DOE/PC/92521--T195

TECHNICAL REPORT

September 1 through November 30, 1994

Project Title: SULFUR REMOVAL IN ADVANCED TWO STAGE PRESSURIZED FLUIDIZED BED COMBUSTION

DOE Cooperative Agreement Number:	DE-FC22-92PC92521 (Year 3)
ICCI Project Number.:	94-1/5.1A-1M
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ABSTRACT

The objective of this study is to obtain data on the rates and the extent of sulfation reactions involving partially sulfided calcium-based sorbents, and oxygen as well as sulfur dioxide, at operating conditions closely simulating those prevailing in the second stage (combustor) of Advanced Two-Stage Pressurized Fluidized-Bed Combustors (PFBC). In these systems the CO_2 partial pressure generally exceeds the equilibrium value for calcium carbonate decomposition. Therefore, calcium sulfate is produced through the reactions between SO_2 and calcium carbonate as well as the reaction between calcium sulfide and oxygen.

To achieve this objective, the rates of reaction involving SO_2 and oxygen (gaseous reactant); and calcium sulfide and calcium carbonate (solid reactants), will be determined by conducting tests in a pressurized thermogravimetric analyzer (HPTGA) unit. The effects of sorbent type, sorbent particle size, reactor temperature and pressure; and O_2 as well as SO_2 partial pressures on the sulfation reactions rate will be determined.

During this quarter, samples of the selected limestone and dolomite were sulfided in the fluidized-bed reactor. These tests were conducted in both calcining and non-calcining operating conditions to produce partially-sulfided sorbents containing calcium oxide and calcium carbonate, respectively. These samples which represent the carbonizer discharge material, will be used as the feed material in the sulfation tests to be conducted in the HPTGA unit during the next 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 SO_2 emissions.

In the two-stage PFBC processes supported by the United Stated 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 (combustor) where the unreacted calcium carbonate is reacted with SO_2 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 CO_2 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). The rate of direct sulfidation reaction at carbonizer conditions were determined in an earlier ICCI-funded project (Ref. No. R93-1/2.1A-1M). This project is a follow-up of the earlier project to determine the rates and the extent of sulfation reactions involving partially sulfided Ca-based sorbents (containing CaS and $CaCO_3$), at the operating conditions prevailing in the second stage (combustor) of the advanced PFBC processes.

A systematic study of the sulfation reactions occurring in the combustor stage of the two-stage PFBC is necessary 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 and the extent of sulfations reactions involving partially sulfided calcium-based sorbents, sulfur dioxide, and oxygen under operating conditions expected in the combustor stage of the two-stage PFBC processes.

This study will focus on the determination of the effects of sorbent type (i.e. limestone or dolomite), sorbent particle size; SO_2 and O_2 partial pressures, as well as reactor temperature and pressure, on the sulfation reactions. The rate of reaction with fully calcined sulfided sorbents at near equilibrium CO_2 partial pressure will also be measured

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to determine the relative rates of sulfation 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.

OBJECTIVES

The overall objective of this project is to obtain data on the rates of reactions involving calcium sulfide, calcium carbonate, sulfur dioxide, and oxygen, under the operating conditions expected in the combustion stage of the two-stage PFBC processes, where, in general, because of high CO_2 partial pressures, the calcium carbonate in the partially sulfided limestone (or dolomite) does not decompose. Under such circumstances, the sulfur compounds in char are converted to sulfur dioxide which should be removed by the uncalcined calcium carbonate in the combustor.

The specific objectives of this project are to -

1. Obtain experimental data on the rates and extent of sulfation reactions involving calcium sulfide and uncalcined calcium carbonate (in partially sulfided limestone and dolomite); and oxygen and sulfur dioxide, at operating conditions expected in the combustor reactor in PFBC.

2. Determine the effects of operating variables such as reactor temperature and pressure, sorbent type and particle size; and O_2, CO_2 and SO_2 partial pressures, on the sulfation reaction rates.

3. Provide a direct comparison between the rates of sulfation reactions involving calcium-based sorbent at CO_2 partial pressure in the vicinity of the equilibrium value for calcination of calcium carbonate.

4. Estimate the extent of desulfurization in the second stage (combustor) 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 conversion of sulfur dioxide and calcium sulfide to calcium sulfate.

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, Advanced Two Stage Fluidized Bed Combustion (PFBC)(1-6), 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.(7-11) With either option, sulfur removal efficiencies of at least 90% are expected by using calcium-based sorbents as in-situ capture agents.

One proposed plant concept for a two-stage PFBC combined-cycle plant, shown in Figure 1 as a simplified process block diagram, is being developed by Foster Wheeler under a DOE contract.(1) In this design, coal is fed to a pressurized fluidized-bed carbonizer where the coal partially gasifies producing a low-Btu fuel gas and char. The fuel gas is cleaned in a cyclone and filter to remove particulates, and burned in a topping combustor. The topping combustor produces the energy required to drive the gas turbine which drives a generator and a compressor that feeds air to the carbonizer, a Circulating Fluidized Bed Combustor (CPFBC), and a Fluidized-Bed Heat Exchanger (FBHE). The carbonizer char is burned in the CPFBC with a high excess air, and flue gas from the CPFBC is used to support combustion of the fuel gas in the topping combustor. Steam generated in a Heat Recovery Steam Generator (HRSG) downstream of the gas turbine and in the Fluidized Bed Heat Exchanger (FBHE) associated with the CPFBC, drives the steam turbine generator that produces the remainder of electric power delivered by the plant.

A low-Btu gas is produced in the carbonizer by the pyrolysis/mild devolatilization of coal in a fluidized-bed reactor. Char residue is also produced due to the lower operating temperature of the carbonizer as compared to the higher temperature used in "total" gasifiers. Calcium-based sorbents are injected into the carbonizer to promote tar cracking and to capture sulfur as calcium sulfide. Because the sulfur capture is done in-situ, the raw fuel gas can be used without cooling thereby avoiding expensive heat exchangers and chemical or sulfur-capturing bed clean-up systems.

Depending on the partial pressure of CO_2 in the carbonizer, the $CaCO_3$ in the sorbent will either exist as $CaCO_3$ or calcine to CaO. Calcination of $CaCO_3$ proceeds by the following reaction:

$$CaCO_3 = CaO + CO_2 \tag{1}$$

H_2S is removed in the carbonizer/gasifier by reaction with uncalcined limestone, as in Reaction (2):

$$CaCO_3 + H_2S = CaS + H_2O + CO_2 \tag{2}$$

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

$$CaO + H_2S = CaS + H_2O \tag{3}$$

The extent to which Reaction (1) proceeds is determined by the bed temperature and the partial pressure of CO_2 in the carbonizer. The following correlation was used to estimate the equilibrium CO_2 partial pressure for the decomposition of $CaCO_3$(11)

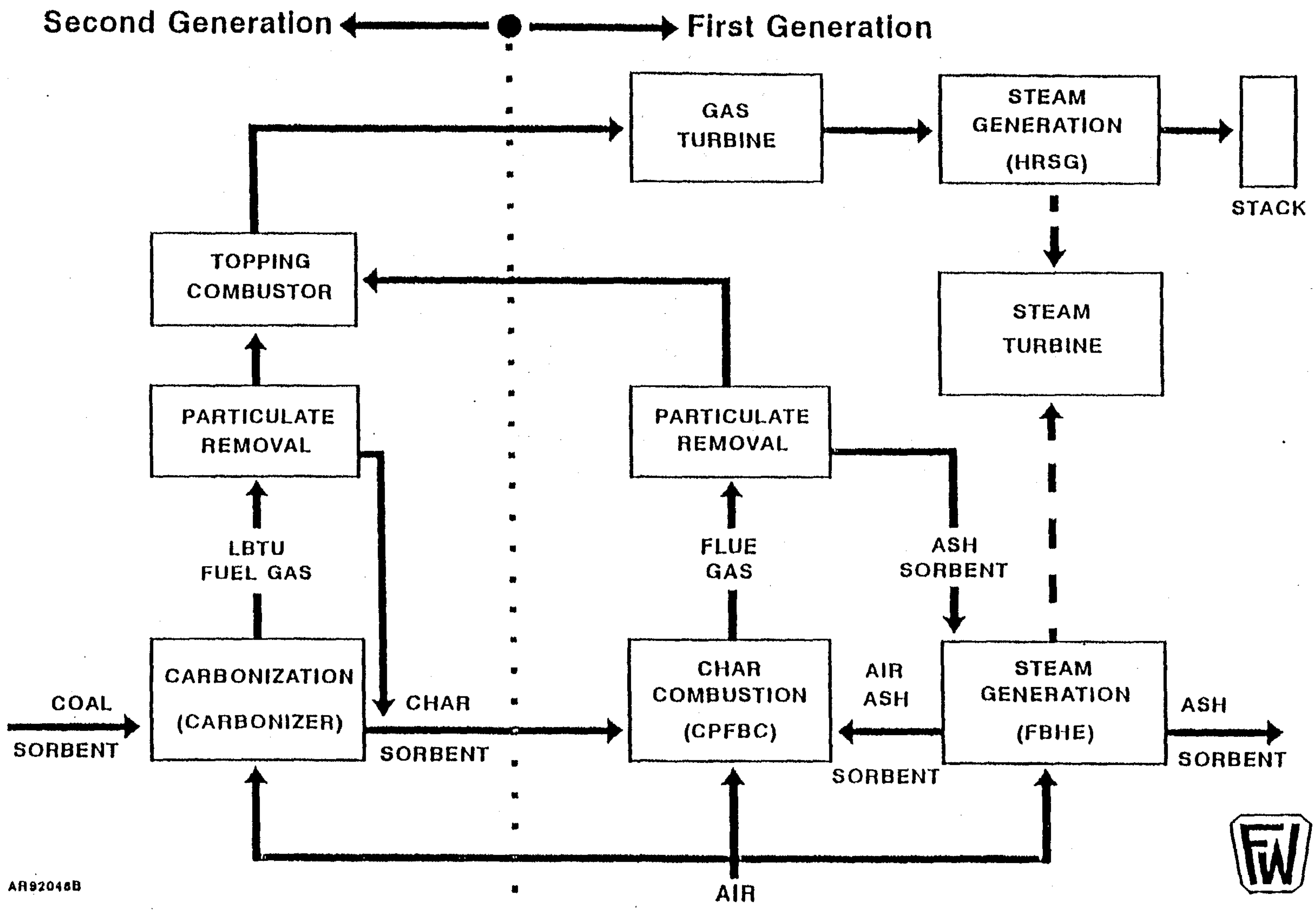

Figure 1. SCHEMATIC DIAGRAM OF AN ADVANCED TWO-STAGE PFBC PLANT (1)

$$P_{CO_2} = 10^{\frac{[-8799.7+7.521]}{T}} \qquad (A)$$

In Equation (A), P_{CO2} 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.

Computer models have been developed, based on published data, to simulate air-blown pyrolysis of coal in a carbonizer. Carbonizer fuel gas compositions predicted by models developed by IGT(5) and M. W. Kellogg(2) are shown in Table 1. The predicted carbonizer product gases are for a Pittsburgh coal feed at 14 atmospheres and 1600°F (IGT) and an Illinois No. 6 coal feed at 15 atmospheres and 1450°F (M. W. Kellogg). The CO_2 partial pressure is seen to be approximately 1.7 atmospheres in both cases. According to equation (A), at this temperature and partial pressure of CO_2, the calcium in the limestone/dolomite injected into the carbonizer for sulfur capture will be in the form of $CaCO_3$, and therefore the H_2S will be removed mainly by Reaction (2). The predicted Ca/S ratio, based on the sulfur in the coal feed, varies from 1.75 in the IGT model to 1.99 in the Kellogg model.

Actual gasifier product gas compositions from a pilot scale fluidized-bed gasifier based on IGT's U-GAS technology, are shown in Table 2. This represents gasification technology being developed as part of an IGCC process. The data shown in Table 2 are from a series of in-situ desulfurization tests with coal and limestone cofeeding in the steam-air gasification mode(12), indicating that the partial pressure of CO_2 in the gasifier may, under certain operating conditions, be high enough to place the calcium carbonate in the noncalcining regime.

The reaction between calcium-based sorbents and hydrogen sulfide [Reactions (2) and (3)] have been studied by many investigators, including the Principal Investigator of this project, over the past two decades. Among these investigators, Abbasian et al(14-20), Borgwardt and Roache(21), Ruth et al.(22), Squires(23), Kamath and Petrie(24), Simon and Raulins(25), Yen et al.(26), Freund(27), Borgwardt et al.(28) However, none of the above studies include experimental data on direct sulfidation reaction (2) with limestone and dolomite at conditions prevalent in the proposed designs of these carbonizers, that is, temperature of 800°-950°C, pressures of 12-20 atmospheres, CO_2 partial pressures near 2 atmospheres and sorbent particle sizes in the range of 100 to 900 μm.

Table 1. MODEL PREDICTED CARBONIZER FUEL GAS COMPOSITION

Operating Conditions	IGT	Kellogg
Coal Type	Pittsburgh No. 8	Illinois No. 6
Temperature, °F	1600	1450
Pressure, psig	192	148
Ca/S Feed Molar Ratio	1.75	1.5
Sorbent Particle Size, μm	100	
Selected Gases	vol %	
Carbon Monoxide	11.04	15.51
Hydrogen	5.90	19.35
Carbon Dioxide	12.32	10.34
Methane	6.23	1.30
Hydrogen Sulfide	0.035	0.01
Water Vapor	8.20	10.03

Table 2. SUMMARY OF U-GAS PDU IN-SITU DESULFURIZATION TEST DATA
Feed Material: Pittsburgh Seam Bituminous Coal - Ireland Mine
Sorbent: New Enterprise Limestone

	Test No.				
	1	2	3	4	5
Bed Temperature, °F	1845	1870	1860	1767	1762
Reactor Pressure, psig	150	303	303	406	290
Ca/S Feed Molar Ratio	2.60	1.72	2.25	4.21	3.80
Sulfur Capture, %	95.9	84.9	74.4	93.4	103.7
Reactor Gas Composition, Vol %					
Carbon Monoxide	10.54	4.31	6.62	1.90	3.53
Hydrogen	12.13	8.34	10.78	4.92	7.35
Carbon Dioxide	13.05	12.53	13.42	11.35	11.95
Methane	2.47	1.55	2.19	1.33	1.99
Nitrogen	38.43	36.45	33.87	37.26	36.34
Hydrogen Sulfide	0.11	0.18	0.22	0.16	0.08
Water Vapor	23.27	36.64	32.90	43.08	38.71

The mathematical models used for estimation of sulfur capture in the carbonizer (2,5) are based on either the extrapolation of the available data on this reaction at lower temperature and atmospheric pressure, or based on the thermodynamic consideration.

The reactivity of calcium-based sorbents (limestone and dolomite) toward H_2S in the direct sulfidation reaction [Reaction (2)] at the carbonizer operating conditions in an earlier ICCI-funded project (Ref. No. 93-01/2.1A-1M) were determined. This information(29,30) is one of the key factors in determination of the optimum calcium to sulfur ratio in the two-stage PFBC processes. 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) --

$$CaCO_3 + SO_2 + 1/2O_2 = CaSO_4 + CO_2 \tag{4}$$

$$CaS + 2O_2 = CaSO_4 \tag{5}$$

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.

Sulfation of calcium sulfide in partially sulfided (and calcined) calcium-based sorbents has been studied by the principal investigator of this project over the past several years under the sponsorship of the ICCI(31-35) The results of these investigations indicate that limestone can only be partially sulfated while dolomite can be nearly completely sulfated at about 800°C. The extent of sulfation depends not only on the sorbent type, but also on the extent of sulfidation in the gasifier (or carbonizer).

The limited conversion of calcium sulfide in limestone to calcium sulfate is believed to be due to plugging of the pores of the sorbent that can prevent diffusion of oxygen inside the particle. Sulfation of limestone involving calcium oxide has also been reported to be limited to a fraction of complete conversion due to pore plugging.(36-38)

The literature on the direct sulfation reaction (Reaction 4) is limited and mostly concentrates on small sorbent particles that are typically used in limestone injection system. Snow et al.(39) showed that the uncalcined limestone particles (3-20 μm diameter) were sulfated at a rate that was higher than that for the corresponding calcine. The higher rate of direct sulfation reaction is believed to be due to more porous nature of the sulfated surface. It was hypothesized that the porosity was created by the outflow of CO_2 through the product sulfate larger and thereby improved the accessibility of SO_2 and oxygen to the reacting surface. A similar result has been reported by Iisa et al.(40)

The results of these studies suggest that the sulfation of both calcium sulfide and calcium carbonate in the partially sulfided calcium-based sorbent, because of the uncalcined nature of the sorbent, may proceed at higher rate and achieve higher conversion compared to the corresponding calcined and sulfided sorbent. The experimental data on sulfation of partially sulfided (and uncalcined) sorbents at the combustion stage in the PFBC process is necessary to verify the suitability of limestone for use in the Advanced Two-Stage PFBC Processes.

This project will focus on the determination of the rate and the extent of reactions involving partially sulfided uncalcined calcium-based sorbents with oxygen and sulfur dioxide at the operating conditions that are expected to prevail in the combustor. This systematic study will include determination of the effects of sorbent type (i.e. limestone or dolomite), sorbent particle size; CO_2, O_2, and SO_2 partial pressures, as well as reaction temperature and pressure, on the direct sulfidation reactions [Reaction (4) and (5)].

EXPERIMENTAL PROCEDURE

This project is divided into the following tasks:

Task 1. Sorbent Preparation and Characterization

Task 2. Sulfidation Reactions Tests

Task 3. Analyses of Sulfation Reactions Data

Because the equilibrium partial pressure of CO_2 at combustor temperatures exceeds one atmosphere, the tests must be conducted in a pressurized reactor. The tests in this project are conducted in a specially designed high-pressure Thermogravimetric Analyzer (HPTGA) unit that is available at IGT.

The schematic diagram and the schematic diagram of the HPTGA unit is shown in Figure 2. This unit has a balanced pressure reactor design, capable of operation at 1000°C at 100 atm. The special design of the inner reactor is suitable for operation in a corrosive environment.

Task 1. Sorbents Preparation and Characterization

The two sorbents selected for testing in this project , including one limestone and one dolomite, have already been tested in earlier ICCI-funded programs. The desired particle sizes of each sorbent were obtained by crushing and screening the selected sorbent. The average particle sizes selected for this study were 100, 300, and 900 µm. The bulk chemical composition of the sorbent as determined in the previous ICCI- funded program is presented in Table 3.

Table 3. CHEMICAL ANALYSES OF SORBENTS

Analyses, wt %	Limestone	Dolomite
Calcium	38.7	22.2
Magnesium	0.59	13.2
Potassium	0.5	0.5
Iron	0.084	0.11
Aluminum	0.05	0.069
Silicon	0.11	0.3
Strontium	0.015	0.005
Carbon Dioxide	44.7	48.0
Oxygen (by Diff.)	15.251	15.616
	100	100

Samples of the selected limestone and dolomite were sulfided in fluidized-bed reactor. These tests were conducted in both calcining and non-calcining operating conditions to produce partially-sulfided sorbents containing calcium oxide and calcium carbonate, respectively. These samples which represent the carbonizer discharge material, will be used as the feed material in the sulfation tests to be conducted in Task 2.

The physical and chemical properties of the sulfided sorbent including porosity, specific surface area, and pore size distribution are currently being determined. This information will be used in the analysis of reaction rate data (Task 3) to correlate the reaction rate to the physical properties of the sorbents.

Task 2. Sulfation Reaction Tests

The objective of this task is to determine the rates of reactions involving partially sulfided limestone and dolomite (produced by direct sulfidation reaction in the carbonizer), and oxygen as well as sulfur dioxide, at operating conditions expected in the second stage (combustor) of two-stage PFBC processes.

The effects of sorbent type, oxygen and SO_2 partial pressures, and reactor pressure and temperature on the reaction rate will be determined. Sulfation 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 800 to 950°F, pressure range of 12 to 20 atmospheres, and both sorbents with an average particle diameter of about 300 μ m.

The schematic diagram of the HPTGA unit is shown in Figure 2. In a typical HPTGA 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. Analysis of Sulfation Reaction Data

The objective of this task is to provide guidelines for estimation of the extent of sulfur removal and the composition of the final solid waste material in the second stage (combustor) of the advanced two-stage PFBC at different operating conditions.

The reaction rate data to be obtained in Task 2 at the prevailing PFBC operating conditions, combined with the data obtained in the previous ICCI-funded project, will provide the necessary information to make a more accurate prediction to the extent of desulfurization and the composition of the solid waste products in the large-scale advanced two-stage PFBC processes.

RESULTS AND DISCUSSION

During this quarter, four sulfidation tests were conducted in the fluidized-bed reactor with the two selected sorbents. These tests were conducted in both calcining and noncalcining conditions to produce partially sulfided sorbent representing carbonizer discharge. These samples will be used as the feed material for the sulifdation tests. To eliminate problems associated with feed sample non-homogeneity in the HPTGA sequential sulfidation/sulfation tests, it was decided to add small quantities of small(d_p = 0.01 cm) and large (d_p = 0.09 cm) particles to the sorbent during sulfidation tests. The partially sulfided sorbent in different particle sizes will be obtained by screening the sulfided samples and analyzing them separately.

The HPTGA unit was installed at IGT's new laboratory and shake down tests were completed. The sulfation tests planned for this project will be initiated during the next quarter.

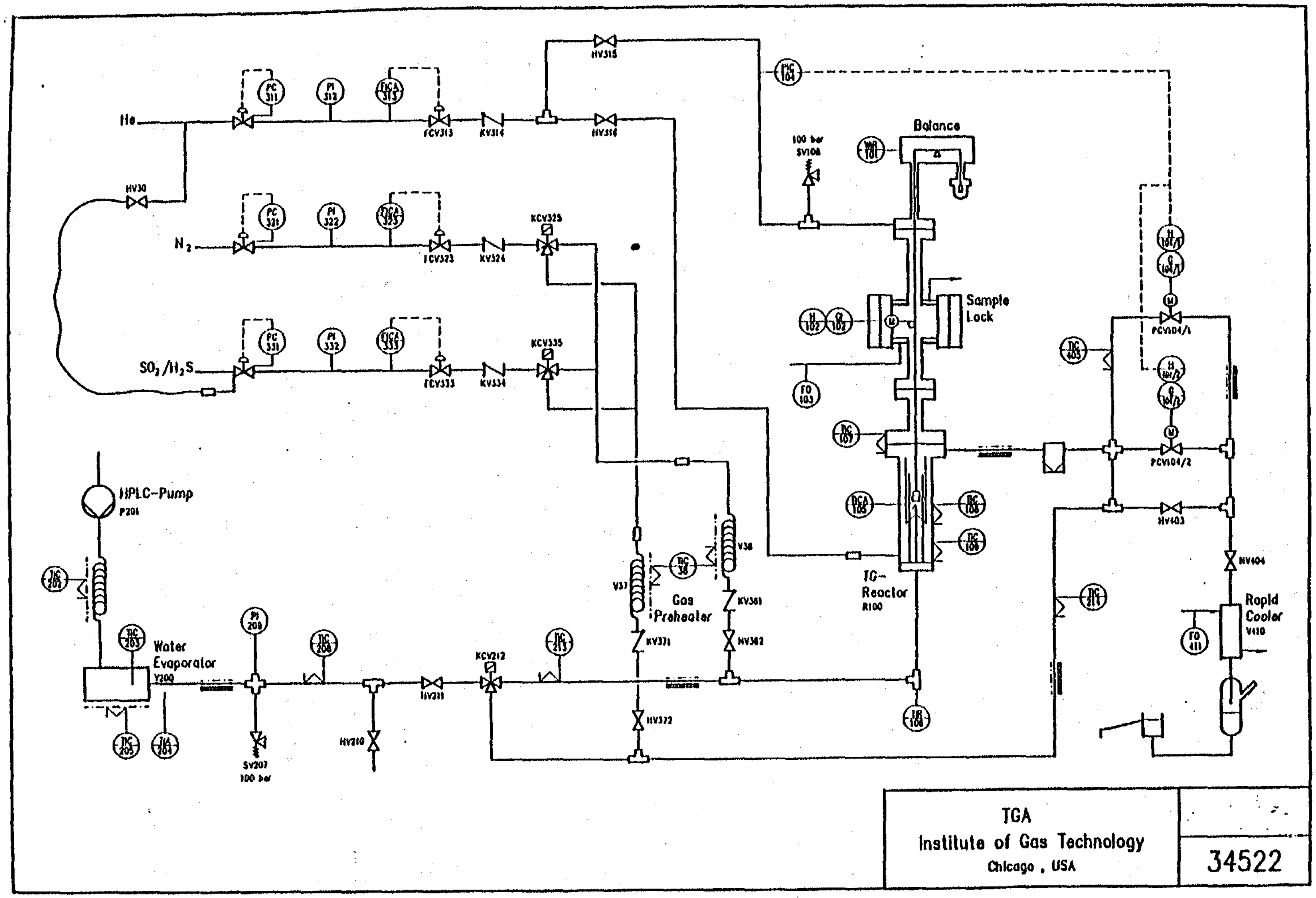

Figure 2. SCHEMATIC DIAGRAM OF THE PRESSURIZED TGA UNIT

CONCLUSIONS AND RECOMMENDATIONS

The results of the sulfidation tests conducted during this quarter are currently being analyzed. Therefore, no conclusions can be made at this time.

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