ABSTRACT

The objective of this study was 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 CO₂ partial pressure generally exceeds the equilibrium value for calcium carbonate decomposition. Therefore, calcium sulfate is produced through the reactions between SO₂ and calcium carbonate as well as the reaction between calcium sulfide and oxygen.

To achieve this objective, the rates of reaction involving SO₂ and oxygen (gaseous reactant); and calcium sulfide and calcium carbonate (solid reactants), were determined by conducting tests in a pressurized thermogravimetric analyzer (HPTGA) unit. The effects of sorbent type, sorbent particle size, reactor temperature and pressure; and O₂ as well as SO₂ partial pressures on the sulfation reactions rate were determined in this study.

The results of sulfation reaction tests conducted in this project indicate that, because of limiting CaS oxidation, the uncalcined limestone tested in this study, is not suitable for PFBC application. Half calcined dolomite is very reactive toward sulfur dioxide at PFBC operating conditions. Both calcium carbonate and magnesium oxide appear to react with SO₂ and oxygen, resulting in an overall sulfur loading of about 10% of the sorbent weight. Formation of magnesium sulfate appears to significantly contribute to pore plugging, limiting the maximum sulfur loading.
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 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 (and magnesium oxide) react 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). The rates of direct sulfidation reaction at carbonizer conditions were determined in an earlier ICCLI-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 CaCO₃), 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 was to obtain data on the rates and the extent of sulfation 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. The parametric study undertaken in this project included the effects of sorbent type (i.e. limestone or dolomite), sorbent particle size; partial pressures, as well as reactor temperature and pressure, on the sulfation reactions.

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.

In this study, a large number of tests were conducted with sulfided half-calcined dolomite and uncalcined limestone in the high pressure/high temperature thermogravimetric analyzer (HPTGA) unit at operating conditions expected to prevail in the second stage of PFBC processes.

In the parametric study, the effects of sorbent type, oxygen (1% - 10%) and sulfur dioxide (375 - 10,000 ppmv) concentration, and reactor pressure (12 - 20 atm) and temperature (750 - 900°C) on the reaction rate were determined. Sulfation tests were also conducted with different CO₂ concentrations (10 - 16%) to determine the effect of excess CO₂ on the sulfation reaction rate.

The main reactions occurring in the combustor include the reactions of calcium carbonate and magnesium oxide with SO₂ and oxygen as well as the calcium sulfided oxidation reaction --

\[ \text{CaCO}_3 + \text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{CaSO}_4 + \text{CO}_2 \]  \hspace{1cm} \text{(A)}

\[ \text{MgO} + \text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{MgSO}_4 \]  \hspace{1cm} \text{(B)}

\[ \text{CaS} + 2\text{O}_2 = \text{CaSO}_4 \]  \hspace{1cm} \text{(C)}

In order to determine the extent of SO₂ removal in the combustor, the rate of Reaction (C) was first determined in the absence of SO₂ and subtracted from the overall rate when both SO₂ and oxygen were present.

The results of this study indicate that the calcium sulfide in the partially sulfided uncalcined limestone tested, could only be sulfated to below 25%, making this sorbent unsuitable for PFBC application. However, the partially sulfided half-calcined dolomite tested was very reactive toward SO₂ and oxygen reaching 85% conversion of calcium sulfide and 10% sulfur loading (per weight of sorbent) at relatively short residence time.

The limiting temperature appears to be around 800-850°C and the overall sulfur loading appears to be lower at higher pressure. The relative selectivity toward calcium carbonate sulfation (relative to MgO) appears to improve by decreasing pressure. Formation of magnesium sulfate appears to significantly contribute to pore plugging, adversely affecting the overall sulfation reaction and limiting the maximum sulfur loading.
OBJECTIVES

The overall objective of this project was 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 CO₂ 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 as well as magnesium oxide in the combustor.

The specific objectives of this project were 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 O₂, CO₂ and SO₂ partial pressures, on the sulfation reaction rates.

3. Provide a direct comparison between the rates of sulfation reactions involving calcium-based sorbents at CO₂ 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 SO₂, unless scrubbers are used which decrease thermal efficiency and increase the cost of electricity (COE). Two technologies, Advanced Two Stage Fluidized Bed Combustion (PFBC)⁴⁻⁵, and Integrated Gasification Combined Cycle (IGCC), are being developed that can use high sulfur coals in an economical and environmentally sound manner.⁴⁻⁶ 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.⁴⁻⁷ 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:

\[
CaCO_3 = CaO + CO_2 \quad (1)
\]

H\(_2\)S is removed in the carbonizer/gasifier by reaction with uncalcined limestone, as in Reaction (2):

\[
CaCO_3 + H_2S = CaS + H_2O + CO_2 \quad (2)
\]

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

\[
CaO + H_2S = CaS + H_2O \quad (3)
\]

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\(_3\)\(^{(11)}\).
In Equation (A), $P_{CO_2}$ 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$_2$S removal will take place by Reaction (3). If the CO$_2$ partial pressure exceeds that equilibrium pressure, H$_2$S 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$_2$S 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$^{(3)}$ 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$_2$S 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 are, Abbasi$^{(14-20)}$, Borgwardt and Roache$^{(21)}$, Ruth$^{(22)}$, Squires$^{(23)}$, Kamath and Petrie$^{(24)}$, Simon and Raulins$^{(25)}$, Yen$^{(26)}$, Freund$^{(27)}$, and 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 800⁰-950⁰C, 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

<table>
<thead>
<tr>
<th>Operating Conditions</th>
<th>IGTT</th>
<th>Kelloggs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal Type</td>
<td>Pittsburgh No. 8</td>
<td>Illinois No. 6</td>
</tr>
<tr>
<td>Temperature, °F</td>
<td>1600</td>
<td>1450</td>
</tr>
<tr>
<td>Pressure, psig</td>
<td>192</td>
<td>148</td>
</tr>
<tr>
<td>Ca/S Feed Molar Ratio</td>
<td>1.75</td>
<td>1.5</td>
</tr>
<tr>
<td>Sorbent Particle Size, µm</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

**Selected Gases**

<table>
<thead>
<tr>
<th></th>
<th>IGTT</th>
<th>Kelloggs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Monoxide</td>
<td>11.04</td>
<td>15.51</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.90</td>
<td>19.35</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>12.32</td>
<td>10.34</td>
</tr>
<tr>
<td>Methane</td>
<td>6.23</td>
<td>1.30</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>0.035</td>
<td>0.01</td>
</tr>
<tr>
<td>Water Vapor</td>
<td>8.20</td>
<td>10.03</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Test No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed Temperature, °F</td>
<td>1845</td>
<td>1870</td>
<td>1860</td>
<td>1767</td>
<td>1762</td>
</tr>
<tr>
<td>Reactor Pressure, psig</td>
<td>150</td>
<td>303</td>
<td>303</td>
<td>406</td>
<td>290</td>
</tr>
<tr>
<td>Ca/S Feed Molar Ratio</td>
<td>2.60</td>
<td>1.72</td>
<td>2.25</td>
<td>4.21</td>
<td>3.80</td>
</tr>
<tr>
<td>Sulfur Capture, %</td>
<td>95.9</td>
<td>84.9</td>
<td>74.4</td>
<td>93.4</td>
<td>103.7</td>
</tr>
</tbody>
</table>

**Reactor Gas Composition, Vol %**

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Monoxide</td>
<td>10.54</td>
<td>4.31</td>
<td>6.62</td>
<td>1.90</td>
<td>3.53</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>12.13</td>
<td>8.34</td>
<td>10.78</td>
<td>4.92</td>
<td>7.35</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>13.05</td>
<td>12.53</td>
<td>13.42</td>
<td>11.35</td>
<td>11.95</td>
</tr>
<tr>
<td>Methane</td>
<td>2.47</td>
<td>1.55</td>
<td>2.19</td>
<td>1.33</td>
<td>1.99</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>38.43</td>
<td>36.45</td>
<td>33.87</td>
<td>37.26</td>
<td>36.34</td>
</tr>
<tr>
<td>Hydrogen Sulfide</td>
<td>0.11</td>
<td>0.18</td>
<td>0.22</td>
<td>0.16</td>
<td>0.08</td>
</tr>
<tr>
<td>Water Vapor</td>
<td>23.27</td>
<td>36.64</td>
<td>32.90</td>
<td>43.08</td>
<td>38.71</td>
</tr>
</tbody>
</table>
The mathematical models used for estimation of sulfur capture in the carbonizer\(^{2,3}\) are based on either the extrapolation of the available data on this reaction at lower temperature and atmospheric pressure, or calculated from thermodynamic equilibrium.

The reactivity of calcium-based sorbents (limestone and dolomite) toward \(\text{H}_2\text{S}\) in the direct sulfidation reaction [Reaction (2)] at the carbonizer operating conditions were determined in an earlier ICCI-funded project (Ref. No. 93-01/2.1A-1M). 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) --

\[
\text{CaCO}_3 + \text{SO}_2 + 1/2\text{O}_2 = \text{CaSO}_4 + \text{CO}_2
\]

\[
\text{MgO} + \text{SO}_2 + 1/2\text{O}_2 = \text{MgSO}_4
\]

\[
\text{CaS} + 2\text{O}_2 = \text{CaSO}_4
\]

A systematic study of the complex desulfurization reactions occurring in 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.\(^{36-37}\)

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 systems. Snow et al.\(^{38}\) showed that uncalcined limestone particles (3-20 \(\mu\)m diameter) were sulfated at a rate that was higher than that for the corresponding calcined particles. The higher rate of direct sulfation reaction is believed to be due to the more porous nature of the sulfated surface. It was hypothesized that the porosity was created by the outflow of \(\text{CO}_2\) through the product sulfate layer and thereby improved the accessibility of \(\text{SO}_2\) and oxygen to the reacting surface. A similar result has been reported by Lisa et al.\(^{39}\)
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 focused 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 included determination of the effects of sorbent type (i.e. limestone or dolomite), sorbent particle size; CO₂, O₂, and SO₂ partial pressures, as well as reaction temperature and pressure, on sulfation reactions [Reactions (4), (5), and (6)].

EXPERIMENTAL PROCEDURE

This project is divided into the following tasks:

Task 1. Sorbent Preparation and Characterization

Task 2. Sulfation Reactions Tests

Task 3. Analyses of Sulfation Reactions Data

Because the equilibrium partial pressure of CO₂ 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 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 150, 300, and 600 µm. The bulk chemical composition of the sorbents as determined in the previous ICCI-funded program is presented in Table 3.
Table 3. CHEMICAL ANALYSES OF SORBENTS

<table>
<thead>
<tr>
<th>Analyses, wt %</th>
<th>Limestone</th>
<th>Dolomite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>38.7</td>
<td>22.2</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.59</td>
<td>13.2</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Iron</td>
<td>0.084</td>
<td>0.11</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.05</td>
<td>0.069</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.11</td>
<td>0.3</td>
</tr>
<tr>
<td>Strontium</td>
<td>0.015</td>
<td>0.005</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>44.7</td>
<td>48.0</td>
</tr>
<tr>
<td>Oxygen (by Diff.)</td>
<td>15.251</td>
<td>15.616</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

To produce sulfided calcium-based sorbent representing discharge material from the first stage of PFBC (Carbonizer) with in-bed sulfur capture, samples of both sorbents were partially sulfided in a fluidized bed reactor. The operating conditions were selected to closely simulate the operating conditions prevailing in the carbonizer, in both calcining and non-calcining regime of operation. The extent of sulfidation in these samples are given in the section under “RESULTS AND DISCUSSION”.

Task 2. Sulfation Reaction Tests

The objective of this task was 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 (1% - 10%) and sulfur dioxide (375 - 10,000 ppm) concentration, and reactor pressure (12 - 20 atm) and temperature (750 - 900°C) on the reaction rate were determined. Sulfation tests were also conducted with different CO₂ concentrations (10 - 16%) to determine the effect of excess CO₂ on the sulfation reaction rate.

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 was to provide guidelines for estimation of the extent of sulfur removal and the composition of the final solid waste material in the second stage (combusitor) of the advanced two-stage PFBC at different operating conditions.

The reaction rate data obtained in Task 2 at the prevailing PFBC operating conditions, were used to make a more accurate prediction to the extent of desulfurization and the composition of the solid waste products in the advanced two-stage PFBC processes.

**RESULTS AND DISCUSSION**

The results of chemical analyses of the partially sulfided sorbents are given in Table 4. These samples, which were used as feed material for the sulfation tests, were screened into three particle sizes with average diameters of .015, .03, and .06 cm. The operating condition for preparations of the partially sulfided sorbents were selected to closely simulate the operating condition in the carbonizer. The solid residence time were selected to achieve 25 to 50% sulfidation representing Ca/s ratio of 2 to 4 in the carbonizer.

The main reactions occurring in the combustor include the reactions of calcium carbonate and magnesium oxide with SO₂ and oxygen as well as the calcium sulfided oxidation reaction --

\[
\text{CaCO}_3 + \text{SO}_2 + 1/2\text{O}_2 = \text{CaSO}_4 + \text{CO}_2 \quad (4)
\]

\[
\text{MgO} + \text{SO}_2 + 1/2\text{O}_2 = \text{MgSO}_4 \quad (5)
\]

\[
\text{CaS} + 2\text{O}_2 = \text{CaSO}_4 \quad (6)
\]

To determine the extent of SO₂ removal in the combustor, the rate of CaS oxidation reaction was determined by reacting the partially sulfided sorbents with a reactant gas mixture that did not contain SO₂. The range of operating parameters used during calcium sulfide oxidation [i.e. Reaction (6)] are given in Table 5.

The rate of sulfation reaction [i.e., Reaction (6)] at the baseline condition is shown in Figure 3 in terms of calcium sulfide conversion versus time. The solid line in Figure 3 represents the best fit to the experimental data. Because of the number of data points collected during each test is large, the equations representing the best fit are used when comparing the results of different tests. To determine the magnitude of random variation
in the results obtained in the HPTGA experiments, a series of independent tests were conducted at baseline condition. The results of these tests indicate that the rate of reaction can be determined with excellent accuracy and repeatability. To eliminate the effect of inter-particle diffusion, and “Starvation Condition”, a series of tests were conducted with the sample weight ranging from 5 to 50 mg. The rates of reaction obtained in this series of tests were very similar, indicating that the sample weight did not have any effect on the rate of sulfation reaction.

Table 4. CHEMICAL COMPOSITION OF SULFIDED SORBENTS

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>State of Calcination</th>
<th>Extent of Sulfidation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite</td>
<td>Calcined</td>
<td>50.1</td>
</tr>
<tr>
<td>Dolomite</td>
<td>Half-Calcined</td>
<td>41.0</td>
</tr>
<tr>
<td>Limestone</td>
<td>Calcined</td>
<td>22.9</td>
</tr>
<tr>
<td>Limestone</td>
<td>Uncalcined</td>
<td>21.2</td>
</tr>
</tbody>
</table>

Table 5. RANGES OPERATING CONDITIONS FOR CaS OXIDATION

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorbent</td>
<td>Sulfided half-calcined dolomite</td>
</tr>
<tr>
<td>Pressure</td>
<td>12-20 atm</td>
</tr>
<tr>
<td>Temperature</td>
<td>750-900°C</td>
</tr>
<tr>
<td>Particle size</td>
<td>.015-.06 cm</td>
</tr>
<tr>
<td>CO₂</td>
<td>12-16%</td>
</tr>
<tr>
<td>O₂</td>
<td>1-10%</td>
</tr>
<tr>
<td>SO₂</td>
<td>none</td>
</tr>
</tbody>
</table>

The effect of reaction temperature on the rate of sulfation reaction is shown in Figure 4, indicating that the reaction rate is very sensitive to the reaction temperature (i.e. high activation energy). The extent of conversion at 900°C appears to level off at lower value compared to results obtained in the test at 850°C, suggesting that a fraction of calcium sulfide may have been converted to SO₂ through Reaction (6). The effect of oxygen concentration is shown in Figure 5, indicating that although the rate of reaction generally increases with increasing oxygen concentration, the effect is more pronounced at higher oxygen concentration (i.e. 10%). This may be due to the extreme exothermic nature of the reaction which can lead to a small increase in the temperature at higher reaction rate. The effect of CO₂ concentration on the reaction rate is shown in Figure 6. The results indicate that the reaction rate is generally lower at higher CO₂ concentration. This decrease in the reaction rate may be attributed to lower rate of outward diffusion of CO₂ produced during the course of the reaction.
The effect of sorbent particle size on the reaction rate at two levels of CO₂ partial pressure are given in Figures 7 and 8, indicating that the rate of reaction increases with decreasing sorbent particle size.

The effect of overall pressure is shown in Figure 9, suggesting that the reaction rate increases with increasing reactor pressure. This generally indicates that the positive effect of higher oxygen partial pressure on the reaction rate is more pronounced than the adverse effect of higher CO₂ partial pressure. Because the effect of CO₂ particle pressure is believed to be due to diffusion, which is a first order dependence, it may be concluded that the dependence of the reaction rate on the oxygen concentration is higher than first order.

The extent of CaS oxidation in the uncalcined limestone is shown in figure 10 indicating that despite the low sulfide content of the sorbent, the extent of oxidation of calcium sulfide in uncalcined limestone is limited to below 25%. Because of the expected high fraction of calcium sulfide in the spent sorbent after the combustion stage, limestone based spent sorbents will not be acceptable material for disposal in the landfill. Therefore, this sorbent is not suitable for PFBC application. Based on the results of calcium sulfide oxidation in limestone, no further tests were performed with this sorbent.

To determine the extent of sulfation reactions involving SO₂, it was assumed that because of high concentration of oxygen (relative to SO₂), the rate of CaS oxidation is independent of SO₂ concentration. Under this condition, the rate of sulfation reaction involving SO₂ can be determined by subtracting the sample weight gain corresponding to CaS oxidation under identical operating conditions (except for the presence of SO₂).

Because the magnitude of weight gain per mole of sulfur absorbed during sulfation of calcium carbonate is different from that of magnesium oxide, the sulfur loading in the sulfated samples were determined by analyzing the reacted samples and performing a sulfur balance on the feed and product solids.

The ranges of operating conditions for the SO₂ absorption tests were the same as those presented in Table 5 for CaS oxidation except for SO₂ which was in the range of 500 to 10,000 ppmv.

The effect of temperature on SO₂ absorption at SO₂ concentrations of 2000 and 5000 ppmv are shown in Figures 11 and 12 respectively. The results indicate that the rate of SO₂ absorption generally increases with increasing temperature. However, at high SO₂ concentration and temperature (i.e. SO₂ = 5000 ppm and T = 850°C), although the initial sulfur loading increases with increasing SO₂ concentration, the rate levels off quickly. This may be due to formation of higher levels magnesium sulfate plugging the pore, preventing SO₂ to reach unreacted calcium carbonate.

The sulfur loading after 15 minutes of reaction time for all three particle sizes at different CO₂ and SO₂ concentration are presented in Figure 13. The results indicate that at 2000 ppmv of SO₂, the sulfur loading decreases with increasing particle size. However, at 5000
ppmv SO$_2$, the rate sulfur absorption for fine particles is lower than of medium size particles. The sulfur loading for coarse and medium size particles increases with CO$_2$ partial pressure while the loading is lower for small particles. These phenomena may be attributed to the changes in the relative conversion of MgO and CaCO$_3$ at different operating conditions. For example, the rate of sulfation reaction for the fine particles is initially higher at higher CO$_2$ concentration, but levels off quickly as shown in Figure 14. Figure 15 shows that for the medium size particle, the dependence of the sulfur loading on CO$_2$ concentration is exactly apposite of the phenomena observed with the “fine” particles. A similar trend was observed for coarse particles.

The effect of overall pressure on sulfur loading in combustor is shown in Figure 16, indicating that the overall rate of SO$_2$ absorption decreases with increasing combustor pressure. The effect of oxygen and SO$_2$ concentration on SO$_2$ absorption are shown in Figures 17 and 18 respectively, indicating that the overall SO$_2$ absorption rate increases with both oxygen and SO$_2$ concentrations.

Because of the two competing sulfation reactions, it is not possible to determine the extent of conversion in each reaction from a single TGA experiment. However, qualitative measure of the relative extent of calcium carbonate and magnesium oxide sulfation can be described by a relative selectivity index which is a normalized ratio of the sulfur loading in the combustor to the weight gain observed during the TGA experiment. This stems from the fact that for each gram mole of calcium carbonate sulfate, the net weight gain in the sulfation reaction will be 36 gram [i.e. $136(MW_{CaSO_4}) - 100(MW_{CaCO_3}) = 36$] while the weight gain per gram mole of magnesium oxide is 80 [i.e. $120(MW_{MgSO_4}) - 40(MW_{MgO}) = 80$]. Therefore, higher values of relative selectivity index represent higher calcium carbonate conversion relative to magnesium oxide conversion.

The relative selectivity index for the six tests conducted for effect of temperature are shown in Figure 19. The result indicates that selectivity toward calcium increases with increasing temperature. However, at 850°C at SO$_2$ concentration of 5000 ppmv, the relative selectivity is lower than that of 800°C. Lower relative selectivity and sulfur loading (see Figure 12) indicates that formation of higher levels of magnesium sulfate may plug the pores preventing calcium carbonate from reaction with SO$_2$. This is consistent with the fact that generally, the extent of conversion of calcium carbonate is expected to be higher than that of magnesium oxide, that is much deeper penetration of SO$_2$ is required to convert a high fraction of calcium carbonate to calcium sulfate. Also, there is a higher probability of pore plugging with magnesium oxide sulfation because of formation of much larger molecules, while in the case of calcium carbonate, because of the release of carbon dioxide, probability of pore plugging is much lower.

Figure 20 shows the relative selectivity at different particle sizes for two levels of CO$_2$ and SO$_2$ concentrations. The results indicate that the relative selectivity increases with SO$_2$ concentration. However, the relative selectivity increases with increasing CO$_2$ partial pressure for large particles (dp=.06 cm) and decreases for the small particles. Lower relative selectivity and sulfur loading at high CO$_2$ partial pressure again indicates higher
conversion of magnesium oxide play a role in limiting the overall SO$_2$ absorption. The dependence of relative selectivity on the particle size appears to be mixed. While at the lower SO$_2$ and CO$_2$ levels (i.e. CO$_2$ = 10% and SO$_2$ = 2000 ppmv), the relative selectivity increases with decreasing particle size, at high levels of both gas compounds (i.e. CO$_2$ = 16% and SO$_2$ = 5000 ppmv), the opposite appears to be true. This may be attributed that the rate of magnesium oxide sulfation is not affected by CO$_2$ partial pressure, while in the case of calcium carbonate the sulfation rate is adversely affected by higher CO$_2$ concentrations. Therefore, the relative difference in the speed of the two reactions at different particle sizes combined with the possible plugging potential of the magnesium sulfate can lead to the mixed results that are shown in Figure 20.

The relative selectivity as a function of reaction pressure, oxygen and SO$_2$ concentration are shown in Figures 21 through 23, respectively, indicating that the relative selectivity decreases with increasing total pressure and increases with increasing oxygen or SO$_2$ concentration. Lower relative selectivity at higher pressure indicates that the order of sulfation reactions with respect to SO$_2$ and oxygen is higher for magnesium oxide sulfation compared to that of calcium carbonate.

Because of the complexity of the competing reactions, in order to determine the rate of individual sulfation reactions, it is necessary to determine the extent of sulfation of each reaction at different reaction times by combining the weight gain with chemical analyses of the reacted solids. However, this procedure is very laborious and not cost effective. Also, determination of the rate of individual compounds by using pure compounds, because of differences in the pore structure, is not applicable to actual sorbents.

In order to estimate the extent of SO$_2$ removal in the combustor, the reaction rate was approximated by a first order rate expression. The reaction rate constant as assumed to be independent of oxygen concentration and first order with respect to SO$_2$ concentration. The first order rate expression used along with the uniform fluidized-bed model to estimate the extent of H$_2$S removal in a pilot combustor unit. The overall reaction rate constant in the fluidized bed was described by:

$$\frac{1}{k_{\text{overall}}} = \frac{1}{k_r} + \frac{1}{k_d}$$

(7)

where the $k_{\text{overall}}$ is the overall rate constant, $k_r$ is the chemical reaction rate constant, and $1/k_d$ represents the resistance due to mass transfer in the fluidized bed.

The pilot scale combustor was assumed to be 25 cm in diameter, operating at 800°C and 12 bar. The coal char feed rate and SO$_2$ concentration in the combustor (without the sorbent) was assumed at 227 kg/hr and 5000 ppmv respectively. The results of mathematical simulation of this unit is presented in Figure 24 indicating that at a calcium-to-sulfur ratio of about 2, SO$_2$ can essentially be removed from the combustor with a reactor bed height of about 5 meters. However, the results also suggest that the extent of sulfur removal is very sensitive to Ca/S ratio, and the bed height.
CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be made from the work performed in this project:

- The rate of CaS oxidation involving half calcined dolomite and oxygen increases with:
  - increasing temperatures up to 850°C
  - decreasing particle size
  - increasing oxygen concentration
  - decreasing CO₂ partial pressure
  - increasing reactor pressure

- The rate of CaS oxidation reaction is very fast at temperatures above 850°C which rapidly increases with increasing temperature, achieving more than 85% conversion in less than a few minutes. The reaction appears to continue to completion, however, above 85% conversion, the rate of reaction appears to be low, requiring long residence time to reach complete conversion. Therefore, concentration of the residual calcium sulfide in the solid wastes from the combustor stage is expected to be low.

- The calcium sulfide in the partially sulfided uncalkined limestone tested in this project can only be sulfated to below 25%, making this limestone unsuitable for carbonizer application.

- The rate and the extent of sulfation reaction involving partially sulfided half-calcined dolomite and SO₂ generally increases with:
  - increasing temperature
  - decreasing CO₂ concentration
  - increasing O₂ and SO₂ concentration
  - decreasing pressure

- Because of competing parallel sulfation reactions involving calcium carbonate and magnesium oxide, the extent of conversion in each reaction cannot be determined. The maximum sulfur loading appears to be about 10% of the sorbent weight.

- The overall rate of reaction between half calcined dolomite and SO₂ and oxygen is relatively high, resulting in high desulfurization efficiency in the combustor.

- Formation of magnesium sulfate appears to significantly contribute to pore plugging, limiting the maximum sulfur loading.

- The relative selectivity of sulfation reaction (toward calcium carbonate) appears to increase with:
  - increasing temperature
  - decreasing pressure
  - increasing O₂ and SO₂ concentration.
REFERENCES CITED


5. Rehmat, A. and Goyal, A., 1987, Pressurized Fluidized-Bed Combustion (PFBC): Second-Generation Systems Research and Development. Subtask: Carbonizer:In the HPTGA experiments, to eliminate interparticle diffusion and changes in the reactant gas composition, the amount of sample used are very small (i.e., 2-10 mg), resulting in Model. Final Report to Foster Wheeler Development Corp., under U.S. DOE Contract No.: DE-AC21-86MC231023, November.


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Second Generation ← → First Generation

- Topping Combustion
  - Particulate Removal
    - LBTU Fuel Gas
  - Carbonization (Carbonizer)
    - Char Sorbent
- Steam Turbine
  - Steam Generation (HHSG)
  - Steam Turbine
  - Particulate Removal
    - Flue Gas
  - Char Combustion (CPFBC)
    - Air Ash
  - Steam Generation (FBIE)
    - Air Ash

Figure 1. SCHEMATIC DIAGRAM OF AN ADVANCED TWO-STAGE PFBC PLANT (1)
Figure 3. SULFATION REACTION RATE AT BASELINE CONDITIONS.

Figure 4. EFFECT OF TEMPERATURE ON THE SULFATION REACTION RATE.
Figure 5. EFFECT OF OXYGEN CONCENTRATION ON THE SULFATION REACTION RATE.

Figure 6. EFFECT OF CARBON DIOXIDE CONCENTRATION ON THE SULFATION REACTION RATE.
Figure 7. EFFECT OF SORBENT PARTICLE SIZE ON THE SULFATION REACTION RATE (16% CO₂).

Figure 8. EFFECT OF SORBENT PARTICLE SIZE ON THE SULFATION REACTION RATE (10% CO₂).
Figure 9. EFFECT OF REACTION PRESSURE ON THE SULFATION REACTION RATE.

Figure 10. EFFECT OF LIMESTONE PARTICLE SIZE ON THE SULFATION REACTION RATE (16% CO$_2$).
Figure 11. EFFECT OF TEMPERATURE ON THE SULFUR LOADING (2000 ppmv SULFUR DIOXIDE).

Figure 12. EFFECT OF TEMPERATURE ON THE SULFUR LOADING (5000 ppmv SULFUR DIOXIDE).
Figure 13. EFFECT OF CARBON DIOXIDE CONCENTRATION ON THE SULFUR LOADING.

Figure 14. EFFECT OF CARBON DIOXIDE CONCENTRATION FOR SMALL SIZE PARTICLES.
Figure 15. EFFECT OF CARBON DIOXIDE CONCENTRATION ON THE SULFUR LOADING FOR MEDIUM SIZE PARTICLES.

Figure 16. EFFECT OF REACTION PRESSURE ON THE SULFUR LOADING.
Figure 17. EFFECT OF OXYGEN CONCENTRATION ON THE SULFUR LOADING.

Figure 18. EFFECT OF SULFUR DIOXIDE CONCENTRATION ON THE SULFUR LOADING.
Figure 19. EFFECT OF TEMPERATURE ON THE RELATIVE SELECTIVITY.

Figure 20. EFFECT OF CARBON DIOXIDE CONCENTRATION ON THE RELATIVE SELECTIVITY.
Figure 21. EFFECT OF REACTION PRESSURE ON THE RELATIVE SELECTIVITY.

Figure 22. EFFECT OF OXYGEN CONCENTRATION ON RELATIVE SELECTIVITY.
Figure 23. EFFECT OF OXYGEN CONCENTRATION ON RELATIVE SELECTIVITY.

Figure 24. EFFECT OF (Ca & Mg)/S RATIO ON THE PREDICTED SULFUR DIOXIDE CONCENTRATION PROFILE IN THE FLUIDIZED BED COMBUSTOR.
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
Principal Investigator: Javad Abbasian, Institute of Gas Technology
Other Investigators: Andy Hill and James, R. Wangerow, Institute of Gas Technology
Project Manager: Franklin I. Honea, Illinois Clean Coal Institute

COMMENTS

The project was completed on schedule and all objectives were achieved.
## Expenditures - Exhibit II

**Cumulative Projected and Estimated Expenditures by Quarter**

<table>
<thead>
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<th>Quarter*</th>
<th>Types of Cost</th>
<th>Direct Labor</th>
<th>Fringe Benefits</th>
<th>Materials &amp; Supplies</th>
<th>Travel</th>
<th>Major Equipment</th>
<th>Other Direct Costs</th>
<th>Indirect Costs</th>
<th>Total</th>
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<tr>
<td>Sept. 1, 1994 to Nov. 30, 1994</td>
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<td>926.3</td>
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<td></td>
<td>500</td>
<td>1,000</td>
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<td></td>
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*Cumulative by Quarter*
CUMULATIVE COSTS BY QUARTER - EXHIBIT C

SULFUR REMOVAL IN ADVANCED TWO STAGE PRESSURIZED FLUIDIZED BED COMBUSTION

(In Thousands)

Months and Quarters

O = Projected Expenditures $119,184

A = Actual Expenditures $119,755

Total ICCI Award $119,184
A. Sorbent Preparation and Characterization

B. Sulfation Reaction Tests

C. Analysis of Reaction Rate Data

D. Preparation of Technical Reports

E. Preparation of Project Management Report

SCHEDULE OF PROJECT MILESTONES