Project Title: Stabilization of Solid Wastes From Coal Gasification
ICCI Project Number: 90-1/5.3A-1M
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ABSTRACT

The objective of this investigation was to determine the effects of reactor pressure and temperature on the conversion of calcium sulfide in solid waste from high-pressure coal gasifiers (that utilize calcium-based sorbent for in-bed sulfur capture) to stable and environmentally acceptable solids products for final disposal.

To achieve this objective, selected samples of partially sulfided calcium-based sorbents were reacted with oxygen at a variety of operating conditions. The solid products were then tested for their suitability for disposal in landfills. The parameters that were studied in this investigation included sorbent type, sorbent particle size, reactor pressure, and reactor temperature.

Three calcium-based sorbents were selected for testing in this program which included a limestone, a dolomite, and a dolomitic limestone. Two sizes from each sorbent were used which included coarse particles (dp = 0.07 cm) and fine particles (dp = 0.02 cm). These sorbents were sulfided in an ambient-pressure quartz fluidized-bed reactor at 1650°F. The residence times in these tests were chosen to achieve a 50% sulfidation level. The partially sulfided sorbents were oxidized in the fluidized-bed reactor at ambient pressure using a reactant gas containing 5% oxygen. The effects of oxidation pressure on the conversion of the calcium sulfide were determined by conducting tests in a pressurized thermogravimetric analyzer (TGA) reactor at 1500°F at pressures of 100 and 300 psia.

The results of these tests indicate that the overall conversion of CaS increases with increasing temperature. However, calcium sulfide conversion to calcium sulfate decreases with increasing temperature while conversion to SO₂ significantly increases as temperature increases above 1500°F. The oxidation pressure did not appear to have any effect on the conversion of calcium sulfide at 1500°F. The results of Scanning Electron Microscopy (SEM) analyses of the oxidized sorbent indicate that both sulfidation and sulfation reaction can be described by a shrinking core model and that the sulfur release during oxidation appear to occur through reaction between CaS and CaSO₄ at the interface of these compounds. The results of EPA proposed sulfur leaching tests on the oxidized sorbents indicate that the amount of sulfur released is an order of magnitude below the EPA limit for all the stabilized samples, making them suitable for disposal in landfills.

(This project is funded by the Illinois Department of Energy and Natural Resources as part of its cost-shared program with the U. S. Department of Energy.)
EXECUTIVE SUMMARY

The objective of this investigation was to determine the effects of reactor pressure and temperature on the conversion of solid wastes (calcium sulfide) from coal gasifiers (that utilize calcium-based sorbents for sulfur capture) to stable and environmentally acceptable solid products for final disposal.

The sulfur compounds present in coal are converted to hydrogen sulfide when the coal is gasified. To comply with the New Source Performance Standards (NSPS), a high fraction of the sulfur must be removed from the gas stream. Calcium-based sorbents such as limestone and dolomite are among the prime candidates for in-bed capture of sulfur from the fuel gas. In Integrated Coal Gasification Combined Cycle (IGCC) Systems, where very low levels of $\text{H}_2\text{S}$ in fuel gas are required, more than 90% of the $\text{H}_2\text{S}$ in the fuel gas can be removed in the gasifier by using calcium-based sorbents such as limestone or dolomite. An external hot gas cleanup system using regenerable mixed metal oxides such as zinc ferrite is then used to further reduce the $\text{H}_2\text{S}$ content of the fuel gas to acceptable levels for IGCC application.

The removal of sulfur in the gasifier takes place through the reaction of hydrogen sulfide with calcium oxide or calcium carbonate, which produces calcium sulfide. This compound is not stable, and therefore, is not suitable for direct disposal in landfills. However, calcium sulfide can be further reacted with oxygen to produce calcium sulfate, which is a stable and environmentally acceptable compound for disposal.

Three calcium-based sorbents were tested in this study. These sorbents are the same as those used in a previous study sponsored by CRSC (Subgrant 89-4). The calcium carbonate content of these sorbents were about 100% (limestone), 50% (dolomite) and 75% (dolomitic limestone). The sorbents were crushed and screened into narrow particle size ranges. Two cuts from each sorbent were selected for this investigation which included fine particles (-60+80 mesh) with an average particle diameter of 0.02 cm and coarse particles (-20+30 mesh) with an average particle diameter of 0.07 cm.

Six sulfidation tests were conducted in a 3-inch-diameter quartz fluidized-bed reactor. Samples of both cuts from each sorbent were used in these tests. The tests were designed to produce partially sulfided sorbents with sulfidation levels of about 50%. The partially sulfided sorbents were analyzed and their calcium and sulfur content were determined. The extent of sulfidation for all the six samples were very close to the desired 50% level.

A total of 12 tests were conducted in a pressurized TGA reactor to study the effect of pressure on the extent of sulfation of partially sulfided sorbents. All three sorbents in both particle sizes were sulfated at 1500°F at pressures of 100 and 300 psia. The results of these tests indicate that reactor pressure does not effect the rate and the extent of sulfation reaction. The rate and the extent of sulfation is generally consistent with the ambient pressure sulfation data obtained previously in a CRSC funded project (Subgrant 89-4).

A total of 26 tests were conducted in this program to determine the effect of reaction temperature on the stabilization of partially sulfided Ca-based sorbents. These tests were conducted in a 2-inch-diameter quartz fluidized-
bed reactor with the three sorbents in both particle sizes in the temperature range of 1500° to 1800°F. The data obtained in these tests indicate that the overall CaS conversion increases with increasing temperature. However, calcium sulfide conversion to calcium sulfate decreases with increasing temperature while conversion to SO₂ significantly increases as temperature increases.

The results of Scanning Electron Microscopy (SEM) analyses of the oxidized sorbent indicate that both sulfidation and sulfation reaction can be described by a shrinking core model and that the sulfur release during oxidation appears to occur through reaction between CaS and CaSO₄ at the interface of these compounds.

The results of EPA proposed sulfur leaching tests on the stabilized sorbents indicate that the amount of sulfur released is an order of magnitude below the EPA limit for all the stabilized samples, making them suitable for disposal in landfills.
OBJECTIVES

The overall objective of this investigation is to determine the effects of reactor pressure and temperature on the conversion of solid wastes (calcium sulfide) from coal gasifiers (that utilize limestone or dolomite for sulfur capture) to stable and environmentally acceptable solid products for final disposal.

The program goals were specifically directed toward the waste management, research priority 5.3A: Studies Related to Utilization of Waste Materials. The program was targeted toward the determination of the operating window (i.e., temperature and pressure) that would lead to production of stable and acceptable solid wastes for disposal in landfills.

The specific objectives of the program were to:

1. Obtain experimental data on stabilization of three calcium-based sorbents at different temperatures.
2. Obtain experimental data on stabilization of the three calcium-based sorbents at different pressures.
3. Conduct Scanning Electron Microscopy (SEM) tests on sulfated sorbents to determine the extent of sintering and to determine the composition of different layers of the cross section of the sorbents.
4. Conduct sulfur leaching tests with stabilized sulfided sorbents to determine their suitability as the end product (for disposal) from coal gasification processes that use calcium-based sorbents as sulfur capture media.

INTRODUCTION AND BACKGROUND

The market-share of Illinois high-sulfur coal can be expanded to industrial users as well as power plants if the coal can be used in an environmentally acceptable manner with minimum gas cleanup costs. For example, an integrated coal gasification/combined-cycle power plant offers the potential for both lower cost power and lower emissions than coal-fired plants with flue gas desulfurization for power generation. An attractive system for coal gasification is one in which high-sulfur coal is gasified; sulfur in coal is removed from the fuel gas and is retained within the gasifier with ash, and solid wastes containing sulfur compounds are disposed in an environmentally acceptable manner.

The sulfur compounds present in coal are converted to hydrogen sulfide when the coal is gasified. To comply with the New Source Performance Standards (NSPS), a high fraction of the sulfur must be removed from the gas stream. One approach for removing sulfur compounds from the fuel gas is the use of calcium-based sorbents, such as limestone and dolomite in the gasifier. In such processes, limestone or dolomite react with the sulfur compounds (mainly \( \text{H}_2\text{S} \)) to significantly reduce the sulfur content of the fuel gas (see Figure 1). For IGCC application, where very low levels of \( \text{H}_2\text{S} \) in the fuel gas
GASIFICATION AND IN SITU DESULFURIZATION SECTION

COAL GASIFICATION → PRODUCT GAS CONTAINING H₂S

\[ \text{CaCO}_3 \cdot \text{MgCO}_3 \rightarrow \text{CaO} + \text{MgO} + 2\text{CO}_2 \]

\[ \text{CaO} + \text{H}_2\text{S} \rightarrow \text{CaS} + \text{H}_2\text{O} \]

SULFATION SECTION

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

Figure 1. COAL GASIFICATION REACTOR WITH IN-SITU SULFUR REMOVAL
are required, regenerable mixed metal oxide sorbents can be used to further reduce the H₂S content of the fuel gas to acceptable levels for such applications.

The solid wastes produced from the reactions of calcium-based sorbents with hydrogen sulfide in the fuel gas, contain calcium sulfide which is unstable and has the tendency to decompose when it contacts moisture in the air, releasing hydrogen sulfide to the atmosphere. To dispose the solid waste products in an environmentally acceptable manner, calcium sulfide can be converted to stable calcium sulfate through reaction with oxygen (air) --

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

Researchers in the field of chemical reactions related to sulfur capture\(^{(1-12)}\) have studied the reaction of calcium-based sorbents with hydrogen sulfide. However, the conversion of calcium sulfide to stable calcium sulfate has not been sufficiently addressed in the literature. The experimental data obtained by the principal investigator of this project in a previous CRSC funded project (under Subgrant 89-04) indicated that the maximum level of conversion in Reaction (A) depends on the sorbent type (i.e., limestone or dolomite), sorbent particle size, and the level of sulfidation of the sorbent prior to sulfation reaction.\(^{(13)}\) Figure 2 shows that for coarse sorbent particles (dp = 0.07 cm), the maximum level of conversion in Reaction (A) increases with increasing magnesium content of the sorbent, as well as increasing Ca/S ratio during desulfurization. Figure 3 shows similar results for smaller sorbent particles (dp = 0.02 cm). Comparison of the data presented in Figures 2 and 3 indicates that calcium sulfide in sulfided dolomite particles can be completely converted to stable calcium sulfate as long as the calcium to sulfur ratio in the gasifier is higher than 2. However, in the case of limestone and dolomitic limestone, in order to achieve high levels of conversion, very fine particles and a relatively high Ca/S ratio should be used.

Lower levels of sulfation in limestone are probably due to formation of large calcium sulfate molecules on the outer layer of the sorbent particles and the consequent blocking of the diffusion of oxygen to the interior of the particles. This results in a sorbent particle that is composed of calcium sulfide on the inside surrounded by a layer of calcium sulfate. On the other hand, the magnesium oxide in the dolomite does not react with hydrogen sulfide which keeps the pore size of the sorbent particle open for diffusion of oxygen during the oxidation resulting in a uniform calcium sulfate composition throughout the sorbent particle.

The results of EPA proposed sulfur leaching tests conducted at IGT on the stabilized sulfided Ca-based sorbents (in the previous CRSC-funded projects) indicated that the amount of sulfur released from all samples was below the EPA limit of 500 mg/kg, making the stabilized sorbents suitable for disposal. The use of limestone rather than dolomite is generally desired because the higher fraction of calcium in the limestone compared to dolomite will require utilization of a smaller quantity of the sorbent for fuel gas desulfurization and will result in a smaller quantity of solid wastes for disposal. At gasification temperatures of 1800°F to 1900°F, the sulfidation reaction is very fast. The residence time of the solid and gas stream in the gasifier, dictated by carbon conversion, is long enough for
Figure 2. THE EXTENT OF STABILIZATION OF DIFFERENT SULFIDED Ca-BASED SORBENTS (Coarse Particles)
Figure 3. THE EXTENT OF STABILIZATION OF DIFFERENT SULFIDED Ca-BASED SORBENTS (Fine Particles)
desulfurization of the fuel gas by calcium-based sorbents (limestone or dolomite). If limestone can be sulfated to acceptable solid waste product for disposal, it will be the preferred sorbent for fuel gas desulfurization, which will lead to significant reduction in the amount of solid waste from coal gasification/desulfurization processes.

In the previous CRSC program, a number of tests were conducted to determine the optimum operating temperature for Reaction (A). The results of these tests are presented in Figures 4 and 5 which indicate that the rate of reaction increases with increasing temperature up to 1500°F and is essentially constant in the temperature range of 1500°F to 1800°F. From Figure 5, it appears that the maximum level of sulfation at temperatures above 1500°F is decreasing with increasing temperature.

It should be noted that the conversion values in Figure 5 were based on the initial sulfur content of the sulfided sorbent assuming that only Reaction (A) takes place. However, the calcium sulfate produced by Reaction (A), at temperatures of interest to the overall process (1500°F-1800°F), can also react with the calcium sulfide in an apparent solid-solid reaction to release SO₂:

\[ \text{Cas} + 3\text{CaSO}_4 = 4 \text{CaO} + 4\text{SO}_2 \]  

(B)

Reaction (A) is a highly exothermic reaction (\( \Delta H_{\text{rxn}} > 350 \text{ Kcal/gmole} \)) resulting in a significant increase in the particle temperature. Reaction (B) becomes more favorable as the particle temperature increases, resulting in release of SO₂, and the reducing overall sorbent utilization. The highly exothermic nature of Reaction (A) and its effect on the reactor temperature plays a big role in the final distribution of the products.

The overall reaction for release of SO₂ can be obtained by combining Reactions (A) and (B) [i.e. \( 3(A) + (B) = 4(C) \)]:

\[ \text{Cas} + 3/2\text{O}_2 = \text{CaO} + \text{SO}_2 \]  

(C)

The familiar Reaction (D) for sulfation of calcium oxide --

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

(D)

is also a dependent reaction with regard to independent reactions (A) and (B).

\[(A) - (B) = 4(C)\]

Oxidation of calcium sulfide through Reactions (B) and (C) decreases the sulfur content of the sorbents, resulting in smaller weight gain in TGA experiments, which translate into lower calculated levels of sulfation in Reaction (A). In the cases where both Reactions (A), (B) or (C) are taking place, it is necessary to know the extent of conversion in competing reactions to determine the suitability of the solid products for disposal. In general, it may be assumed that any levels of conversion of calcium sulfide through Reaction (B) would increase the potential for producing solid products with better leaching characteristics. Any amount of SO₂ that is produced in Reaction (B) can be introduced in the gasifier where it is captured by the calcined sorbents.
Figure 4. EFFECT OF TEMPERATURE ON STABILIZATION OF SULFIDED DOLOMITE
Figure 5. EFFECT OF TEMPERATURE ON STABILIZATION OF SULFIDED DOLOMITE
Lower maximum level of conversion at temperatures higher than 1500°F, may have also been caused by sintering of the sulfided sorbents at the higher temperatures which also increases the probability of producing end products with better leaching characteristics.

A careful examination of the effects of temperature on the stabilization of sulfided solid sorbents is therefore necessary to determine the optimum temperature for the stabilization of the solid waste products. The effect of reactor pressure on the stabilization of calcium sulfide has not been reported in the literature. The overall rate of sulfation reaction at elevated pressure, depending on the reaction controlling mechanism, may be much higher than the rate of reaction at ambient pressure. This information is necessary to determine if the stabilization step should be carried out at elevated pressure, in the bottom section of the gasifier (See Figure 1); or in an external low pressure reactor.

The results of this investigation together with those obtained in the previous CRSC funded project provide the baseline information for stabilization of solid wastes.

**EXPERIMENTAL PROCEDURE**

The experiments performed in this program were carried out in a quartz fluidized-bed reactor as well as a high-pressure Thermogravimetric Analyzer (TGA) reactor. Selected samples of the calcium-based sorbents were calcined in a nitrogen atmosphere and reacted with hydrogen sulfide to produce the partially sulfided sorbents for the stabilization tests. The stabilization tests to determine the effect of temperature were also conducted in the quartz fluidized-bed reactor. The TGA reactor was used for high pressure stabilization tests.

**Preparation of Presulfided Samples**

Six sulfidation tests were conducted in a 3-inch-diameter quartz fluidized-bed reactor. Samples of both cuts from each sorbent were used in these tests. The schematic diagram of the unit is presented in Figure 6. The unit essentially consists of a quartz fluidized-bed reactor which is externally heated by two electric furnaces, equipment for feeding and measuring the flow rates of the gases, measuring and controlling the bed temperature, and monitoring the fluidized-bed pressure. The fluidized-bed distributor is made of a quartz fritted disk.

During a sulfidation test, about 750 grams of the sorbent is loaded into the fluidized-bed reactor. The bed is heated up by two electric furnaces while a stream of nitrogen flows through the reactor. The sorbent is calcined during the heat up period and is kept at 1650°F for 30 minutes. Nitrogen and hydrogen sulfide are mixed at a predetermined ratio to achieve the desired mixture composition. The flow rate of the gas mixture is set to fluidize the bed. The reactor off-gas is analyzed to determine the extent of reaction in the fluidized-bed. The data are used to determine the solid residence time needed to achieve the desired level of sulfidation. After this period, the gas is switched to nitrogen and the sample is cooled. During the test, the temperature is controlled by the temperature controller. The reactor
Figure 6. SCHEMATIC FLOW DIAGRAM OF THE QUARTZ FLUIDIZED-BED UNIT
temperature and pressure are monitored by a computer data acquisition system. The reactor off-gas passes through a filter for collection of elutriated fines and then through a liquid scrubber before being vented.

**Effect of Pressure on Stabilization of Sulfided Sorbents**

The objective of this series of tests was to determine the effect of reactor pressure on the rate of sulfation reaction and the maximum level of conversion of calcium sulfide to calcium sulfate. These tests were conducted in the high-pressure/high-temperature TGA (Figure 7) unit using a reactant gas containing 5.25% oxygen at pressures of 100 and 300 psia at 1500°F. The high pressure data obtained in this project, along with those of ambient pressure data obtained in the previous program (CRSC Subgrant 89-4) provides the necessary information for determination of the effect of pressure on the stabilization of calcium sulfide.

The high pressure TGA unit is capable of continuously weighing a sample that is undergoing reaction in a gaseous environment of desired composition at constant pressure. The temperature can be kept constant or varied at a desired rate. The sample (about 2 grams) is contained in a wire-mesh basket. The gas composition is essentially constant because of the large relative gas flow rates used with this system. In a typical test, the wire-mesh basket is initially in the upper cool 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 the inert flow gases. The reactor gas is switched to reactant gas with the desired composition. The basket is lowered into the heated section when the flow rate, temperature, pressure, and gas composition are at the desired level. The basket's weight is continuously recorded while it is in the heated reaction zone. The test is terminated when the basket weight reaches a constant value (that is, no weight loss or gain).

To obtain the desired gas composition in the reactor, the reactant gas (air) is diluted with an inert gas (nitrogen) at a predetermined ratio before the mixture is introduced into the reactor. The flow rates of the two streams are controlled by two mass flow controllers. The sample temperatures are measured by four thermocouples located alongside of the basket at different elevations. The radial distance of these thermocouples from the basket is about 1/4-inch. The flow rates, sample temperature, sample weight, and the reactor pressure are continuously monitored by a computer-based data acquisition system.

A total of 12 tests were conducted in this project to study the effect of pressure on the extent of sulfation of partially sulfided sorbent. All three sorbents in both particle sizes were sulfated at 1500°F at pressures of 100 and 300 psia.

**Effect of Temperature on Stabilization of Sulfided Sorbents**

The objective of this series of tests was to determine the optimum operating temperature for the conversion of calcium sulfide to environmentally stable products for disposal. A total of 26 tests were conducted in a 2-inch-diameter fluidized-bed reactor to study the effect of temperature on stabilization of sulfided sorbents. The schematic diagram of the unit is
Figure 7. SCHEMATIC FLOW DIAGRAM OF THE HIGH-PRESSURE/ HIGH-TEMPERATURE TGA UNIT
shown in Figure 6. The unit essentially consists of a quartz fluidized-bed reactor which is externally heated by two electric furnaces, equipment for feeding and measuring the flow rates of the gases, measuring and controlling the bed temperature, and monitoring the fluidized-bed pressure. The fluidized-bed distributor is made of a quartz fritted disk.

In a typical test, about 50 to 100 grams of the partially sulfided sorbent are loaded into the fluidized-bed reactor. The bed of solids is heated by the external furnace, while a stream of nitrogen flows through the reactor until the reactor reaches the desired temperature. The gas flow rate is then increased to fluidize the bed. At this point, the gas is switched to a reactant gas containing the desired concentration of oxygen. The desired composition of the reactant gas is achieved by mixing a stream of air with nitrogen at predetermined ratios. A slip stream of the reactor off-gas is analyzed to determine the concentration of the sulfur dioxide that may evolve during the reaction. The reaction continues until the desired solids residence time is reached. During the test, the temperature is controlled by the temperature controller. The reactor temperature and pressure are monitored by a computer data acquisition system. The reactor off-gas passes through a filter for collection of elutriated fines and then through a liquid scrubber before being vented. After the test, the reactor solids are analyzed to determine the extent of sulfation and the fraction of sulfur released during the stabilization stage.

RESULTS AND DISCUSSION

Chemical Composition of the Sorbents

The chemical composition of both cuts of the three selected calcium-based sorbents determined in the previous CRSC funded project (Subgrant 89-4) are presented in Table 1. The chemical composition of different cuts of the same sorbents are very similar. The average calcium content of the limestone is 39.2% which corresponds to 98% calcium carbonate. The molar ratio of calcium carbonate to magnesium carbonate in the dolomite is 0.98 indicating that both the limestone and the dolomite are reasonably pure. The dolomitic limestone contains about 85% calcium carbonate and 14% magnesium carbonate. This sorbent contains 66% limestone and 34% dolomite.

Table 1. CHEMICAL ANALYSES OF SORBENTS

<table>
<thead>
<tr>
<th>Analyses, wt %</th>
<th>Limestone</th>
<th>Dolomite</th>
<th>Dolomitic-Limestone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coarse</td>
<td>Fine</td>
<td>Coarse</td>
</tr>
<tr>
<td>Calcium</td>
<td>38.7</td>
<td>39.6</td>
<td>22.2</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.59</td>
<td>0.52</td>
<td>13.2</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Iron</td>
<td>0.084</td>
<td>0.10</td>
<td>0.11</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.05</td>
<td>0.05</td>
<td>0.069</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.11</td>
<td>0.10</td>
<td>0.3</td>
</tr>
<tr>
<td>Stontium</td>
<td>0.015</td>
<td>0.017</td>
<td>0.005</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>44.7</td>
<td>44.5</td>
<td>48.0</td>
</tr>
<tr>
<td>Oxygen (by Diff.)</td>
<td>15.251</td>
<td>14.613</td>
<td>15.616</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Sulfidation of Sorbents

Samples of both cuts (-60+80 mesh and -20+30 mesh) from each sorbent were sulfided in the 3-inch-diameter quartz fluidized-bed reactor. The tests were designed to produce partially sulfided sorbents with sulfidation levels of about 50%.

The partially sulfided sorbents were analyzed and their calcium and sulfur content were determined. The results are presented in Table 2. The extent of sulfidation for all the six samples are very close to the desired value. These samples were used in the stabilization tests.

Table 2. EXTENT OF SULFIDATION IN PARTIALLY SULFIDED SORBENTS

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Particle Size, cm</th>
<th>Extent of Sulfidation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>0.07</td>
<td>49.9</td>
</tr>
<tr>
<td>Limestone</td>
<td>0.02</td>
<td>51.5</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0.07</td>
<td>50.9</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0.02</td>
<td>51.9</td>
</tr>
<tr>
<td>Dolomitic Limestone</td>
<td>0.07</td>
<td>53.8</td>
</tr>
<tr>
<td>Dolomitic Limestone</td>
<td>0.02</td>
<td>45.6</td>
</tr>
</tbody>
</table>

Effect of Pressure on Stabilization of Sulfided Sorbents

The partially sulfided samples of all three sorbents were reacted with oxygen in the high pressure TGA unit at 1500°F at 100 and 300 psia. Both fine (dp = 0.02 cm) and coarse (dp = 0.07 cm) material from each sorbent were used in the tests. The complete test conditions for this series of tests is given in Table 3.

The weight-versus-time data obtained in the TGA experiments were converted into conversion-versus-time. Conversion of calcium sulfide to calcium sulfate is calculated using the following formula:

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

(A)

\[
\% \text{ Gas Conversion} = \frac{(\text{Sample weight gain}) \times 32}{(\text{Initial sample weight}) \times (\text{fraction of sulfur in the sample}) \times (4 \times 16)} \times 100
\]

(1)
Table 3. TEST CONDITIONS FOR THE EFFECT OF PRESSURE

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Particle Diameter, cm</th>
<th>Pressure, psia</th>
<th>Temperature, °F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite</td>
<td>0.02</td>
<td>100</td>
<td>1500</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0.02</td>
<td>300</td>
<td>1500</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0.07</td>
<td>100</td>
<td>1500</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0.07</td>
<td>300</td>
<td>1500</td>
</tr>
<tr>
<td>Limestone</td>
<td>0.02</td>
<td>100</td>
<td>1500</td>
</tr>
<tr>
<td>Limestone</td>
<td>0.02</td>
<td>300</td>
<td>1500</td>
</tr>
<tr>
<td>Limestone</td>
<td>0.07</td>
<td>100</td>
<td>1500</td>
</tr>
<tr>
<td>Limestone</td>
<td>0.07</td>
<td>300</td>
<td>1500</td>
</tr>
<tr>
<td>Dolomitic Limestone</td>
<td>0.02</td>
<td>100</td>
<td>1500</td>
</tr>
<tr>
<td>Dolomitic Limestone</td>
<td>0.02</td>
<td>300</td>
<td>1500</td>
</tr>
<tr>
<td>Dolomitic Limestone</td>
<td>0.07</td>
<td>100</td>
<td>1500</td>
</tr>
<tr>
<td>Dolomitic Limestone</td>
<td>0.07</td>
<td>300</td>
<td>1500</td>
</tr>
</tbody>
</table>

The effects of pressure on sulfation of coarse and fine limestone particles are shown in Figures 8 and 9, respectively, which indicate that reactor pressure and particle diameter do not have any effect on the rate and the extent of sulfation reaction. The rate and the extent of sulfation is generally consistent with the sulfation data obtained previously in a CRSC funded project (Subgrant 89-4), indicating that limestone can only be partially sulfated (about 30-40%). This suggests that the rate of reaction is controlled by diffusion. Since the O₂ concentration is proportional to pressure and the diffusion coefficient is inversely proportional to pressure, the rate of oxidation is unaffected by the pressure increase.

The effect of pressure on sulfation of coarse and fine dolomitic limestone particles is shown in Figures 10 and 11. The extent of sulfation involving sulfided dolomitic limestone is also consistent with ambient pressure data. Figure 12 shows the rate of sulfation reaction involving partially sulfided dolomite particles which is also consistent with low pressure data, indicating that sulfided dolomite can be sulfated to near completion.

**Effect of Temperature on Stabilization of Sulfided Sorbents**

A total of 26 tests were conducted in this program to determine the effect of reaction temperature on the stabilization of partially sulfided Ca-based sorbents. These tests were conducted in the 2-inch-diameter quartz fluidized bed reactors.

The first seven tests were conducted using air as the reactant gas. However, because of the significant amount of heat released during the reaction, the bed temperature could not be controlled. Several attempts were made to control the bed temperature which included cycling air and nitrogen flow, changing bed volume, and lowering the gas flow rate. However, the bed temperature could not be fully controlled in these initial tests.
Figure 8. EFFECT OF PRESSURE ON STABILIZATION OF PARTIALLY SULFIDED COARSE LIMESTONE PARTICLES
Figure 9. EFFECT OF PRESSURE ON STABILIZATION OF PARTIALLY SULFIDED FINE LIMESTONE PARTICLES

SORBENT: LIMESTONE (51.5% Sulfided)
TEMPERATURE: 1500°F
PARTICLE DIAMETER: 0.02 cm
O₂ IN GAS: 5.25%
Figure 10. EFFECT OF PRESSURE ON STABILIZATION OF PARTIALLY SULFIDED COARSE DOLOMITIC LIMESTONE PARTICLES
Figure 11. EFFECT OF PRESSURE ON STABILIZATION OF PARTIALLY SULFIDED FINE DOLOMITIC LIMESTONE PARTICLES
Figure 12. STABILIZATION OF SULFIDED DOLOMITE AT ELEVATED PRESSURES
Figure 13 shows the time-temperature history of the fluidized-bed reactor along with the concentration of evolved \( \text{SO}_2 \) in the reactor off-gas for the fine dolomite particles. The temperature rose 300°F in 2 minutes resulting in significant \( \text{SO}_2 \) release. This test was the least severe test conducted with pure air because fine dolomite particles required a low air flow rate for fluidization while containing the lowest amount of sulfide in the solid. It was concluded that the only way to maintain the bed temperature was by lowering the oxygen concentration through mixing air and nitrogen. All subsequent tests were conducted with the gas containing 5.25% oxygen in which the bed temperature could be controlled.

Figures 14 through 16 show the reactor temperature along with the \( \text{SO}_2 \) content of the reactor off-gas in the tests conducted with fine sulfided dolomite particles while using a reactant gas containing 5.25% oxygen. These figures clearly indicate that the amount of \( \text{SO}_2 \) released significantly increases above 1600°F. The reactor bed temperature drops as soon as \( \text{SO}_2 \) evolution is completed indicating that the heat of reaction is the major source of heat controlling the fluidized-bed temperature.

Similar results were obtained with all other samples. The time temperature history and the \( \text{SO}_2 \) content of the reactor off-gas as a function of reaction time for all tests conducted at three temperatures with three sorbents in two particle sizes (18 tests) are presented in Appendix A.

The sulfur distribution during oxidation of fine sulfided limestone particles are presented in Figures 17 through 19 indicating that the total conversion of \( \text{CaS} \) to \( \text{CaSO}_4 + \text{SO}_2 \) increases with increasing temperature. However, the conversion to \( \text{CaSO}_4 \) decreases with increasing temperature. The distribution of sulfur during oxidation of fine sulfided dolomite particles is presented in Figures 20 through 22. In the case of sulfided dolomite, although the total conversion of \( \text{CaS} \) (to \( \text{CaSO}_4 + \text{SO}_2 \)) is not dependent on the temperature (as all are above 98%), the distribution of sulfur in \( \text{SO}_2 \) and \( \text{CaSO}_4 \) changes dramatically with increasing temperatures, from essentially all \( \text{CaSO}_4 \) at 1500°F to essentially all \( \text{SO}_2 \) at 1800°F. The sulfur distribution for all the 18 successful tests are also presented in Appendix A.

The maximum conversion of \( \text{CaS} \) to \( \text{CaSO}_4 + \text{SO}_2 \) and \( \text{CaSO}_4 + \text{SO}_2 \) for all the tests conducted with the fine sorbent particles are presented in Figures 23-25, respectively. Figure 23 shows that the conversion of \( \text{CaS} \) to \( \text{CaSO}_4 \) increases with the increase in magnesium content (dolomite content) of the sorbent. The conversion of \( \text{CaS} \) to \( \text{CaSO}_4 \) increases in the temperature range of 1500°F to 1650°F for limestone while it decreases for the dolomite and dolomitic limestone sorbents. The conversion to \( \text{CaSO}_4 \) drops to very low values (<12%) at 1800°F for all the sorbents because of the significant \( \text{SO}_2 \) production as is shown in Figure 24. The total conversion (\( \text{CaSO}_4 + \text{SO}_2 \)) increases with increasing temperature and is higher for sorbents with higher dolomite content (Figure 25). The unreacted \( \text{CaS} \) remaining after oxidation for all three fine sorbent particles is presented in Figure 26. The maximum conversions of \( \text{CaS} \) and unreacted \( \text{CaS} \) for all the tests conducted with the coarse sorbent particles are presented in Figures 27 through 30. The results are very similar to those obtained for the fine particles. Increasing temperatures in the range of 1500°F to 1800°F result in a decreasing \( \text{CaS} \) to \( \text{CaSO}_4 \) conversion, an increasing \( \text{CaS} \) to \( \text{SO}_2 \) conversion, and an increasing overall \( \text{CaS} \) conversion.
Figure 13. REACTOR TEMPERATURE AND SO$_2$ CONTENT OF REACTOR OFF-GAS DURING AIR OXIDATION OF PARTIALLY SULFIDED FINE DOLOMITE PARTICLES
Figure 14. REACTOR TEMPERATURE AND $\text{SO}_2$ CONTENT OF REACTOR OFF-GAS DURING OXIDATION OF PARTIALLY SULFIDED FINE DOLOMITE PARTICLES AT 1500°F
Figure 15. REACTOR TEMPERATURE AND SO$_2$ CONTENT OF REACTOR OFF-GAS DURING OXIDATION OF PARTIALLY SULFIDED FINE DOLOMITE PARTICLES AT 1650°F
Figure 16. Reactor Temperature and SO₂ Content of Reactor Off-Gas during Oxidation of Partially Sulfided Fine Dolomite Particles at 1800°F.
Figure 17. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED FINE LIMESTONE PARTICLES AT 1500°F
SORBENT: LIMESTONE (51.5% Sulfided)
TEMPERATURE: 1650 °F
PARTICLE DIAMETER: 0.02 cm
PRESSURE: 1 atm
O₂ IN GAS: 5.25%

Figure 18. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED FINE LIMESTONE PARTICLES AT 1650°F
Figure 19. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED FINE LIMESTONE PARTICLES AT 1800°F
Figure 20. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED FINE DOLOMITE PARTICLES AT 1500°F

SORBENT: DOLOMITE (51.9% Sulfided)
TEMPERATURE: 1500°F
PARTICLE DIAMETER: 0.02 cm
PRESSURE: 1 atm
O₂ IN GAS: 5.25%
Figure 21. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED FINE DOLOMITE PARTICLES AT 1650°F
Figure 22. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED FINE DOLOMITE PARTICLES AT 1800°F

SORBENT: DOLOMITE (51.9% Sulfided)
TEMPERATURE: 1800 °F
PARTICLE DIAMETER: 0.02 cm
PRESSURE: 1 atm
O₂ IN GAS: 5.25%
Figure 23. MAXIMUM CONVERSION OF CaS TO CaSO\textsubscript{4} (FINE PARTIALLY SULFIDED SORBENTS)
Figure 24. Maximum conversion of CaS to SO$_2$ (fine partially sulfided sorbents)
Figure 25. Maximum conversion of CaS to $\text{SO}_2 + \text{CaSO}_4$ (fine partially sulfided sorbents)
Figure 26. UNREACTED CaS REMAINING AFTER OXIDATION (FINE PARTIALLY SULFIDED SORBENTS)
Figure 27. MAXIMUM CONVERSION OF CaS to CaSO$_4$ (COARSE PARTIALLY SULFIDED SORBENTS)

- DOLOMITIC LIMESTONE
- DOLOMITE
- LIMESTONE

PARTICLE DIAMETER: 0.07 cm
PRESSURE: 1 atm
O$_2$ IN GAS: 5.25%
Figure 28. MAXIMUM CONVERSION OF CaS to SO$_2$ (COARSE PARTIALLY SULFIDE SORBENTS)
Figure 29. MAXIMUM CONVERSION OF CaS to SO$_2$ + CaSO$_4$ (COARSE PARTIALLY SULFIDED SORBENTS)
Figure 30. UNREACTED CaS REMAINING AFTER OXIDATION (COARSE PARTIALLY SULFIDED SORBENTS)
Scanning Electron Microscopy (SEM) Analyses

The objective of the SEM analysis was to determine the extent of sintering (if any) in the stabilized samples and determine the composition of different layers of the cross section of the stabilized solid sorbent. This information is useful in determining the mechanism of the reactions involved during oxidation of partially sulfided sorbents.

Petrographic samples of the partially sulfided sorbents were mounted, sectioned, and polished according to the method (ASTM D2797) used in coal petrography (21), and analyzed by scanning electron microscope. The partially sulfided samples of the sorbents were prepared by mounting the samples in a 1-inch-diameter briquette mold with a mixture of BUEHLER epoxy that contained 10% TiO₂ pigment. While the epoxy was still fluid, the samples were subjected to a vacuum to force the epoxy and pigment into cracks and pores. This was done to ensure that the sample would not be pulled out of the epoxy binder during the grinding and polishing steps. The epoxy was allowed to harden overnight. The hardened briquettes were removed from the mold and were polished without water to prevent decomposition of calcium sulfide.

Figure 31 shows the close-up picture and the sulfur map of a partially sulfided limestone particle. The average particle diameter of this sample was 0.02 cm (70 mesh). This sample was 50% sulfided in the ambient-pressure quartz fluidized-bed reactor. From Figure 31, one can conclude that the shrinking-core model is an appropriate model because the partially sulfided particle consists of calcium oxide in the center and calcium sulfide in the outer layer.

The close-up pictures and the sulfur map of a partially sulfided coarse limestone particle after oxidation at 1550°F is shown in Figure 32. From this figure it appears that both the sulfidation and the sulfation reactions can be described by a shrinking core model. Comparison of Figures 32b and 32c indicate that the outer layer consists of mainly calcium sulfate, the middle layer is mainly calcium sulfide and the inner layer is essentially calcium oxide.

The close-up picture and sulfur map of a partially sulfided limestone particle oxidized at 1650°F are presented in Figure 33 indicating that the sample has lost sulfur mostly around the edge of the particle. This picture is consistent with the assumption that the sulfur is released as the result of the reaction between CaS and CaSO₄. Because these compounds are only around the edges of the particle the sulfur loss occurs at these locations as shown in Figure 33b.

The closeup picture and sulfur map of a sulfided dolomitic limestone particle after oxidation at 1800°F is presented in Figure 34. The sulfur map presented in Figure 34a indicates that only a small amount of sulfur is left at the center of the particle. This is consistent with the picture of the oxidized particle at 1650°F presented in Figure 33 that the release of SO₂ is through the reaction of CaS and CaSO₄ at the interface of the two compounds. A close-up picture of the edge of this particle shows that small grains of the particle at the edges are sintering. No interparticle sintering, bridging, or
Figure 31. PARTIALLY SULFIDED FINE LIMESTONE PARTICLES
a) CLOSEUP OF THE PARTICLE, b) SULFUR MAP
Figure 32. PARTIALLY SULFIDED COARSE LIMESTONE PARTICLE AFTER OXIDATION AT 1500°F. a) CLOSEUP OF THE PARTICLE, b) CLOSEUP OF THE PARTICLE EDGE, c) SULFUR MAP OF THE EDGE
Figure 33. PARTIALLY SULFIDED FINE LIMESTONE PARTICLE AFTER OXIDATION
AT 1650°F.  a) CLOSEUP OF THE PARTICLE,
b) SULFUR MAP
Figure 34. Partially sulfided fine dolomitic limestone, particle after oxidation at 1800°F.

a) Sulfur map, b) closeup of the particle, c) closeup of the edge of the particle.
agglomerating was observed for particles oxidized at 1800°F. A close-up picture of a coarse limestone particle that was oxidized at temperatures above 2000°F is shown in Figure 35. Figure 35a shows that interparticle bridge was formed during this high temperature oxidation while Figure 35b shows a close-up picture of the bridge that indicates melting and sintering occurred at this temperature. All the sulfur in this sample was released during oxidation.

Sulfur Leaching Tests

Samples of the oxidized sulfided sorbents produced in this program were subjected to the EPA proposed sulfur leaching test described in an earlier report.(13). The results are presented in Table 4. The levels of sulfur released were an order of magnitude below the limit for all the stabilized samples making these then suitable for disposal in landfills.

Table 3. RESULTS OF EPA PROPOSED SULFIDE LEACHING TEST

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Particle Diameter, cm</th>
<th>Oxidation Temperature, °F</th>
<th>Sulfur Released in EPA Test, mg/Kg Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite</td>
<td>0.02</td>
<td>1500</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0.02</td>
<td>1650</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0.02</td>
<td>1800</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0.07</td>
<td>1500</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0.07</td>
<td>1650</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Dolomite</td>
<td>0.07</td>
<td>1800</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Dolomitic Limestone</td>
<td>0.02</td>
<td>1500</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Dolomitic Limestone</td>
<td>0.02</td>
<td>1650</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Dolomitic Limestone</td>
<td>0.02</td>
<td>1800</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Dolomitic Limestone</td>
<td>0.07</td>
<td>1500</td>
<td>48</td>
</tr>
<tr>
<td>Dolomitic Limestone</td>
<td>0.07</td>
<td>1650</td>
<td>12</td>
</tr>
<tr>
<td>Dolomitic Limestone</td>
<td>0.07</td>
<td>1800</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Limestone</td>
<td>0.02</td>
<td>1500</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Limestone</td>
<td>0.02</td>
<td>1650</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Limestone</td>
<td>0.02</td>
<td>1800</td>
<td>&lt;10</td>
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<tr>
<td>Limestone</td>
<td>0.07</td>
<td>1500</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Limestone</td>
<td>0.07</td>
<td>1650</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Limestone</td>
<td>0.07</td>
<td>1800</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions are made from the work performed in this project.

- The rate and the extent of sulfidation is not sensitive to pressure in the range of 0 to 300 psia.

- The fraction of CaS converted to SO₂ during CaS oxidation significantly increases with increasing temperature in the range of 1500°F to 1800°F. The fraction of CaS converted to CaSO₄ decreases with increasing temperature. Overall, the fraction of CaS remaining as unreacted decreases with increasing temperature.
Figure 35. PARTIALLY SULFIDED COARSE LIMESTONE PARTICLE AFTER OXIDATION AT T>2000°F. a) INTERPARTICLE BRIDGING, b) CLOSEUP OF THE BRIDGE
The overall conversion of CaS as well as selectivity towards conversion to CaSO₄ is higher for dolomite compared to limestone.

The extent of conversion of CaS to CaSO₄ and SO₂ for dolomitic limestone is generally between those of dolomite and limestone.

Based on SEM analyses, both sulfidation and sulfation reactions can be described by a shrinking core model. The sulfur release during oxidation appears to occur through the reactions between calcium sulfide (CaS) and calcium sulfate (CaSO₄) at the interface of the two compounds.

All the oxidized sulfided calcium-based sorbents meet the EPA limit for sulfur release and can be regarded as non-hazardous, and suitable for disposal in landfills.
REFERENCES CITED


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SORBENT: LIMESTONE (51.5% Sulfided)
PARTICLE DIAM: 0.02 cm
PRESSURE: 1 atm
O₂ IN GAS: 5.25%

Figure A-1. REACTOR TEMPERATURE AND SO₂ CONTENT OF REACTOR OFF-GAS DURING OXIDATION OF PARTIALLY SULFIDED FINE LIMESTONE PARTICLES AT 1500°F
Figure A-2. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED FINE LIMESTONE PARTICLES AT 1500°F
Figure A-3. REACTOR TEMPERATURE AND SO₂ CONTENT OF REACTOR OFF-GAS DURING OXIDATION OF PARTIALLY SULFIDED LIMESTONE PARTICLES AT 1650°F
Figure A-4. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED FINE LIMESTONE PARTICLES AT 1650°F
Figure A-5. Reactor temperature and SO₂ content of reactor off-gas during oxidation of partially sulfided fine limestone particles at 1800°F.
Figure A-6. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED FINE LIMESTONE PARTICLES AT 1800°F
Figure A-7. REACTOR TEMPERATURE AND SO₂ CONTENT OF REACTOR OFF-GAS DURING OXIDATION OF PARTIALLY SULFIDED FINE DOLOMITE PARTICLES AT 1500°F
Figure A-8. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED FINE DOLOMITE PARTICLES AT 1500°F
Figure A-9. REACTOR TEMPERATURE AND SO₂ CONTENT OF REACTOR OFF-GAS DURING OXIDATION OF PARTIALLY SULFIDED FINE DOLOMITE PARTICLES AT 1650°F
Figure A-10. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED FINE DOLOMITE PARTICLES AT 1650°F
Figure A-11. REACTOR TEMPERATURE AND SO$_2$ CONTENT OF REACTOR OFF-GAS DURING OXIDATION OF PARTIALLY SULFIDED FINE DOLOMITE PARTICLES AT 1800°F
Figure A-12. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED FINE DOLOMITE PARTICLES AT 1800°F
Figure A-13. REACTOR TEMPERATURE AND SO$_2$ CONTENT OF REACTOR OFF-GAS DURING OXIDATION OF PARTIALLY SULFIDED FINE DOLOMITIC LIMESTONE PARTICLES AT 1500°F
Figure A-14. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED DOLOMITIC LIMESTONE PARTICLES AT 1500°F

SORBENT: DOLOMITIC LIMESTONE (45.6% Sulfided)
TEMPERATURE: 1500 °F
PARTICLE DIAMETER: 0.02 cm
O₂ IN GAS: 5.25%

TIME, min

CaSO₄

SO₂

SULFUR DISTRIBUTION % OF TOTAL S IN SORBENT
SORBENT: DOLOMITIC LIMESTONE
(45.6% Sulfided)

PARTICLE DIAM: 0.02 cm

PRESSURE: 1 atm

$O_2$ IN GAS: 5.25%

Figure A-15. REACTOR TEMPERATURE AND $SO_2$ CONTENT OF REACTOR OFF-GAS DURING OXIDATION OF PARTIALLY SULFIDED FINE DOLOMITIC LIMESTONE PARTICLES AT 1650°F.
Figure A-16. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED FINE DOLOMITE LIMESTONE PARTICLES AT 1650°F
Figure A-17. REACTOR TEMPERATURE AND SO\textsubscript{2} CONTENT OF REACTOR OFF-GAS DURING OXIDATION OF PARTIALLY SULFIDED FINE DOLOMITIC LIMESTONE PARTICLES AT 1800°F
Figure A-18. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED FINE DOLOMITIC LIMESTONE PARTICLES AT 1800°F
Figure A-19. REACTOR TEMPERATURE AND SO₂ CONTENT OF REACTOR OFF-GAS DURING OXIDATION OF PARTIALLY SULFIDED COARSE LIMESTONE PARTICLES AT 1500°F
Figure A-20. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED COARSE LIMESTONE PARTICLES AT 1500°F
Figure A-21. REACTOR TEMPERATURE AND SO$_2$ CONTENT OF REACTOR OFF-GAS DURING OXIDATION OF PARTIALLY SULFIDED COARSE LIMESTONE PARTICLES AT 1650°F
Figure A-22. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED COARSE LIMESTONE PARTICLES AT 1650°F
Figure A-23. REACTOR TEMPERATURE AND SO$_2$ CONTENT OF REACTOR OFF-GAS DURING OXIDATION OF PARTIALLY SULFIDED COARSE LIMESTONE PARTICLES AT 1800°F
Sulfur Distribution, % of Total S in Sorbent

Figure A-24. Sulfur Distribution during Oxidation of Partially Sulfided Coarse Limestone Particles at 1800°F
Figure A-25. REACTOR TEMPERATURE AND SO₂ CONTENT OF REACTOR OFF-GAS DURING OXIDATION OF PARTIALLY SULFIDED COARSE DOLOMITE PARTICLES AT 1560°F
Figure A-26. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED COARSE DOLOMITE PARTICLES AT 1560°F
Figure A-27. Reactor temperature and $\text{SO}_2$ content of reactor off-gas during oxidation of partially sulfided coarse dolomite particles at 1690°F.
Figure A-28. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED COARSE DOLOMITE PARTICLES AT 1690°F
Figure A-29: Reactor temperature and SO$_2$ content of reactor off-gas during oxidation of partially sulfided coarse dolomite particles at 1840°F
Figure A-30. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED COARSE DOLOMITE PARTICLES AT 1840°F
SORBENT: DOLOMITE LIME STONE
(53.8% Sulfided)

PARTICLE DIAM: 0.07 cm

PRESSURE: 1 atm

O₂ IN GAS: 5.25%

Figure A-31. REACTOR TEMPERATURE AND SO₂ CONTENT OF REACTOR OFF-GAS DURING OXIDATION OF PARTIALLY SULFIDED COARSE DOLOMITE LIME STONE PARTICLES AT 1560°F
Figure A-32. Sulfur distribution during oxidation of partially sulfided coarse dolomitic limestone particles at 1560°F.
SORBENT: DOLOMITIC LIMESTONE
(53.8% Sulfided)

PARTICLE DIAM: 0.07 cm

PRESSURE: 1 atm

O2 IN GAS: 5.25%

Figure A-33. REACTOR TEMPERATURE AND SO2 CONTENT OF REACTOR OFF-GAS DURING OXIDATION OF PARTIALLY SULFIDED COARSE DOLOMITIC LIMESTONE PARTICLES AT 1630°F
Sorbent: Dolomitic Limestone (53.8% Sulfided)
Temperature: 1630 °F
Particle Diameter: 0.07 cm
Pressure: 1 atm
O₂ in gas: 5.25%

Figure A-34. Sulfur Distribution During Oxidation of Partially Sulfided Coarse Dolomitic Limestone Particles at 1630°F
Figure A-35. REACTOR TEMPERATURE AND SO₂ CONTENT OF REACTOR OFF-GAS DURING OXIDATION OF PARTIALLY SULFIDED COARSE DOLOMITIC LIMESTONE PARTICLES AT 1790°F
Figure A-36. SULFUR DISTRIBUTION DURING OXIDATION OF PARTIALLY SULFIDED COARSE DOLOMITIC LIMESTONE PARTICLES AT 1790°F