetric Analyzer (TGA) unit, as well as a High-Pressure/High-Temperature Batch Fluidized Bed Reactor (HPTR). Both of these units are capable of operation at elevated pressure and temperature. The HPTR unit is currently available at IGT and the pressurized TGA unit has been purchased by IGT for use in this project. The delivery and installation of the TGA unit is expected to be completed during the second quarter of this project.

The TGA experiments will determine the rate of the sulfidation reactions at various operating conditions. The HPTR tests are designed to confirm the applicability of the reaction rate determined by the TGA experiments, to the fluidized-bed operation.

The schematic diagram the HPTR reactor is shown in Figure 1, and the schematic diagram of the pressurized TGA unit is shown in Figure 2. The detailed description of the experimental procedures involving these units are given in the section under "Task 2" and "Task 3".

Sorbents Preparation and Characterization

Two sorbents will be tested in this program. These sorbents, including one limestone and one dolomite, have already been tested in the previous ICCI-funded programs. The desired particle sizes of each sorbent will be obtained by crushing and screening the selected sorbent. The average particle sizes to be used in this program will be 100, 300, and 900 μm . The weight fraction of the key components including calcium, magnesium, and carbon dioxide will be determined for each cut for both sorbents to ensure the accuracy of the TGA analyses which is totally based on the composition of the starting solid. Physical properties of all batches of the sorbents such as porosity, specific surface area, and pore size distribution will also be determined. This information will be used in analyses of the reaction rate data to correlate the reaction rate to physical properties of the sorbents.

Task 2. Sulfidation Reaction Tests in the Pressurized TGA

The objective of this task is to determine the rate of reaction between H_2S and uncalcined limestone (and half-calcined dolomite) at operating conditions expected in the first stage (carbonizer) of two-stage PFBC processes. The effects of sorbent type, sorbent particle size, CO_2 and H_2S

Figure 1. SCHEMATIC DIAGRAM FOR THE HIGH-PRESSURE/HIGH-TEMPERATURE FLUIDIZED-BED REACTOR (HPTR)

Figure 2. SCHEMATIC DIAGRAM OF THE PRESSURIZED TGA UNIT

partial pressures, and reactor pressures and reaction temperatures on the reaction rate will be determined. Sulfidation tests will also be conducted with CO_2 partial pressures slightly below the equilibrium values, to determine the rate of reaction with calcined sorbents in the vicinity of equilibrium. These tests will be conducted with both sorbents, in the temperature range of 1500 to 1800°F, pressure range of 10 to 20 atmospheres, and a sorbent particle size in the range of 100 μm to 900 μm .

The schematic diagram of the TGA unit is shown in Figure 2. In a typical TGA test, the wire mesh basket containing the sample is initially in the upper section of the reactor in which a downward flow of an inert gas at ambient temperature is maintained. During this time the desired conditions are established in the lower, heated section of the reactor in the presence of flowing inert gases. The reactor gas is then changed to a gas mixture with the desired composition when the reactor temperature has reached the desired value. The test is initiated by lowering the sample into the heated zone while its weight is continually monitored and recorded as the sorbent reacts with the gas. The test is terminated when the sample weight reaches a constant value (no weight loss or gain).

Because the gas flow rates in the reactor are sufficiently high to essentially eliminate changes in the gas composition, the reactions occur under a constant and known environment. Under these conditions the weight loss-versus-time characteristics can be used to determine the reaction rates under constant conditions.

Task 3. Pressurized Fluidized-Bed Tests

The objective of this task is determine the extent of desulfurization in pressurized fluidized-bed environment to confirm the applicability of the TGA data to the fluidized-bed operation. Four tests are planned in this task. These tests will be conducted in a 3-inch pressurized fluidized-bed reactor (HPTR) at 1650°F and 12 atmospheres. Two tests will be conducted at the baseline operating conditions described earlier and the other two tests will be conducted at lower CO_2 partial pressure with calcined sorbents.

The schematic diagram of the HPTR unit is shown in Figure 1. In a typical fluidized bed sulfidation tests, about 500 grams of the sorbent are heated in the reactor in an inert gas containing the desired concentration of CO_2 . The gas is switched to a reactant gas containing CO_2 and H_2S when the reactor pressure and temperature reach the desired level. The reactor effluent is continually monitored by an on line gas

chromatograph to determine the extent of the H₂S removal. The test is terminated by stopping the flow of the H₂S to the reactor. The reactor is depressurized and the heat is then turned off to allow the temperature to reach ambient conditions. The reacted sorbents are removed from the reactor and are analyzed to determine the extent of sulfidation. The results of solid analyses and those of GC analysis of the reactor effluent are used to determine the sulfur balance in the test. The results of these tests couples with those from the TGA tests will be used to estimate sulfur removal from carbonizers/gasifiers.

Task 4. Analyses of Reaction Rate Data

The objective of this task is to provide guidelines for estimation of sulfur removal from a carbonizer/gasifier at different operating conditions.

The reaction rate data to be obtained in Task 2 will be used to estimate the extent of sulfur removal in the 3-inch pressurized fluidized-bed reactor using classical hydrodynamic models. Comparison of the estimated and actual sulfur removal from the fluidized-bed reactor will provide the necessary information to make more accurate predictions on the extent of desulfurization in a large-scale carbonizer/gasifier.

RESULTS AND DISCUSSION

The high-pressure TGA unit has been ordered. The installation of this unit is expected to be completed during the next quarter. The two calcium-based sorbents selected for this study have been ordered and are expected to be available for preparation and characterization during December. Due to availability of the pressurized TGA unit, no experimental work has been performed during this quarter.

CONCLUSIONS AND RECOMMENDATIONS

Due to availability of the pressurized TGA unit, no experimental work has been performed during this quarter.

REFERENCES CITED

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PROJECT MANAGEMENT REPORT
September 1 through November 30, 1993

Project Title: **SULFUR REMOVAL IN ADVANCED TWO-STAGED
PRESSURIZED FLUIDIZED-BED COMBUSTION**

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Project Manager: Franklin I. Honea, Illinois Clean
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COMMENTS

Due to the unavailability of the pressurized TGA unit, no experimental work was initiated during this quarter.

Installation of the TGA unit is expected to be completed during the second quarter. Despite the delay encountered during the installation of the unit, the project is expected to be completed within the schedule.

SULFUR REMOVAL IN ADVANCED TWO-STAGE PRESSURIZED FLUIDIZED-BED COMBUSTION

EXPENDITURES - EXHIBIT B

CUMULATIVE PROJECTED AND ESTIMATED EXPENDITURES BY QUARTER

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials & Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1993 to Nov. 30, 1993	Projected ----- Estimated	10,905 ----- 300	----- -----	400 ----- 0	----- -----	----- -----	----- -----	19,255 ----- 527	30,560 ----- 827
Sept. 1, 1993 to Feb. 28, 1994	Projected ----- Estimated	21,810 ----- -----	----- -----	1,900 ----- -----	----- -----	----- -----	----- -----	38,749 ----- -----	62,459 ----- -----
Sept. 1, 1993 to May 31, 1994	Projected ----- Estimated	32,715 ----- -----	----- -----	3,400 ----- -----	----- -----	----- -----	----- -----	58,240 ----- -----	94,355 ----- -----
Sept. 1, 1993 to Aug. 31, 1994	Projected ----- Estimated	43,314 ----- -----	----- -----	4,000 ----- -----	560 ----- -----	----- -----	----- -----	77,116 ----- -----	124,990 ----- -----

*Cumulative by Quarter

CUMULATIVE COSTS BY QUARTER - EXHIBIT C

**Sulfur Removal in Advanced Two Staged Pressurized Fluidized Bed Combustion
(IN THOUSANDS)**

Months and Quarters

O = Projected Expenditures \$30,560

Δ = Actual Expenditures 827

Total ICCI Award \$ 124,990

SULFUR REMOVAL IN ADVANCED TWO-STAGE
PRESSURIZED FLUIDIZED-BED COMBUSTION

- A. Sorbents Preparation and Characterization
- B. Sulfidation Reaction Tests in Pressurized TGA
- C. Pressurized Fluidized-Bed Tests
- D. Analysis of Reaction Rate Data
- E. Preparation of Technical Reports
- F. Preparation of Project Management Reports

SCHEDULE OF PROJECT MILESTONES

DATE

FILMED

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END