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TECHNICAL REPORT
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Project Title:	Stabilization and/or Regeneration of Spent Sorbents From Coal Gasification DE-FG22-91PC91334
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ABSTRACT

The objective of this investigation is to determine the effects of SO_2 partial pressure and reaction temperature on the conversion of sulfide containing solid wastes from coal gasifiers to stable and environmentally acceptable calcium-sulfate, while preventing the release of sulfur dioxide through undesirable side reactions during the stabilization step. An additional objective of this program is to investigate the use of the Spent Sorbent Regeneration Process (SSRP) to regenerate spent limestone, from a fluidized-bed gasifier with in-bed sulfur capture, for recycling to the gasifier.

To achieve these objectives, selected samples of partially sulfided sorbents will be reacted with oxygen at a variety of operating conditions under sufficient SO_2 partial pressure to prevent release of sulfur from the solids during stabilization that reduces the overall sorbent utilization. Partially sulfided limestone will also be regenerated with water to produce calcium hydroxide and release sulfur as H_2S. The regenerated sorbent will be dewatered, dried and pelletized. The reactivity of the regenerated sorbent toward H_2S will also be determined.

During this quarter sulfidation tests were conducted in a quartz fluidized-bed reactor in which the selected calcium-based sorbents were first calcined and then were reacted with hydrogen sulfide at ambient pressure and 1650°F. These tests were conducted with each sorbent in two particle sizes. chemical analyses of the partially sulfided sorbents indicate that the extent of sulfidation was in the range of 40-50%. The partially sulfided material will be reacted with oxygen to determine the effects of temperature and SO_2 partial pressure on the stabilization of the calcium sulfide in solid waste materials.

DISCLAIMER

MASTER

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EXECUTIVE SUMMARY

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.

High efficiency advanced electric power generation systems using Integrated Coal Gasification Combined Cycle (IGCC) or advanced/staged pressurized fluidized-bed combustion, require very low levels of H_2S in the fuel gases. More than 90% of the H_2S 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 H_2S content of the fuel gas to acceptable levels for IGCC application.

The removal of sulfur takes place through the reaction of hydrogen sulfide with calcium oxide, calcium carbonate, or calcium hydroxide and produces calcium sulfide. This compound is not stable, and therefore, is not suitable for direct disposal. However, calcium sulfide can be either reacted with oxygen (or air) to produce calcium sulfate, which is a stable and environmentally acceptable compound for disposal, or reacted with water to regenerate the sorbent and release sulfur as hydrogen sulfide.

The extent of the conversion of calcium sulfide to stable calcium sulfate has been shown to depend on the sorbent type (i.e., limestone or dolomite), the extent of sulfidation reaction (i.e., Ca/S ratio in the gasifier), sorbent particle size, and magnesium content of the sorbent. The reaction temperature has been shown to have a significant effect on the overall sorbent utilization. Stabilization is generally accompanied by release of sulfur in the form of SO_2 through a side reaction. The fraction of sulfur released as SO_2 increases with increasing temperatures. The release of sulfur during stabilization should be prevented in order to maintain the overall sorbent utilization. This is essential to the development of an economical process scheme for successful stabilization of sulfide containing solid waste products from gasification or staged combustion of high sulfur Illinois coal.

The spent sorbents may also be regenerated in the Spent Sorbent Recovery Process (SSRP). In the proposed process, the ash discharge from a fluidized-bed gasifier, consisting essentially of spent limestone containing CaS and coal ash, is sent to a reactor containing water at temperatures of 150-300°F and pressures of 25 to 350 psia. Process derived CO_2 is bubbled through the ash-water slurry. Under these conditions, the water and CO_2 will react with the CaS to liberate H_2S and produce $Ca(OH)_2$ and/or $CaCO_3$, depending upon the amount of CO_2 used. The subsequent stages of dewatering, drying, pelletizing and recycling of the regenerated materials need to be investigated to determine the viability of the SSRP.

The objective of this investigation is to determine the effects of SO_2 partial pressure, reaction temperature and sorbent type for conversion of sulfide containing solid wastes from coal gasification (that utilize calcium-based sorbents for in-bed sulfur capture) to stable and environmentally acceptable calcium sulfate while preventing the release of sulfur dioxide during the stabilization step. An additional objective of the program is to investigate the viability of the spent sorbent regeneration using the SSRP.

Two calcium-based sorbents were tested in this study which included one limestone and one dolomite. These sorbents are the same as those used in previous projects sponsored by CRSC (Subgrant 89-4 and 90-8). The sorbents were crushed and screened into narrow particle size ranges. Two cuts from each sorbent were selected for this investigation which include 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.

Sulfidation tests were conducted with both coarse and fine particles of each sorbent. The tests were conducted in a 3-inch-diameter quartz fluidized-bed reactor. The reactor temperature was 1650°F and the tests were conducted at atmospheric pressure. The samples were calcined in nitrogen atmosphere. The calcined sorbents were later fluidized by a reactant gas containing 5% hydrogen sulfide for a predetermined period. The sulfided samples were analyzed to determine the extent of sulfidation.

OBJECTIVES

The goal of this program is to develop processes for stabilization and/or regeneration of spent calcium-based sorbent that have been used to capture sulfur in fluidized-bed gasification of high sulfur coals.

The overall objective of this program is to determine the effect of sorbent type, SO_2 partial pressure, and reactor temperature, on the conversion of calcium sulfide to calcium sulfate while preventing the release of sulfur dioxide during the stabilization process. An additional objective of this program is to investigate regeneration of spent Ca-based sorbent using Spent Sorbent Regeneration Process (SSRP) in which spent limestone containing calcium sulfide is reacted with water and carbon dioxide to release sulfur as H_2S and product calcium hydroxide and/or calcium carbonate that can be recycled back to the gasifier.

The proposed program goal is specifically directed towards waste management, Research Priority Section 5.4A: Studies related to disposal and utilization of waste materials generated in gasifiers, or fluidized-bed combustors, or flue gas scrubbers, including in-duct injection. The specific objectives of this program are to:

1. Prepare partially sulfided samples of a limestone and a dolomite (that have been used in previous CRSC funded projects)
2. Obtain experimental data on oxidation of the sulfided sorbents in a quartz batch fluidized-bed reactor. The test parameters will include reaction temperature, SO_2 concentration, oxygen concentration and solid residence time.
3. Analyze oxidized sorbents in terms of their physical and chemical properties to determine the reaction path during oxidation.
4. Conduct sulfur leaching tests with the stabilized sorbent to determine their suitability as the end product.
5. Determine the effects of regeneration on recycling limestone.
6. Analyze and characterize both original limestone and regenerated pellets.
7. Evaluate the reactivity of regenerated sorbent toward H_2S.

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 the 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.

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 to capture the sulfur compounds from the fuel gas.

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) --

$$CaS + 2O_2 \rightarrow CaSO_4 \qquad (A)$$

However, the calcium sulfate produced by reaction (A), at temperatures of interest to the overall process (1500°-1800°F), can also react with the calcium sulfide in an apparent solid-solid reaction to release SO_2 -

$$CaS + 3CaSO_4 \rightarrow 4CaO + 4SO2 \qquad (B)$$

Reaction (A) is a highly exothermic reaction (ΔH_{rxn} > 350 Kcal/g mole) resulting in a significant increase in the particle temperature. Reaction (B) becomes more favorable as the particle temperature increases, resulting in release of SO_2, and reducing overall sorbent utilization. The highly exothermic nature of reaction (A) and its effect on the reaction temperature significantly affects the final distribution of the product.

The spent sorbent containing calcium sulfide can also be regenerated to release sulfur as H_2S and produce calcium hydroxide and/or calcium carbonate that can be recycled back to the gasifier.

$$CaS + 2H_2O \rightarrow Ca(OH)_2 + H_2S \qquad (C)$$

$$CaS + CO_2 + H_2O \rightarrow CaCO_3 + H_2S \qquad (D)$$

Reactions (C) and (D) can be carried out at temperatures of 250-300°F at the gasifier pressures of 25 to 350 psia.

The results of investigations on the stabilization of calcium sulfide in previous CRSC funded projects(1-5) indicate that limestone can only be partially sulfated while dolomite can be essentially completely sulfated at 1500°F. The extent of sulfation depends not only on the sorbent type but also on the extent of sulfidation in the gasifier. The results of previous studies also indicate that the fraction of sulfur in calcium sulfide converted to SO_2 significantly increases with increasing temperature.(6-14)

To prevent SO_2 evolution during stabilization, Reaction (B) must be suppressed. One approach for suppression of SO_2 release during stabilization is to carry out the stabilization at a lower temperature (T<1500°F) while effectively controlling the reactor temperature by using a low concentration of O_2 in the reactant gas. Lower reaction temperature coupled with low oxygen concentration will result in a slow rate of sulfation reaction requiring large reactors to carry out the stabilization step.

A more attractive approach is to carry out the stabilization step in the presence of a significant concentration of SO_2 in the reactant gas. In order to carry out the stabilization of calcium sulfide according to Reaction (A) and to prevent Reaction (B) from occurring, the partial pressure SO_2 in the reactant gas must exceed the equilibrium value at the selected reaction temperature. The overall reaction for release of SO_2 can be obtained by a combination of Reactions (A) and (B) [i.e. 3(A) + (B) = 4(E)] -

$$CaS + 3/2O_2 = CaO + SO_2 \qquad (E)$$

The familiar reaction (F) for sulfation of calcium oxide --

$$CaO + SO_2 + 1/2O_2 = CaSO_4 \qquad (F)$$

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

$$(A) - (B) = 4(F)$$

Based on the Gibbs free energies of these reactions, the thermodynamic equilibrium of reaction (B) dictates the reaction path, as long as all four substances (i.e., CaO, CaS, $CaSO_4$, SO_2) are present. By maintaining the desired concentration of SO_2 during oxidation, partially sulfided calcium-based sorbents can be stabilized through Reaction (A) while the release of SO_2 through Reaction (B) is prevented.

A number of researchers have investigated different methods of CaS regeneration using steam(15-23) with regeneration efficiencies up to 96%. Regeneration of spent sorbents in the SSRP process has also been investigated in a previous CRSC funded project (under Subgrant 90-8). The results of this work indicate that up to 99% of the calcium sulfide can be regenerated in a reactor containing water at temperatures of 150-300°F and pressure of 25 to 350 psia. The regenerated sorbent can be dewatered, dried, pelletized and recycled back to the gasifier. To prevent buildup of coal ash, a slipstream of the treated slurry is removed from the system and dried to be used as fertilizer to adjust soil Ph or fully carbonated to be used aggregate for concrete.

This investigation is targeted toward determination of the sulfur capturing capabilities of both limestone and dolomite during stabilization of partially sulfided sorbents in the presence of excess SO_2. The investigation on regeneration of spent sorbent will expand the current process to include the subsequent stages of dewatering, drying, pelletizing, and recycling of the regenerated material. The result of this work will provide the necessary information in the development of economically attractive processes for the stabilization and/or regeneration of calcium sulfide containing spent sorbents from gasification of Illinois high sulfur coal.

EXPERIMENTAL PROCEDURES

The experiments performed during this quarter were conducted in a 3-inch-diameter quartz fluidized-bed, wherein, selected samples of the sorbents were calcined in nitrogen atmosphere and reacted with hydrogen sulfide.

Sorbent Selection

Two calcium-based sorbents (one limestone and one dolomite) were used for this investigation. These sorbents had already been tested in previous projects sponsored by CRSC (Subgrant 89-4 and 90-8). The selection of these sorbents was primarily based on their calcium carbonate content. The sorbents were crushed and screened into narrow particle size ranges. Two cuts from each sorbent were selected for testing in this program. These selected cuts include coarse particles (-20+30 mesh) and fine particles (-60+80 mesh).

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 1. The unit essentially consists of a quartz fluidized-bed rector which is externally heated by two electrical furnaces, equipment for feeding and measuring the flow rates of the gases, measuring and controlling the bed temperature, and monitoring the fluidized-bed pressure.

During a sulfidation tests, about 750 grams of the sorbent is loaded into the fluidized-bed reactor. The fluidized-bed distributor is made of quartz fritted disk. The bed is heated up by two electrical furnaces while a stream of nitrogen flows through the reactor. The sorbent is calcined during the heatup period and is kept at 1650°F for 30 minutes. Nitrogen and hydrogen sulfide are mixed at a predetermined ratio to achieve the desirable mixture composition. The flow rate of gas mixture is set to fluidize the bed. The gas containing hydrogen sulfide flows through the reactor. A slip stream of the reactor off gases are analyzed to determine the extent of reaction in the fluidized bed. This data is 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 run the temperature is controlled by the temperature controller. The reactor temperature and pressure are monitored by a computer data acquisition system. The reactor off-gases pass through a filter for collection of elutriated fines and then through a liquid scrubber before being vented.

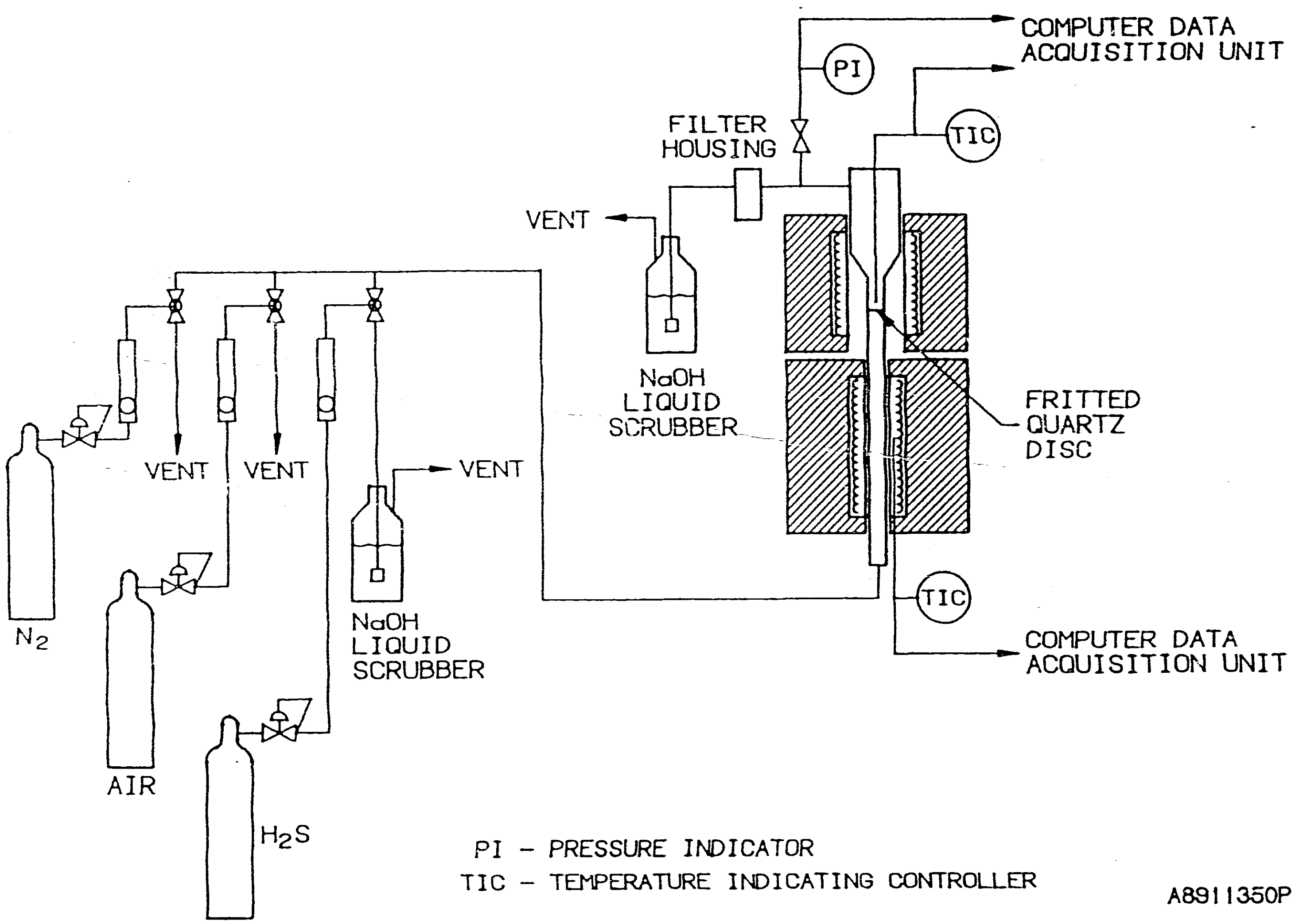

Figure 1. SCHEMATIC FLOW DIAGRAM OF THE QUARTZ FLUIDIZED-BED UNIT

RESULTS AND DISCUSSION

Chemical Compositions of the Sorbents

The chemical composition of both cuts of the two 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% that 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.

Table 1. CHEMICAL ANALYSES OF SORBENTS

	Limestone		Dolomite	
Analyses, wt %	Coarse	Fine	Coarse	Fine
Calcium	38.7	39.6	22.2	22.3
Magnesium	0.59	0.52	13.2	14.1
Potassium	0.5	0.5	0.5	0.5
Iron	0.084	0.10	0.11	0.16
Aluminum	0.05	0.05	0.069	0.071
Silicon	0.11	0.10	0.3	0.25
Stontium	0.015	0.017	0.005	0.005
Carbon Dioxide	44.7	44.5	48.0	48.2
Oxygen (by Diff.)	15.251	14.613	15.616	14.414
	100	100	100	100

Sulfidation of Sorbents

Samples of both cuts (-60+80 mesh and -20+30 mesh) from both sorbents 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 40-50%.

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 six samples are within the desired range. These samples will be used in the sulfation tests.

Table 2. EXTENT OF SULFIDATION IN PARTIALLY SULFIDED SORBENTS

Sorbent	Particle Size, cm	Extent of Sulfidation, %
Limestone	0.07	47.98
Limestone	0.02	40.49
Dolomite	0.07	47.12
Dolomite	0.02	44.46

CONCLUSIONS AND RECOMMENDATIONS

Based on the analyses of the extent of sulfidation of the sulfided samples produced during this quarter, these samples are suitable for sulfation tests.

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