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Title:
Advanced Hot-Gas Desulfurization Sorbents

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Introduction

Advanced high-efficiency integrated gasification combined cycle (IGCC) power systems are being developed to produce power from coal under the U.S. Department of Energy's (DOE's) multibillion dollar Clean Coal Technology (CCT) Program (Gangwal et al., 1993). In these advanced systems, coal is gasified to produce a gas at high-temperature and high-pressure (HTHP) conditions. The hot gas is cleaned of contaminants, primarily particulates and sulfur gases such as hydrogen sulfide (H_2S) and burned in a combustion turbine. IGCC systems are capable of lower gaseous, liquid, and solid discharges than conventional pulverized-coal-fired power plants. Hot gas cleanup offers the potential for higher plant thermal efficiencies and lower costs due to the elimination of fuel gas cooling and associated heat exchangers.

Sulfur sorbents based on zinc oxide are currently the leading candidates and are being developed for moving- and fludized-bed reactor applications. Zinc oxide sorbents can effectively reduce the H_2S in coal gas to around 10 ppmv and can be regenerated for multicycle operation. However, all of the current first-generation leading sorbents undergo significant loss of reactivity with cycling, as much as 50% or greater loss in only 25 to 50 cycles. Stability of the hot-gas desulfurization step over hundreds of cycles is essential for improved IGCC economics over conventional power plants.

Most hot-gas desulfurization sorbents in the past have been developed for hot-gas cleanup at temperatures greater than 538 °C (1,000 °F). Recent economic evaluations (NOVEM, 1991; Leininger et al., 1992; Rutkowski et al., 1993) have indicated that the thermal efficiency of IGCC systems increases rapidly with the temperature of hot-gas cleanup up to 350 °C and then very slowly as the temperature is increased further. This suggests that the temperature severity of the hot-gas cleanup devices can be reduced without significant loss of thermal efficiency. For this reason, this project aims to develop hot-gas cleanup sorbents for relatively low-temperature applications, 343 to 538 °C, with emphasis on the temperature range from 400 to 500 °C.

Objectives

The objective of this project is to develop advanced hot-gas desulfurization sorbents for relatively low-temperature application that show stable and high sulfidation reactivity at 343 to 538 °C.

Approach

A number of zinc-based formulations will be prepared and screened for testing in a fixed-bed reactor at high pressure (1 to 20 atm) and high temperatures using simulated coal-derived fuel gases. One of the superior formulations will be tested for long-term durability and chemical reactivity in the reactor. To prevent sulfation, catalyst additives will be investigated, which would promote a lower regeneration temperature.

Project Description

Sorbent Preparation

A highly promising method was recently developed under this project in coopearation with a commercial sorbent manufacturer for preparing suitable sorbents. Various sorbents were prepared using this proprietary technique. The role of the commercial manufacturer was to ensure scalability of the manufacturing process and to keep the cost competitive. The following analytical techniques were used to characterize the fresh, sulfided, and regenerated sorbents: (1) X-ray Diffraction (XRD) for the crystalline phase; (2) the standard BET method for surface area measurement; (3) Hg-porosimetry for determination of pore volume, bulk density, average pore diameter, and pore size distribution; and (4) Atomic Absorption (AA) Spectrometry for elemental composition analysis.

Experimental Setup

The materials prepared were tested in a laboratory-scale, high-pressure and high-temperature fixed-bed reactor. Briefly, the experimental setup consisted of a gas delivery system, a fixed-bed reactor, and a gas analysis system. In the gas delivery system, a simulated fuel gas of any desired composition could be generated using bottled gases, a set of mass flow controllers, and high-pressure syringe pumps. Steam was added to the mixed dry gas by vaporizing liquid water and injecting it into the gas stream at a controlled rate by a high-pressure syringe pump. The reactor was constructed of stainless steel pipe. Inside the pipe there was a removable 316 stainless steel 1.0 cm I.D. tube with a porous alumina plate in the bottom that acts as a gas distributor. The inside of the pipe was Alon-processed to prevent corrosion of stainless steel by sulfurous gases in the presence of steam. The pressure inside the reactor was controlled by a back pressure regulator and measured by an electronic pressure sensor. The thermocouples were positioned to measure the temperatures of the preheated feed gas, the reactor bed, and the product gas. The tests were conducted with a simulated gas containing 10% H_2, 15% CO, 5 mol% CO_2, 1 mol% H_2S, 15 mol% H_2O, and balance N_2. The outlet H_2S and SO_2 concentrations were monitored using detector tubes and gas chromatography.

A typical run consisted of loading approximately 1 g of the sorbent in a particle size range of -32+ 64 mesh and heating the reactor to a desired temperature of 300 to 500 °C with continuous flow of nitrogen. Once the desired temperature was attained, the flow of fuel gas to the reactor was started and the concentration of H_2S was measured continuously in the effluent gas. When the H_2S concentration in the effluent gas reached 300 ppmv, indicating breakthrough, the sulfidation was stopped and the system was prepared for regeneration. The regeneration of sulfided material was carried out at the desired temperature ranging between 400 and 650 °C with 2 to 4% oxygen in nitrogen. In all runs, the space velocity used was in the range of 2,000 to 3,000 h^1. The regeneration of the sulfided material was carried out until the SO_2 concentration in the reactor effluent chopped below 50 ppmv. These sulfidation-regeneration cycles were repeated as many times as desired. Typically each material was tested for 5 to 10 cycles to obtain meaningful data on material durability. At the end of a 5- to 10-cycle run, the material was removed from the reactor and all physical and chemical characterizations, as listed above, were carried out on the reacted material to determine changes due to the reaction.

Results

The ZnO-based sorbent (MCRH-1) was evaluated in a sulfidation gas mixture containing (in mole%): $H_2=10\%$, $CO=15\%$, $CO_2=5\%$, $H_2S=1\%$, $H_2O=15\%$, and balance N_2. Figure 1 shows the H_2S breakthrough profiles as a function of normalized time. In tests with the MCRH-1 sorbent conducted at 427 °C , the sorbent conversion at breakthrough was 80 percent. In fact, the H_2S
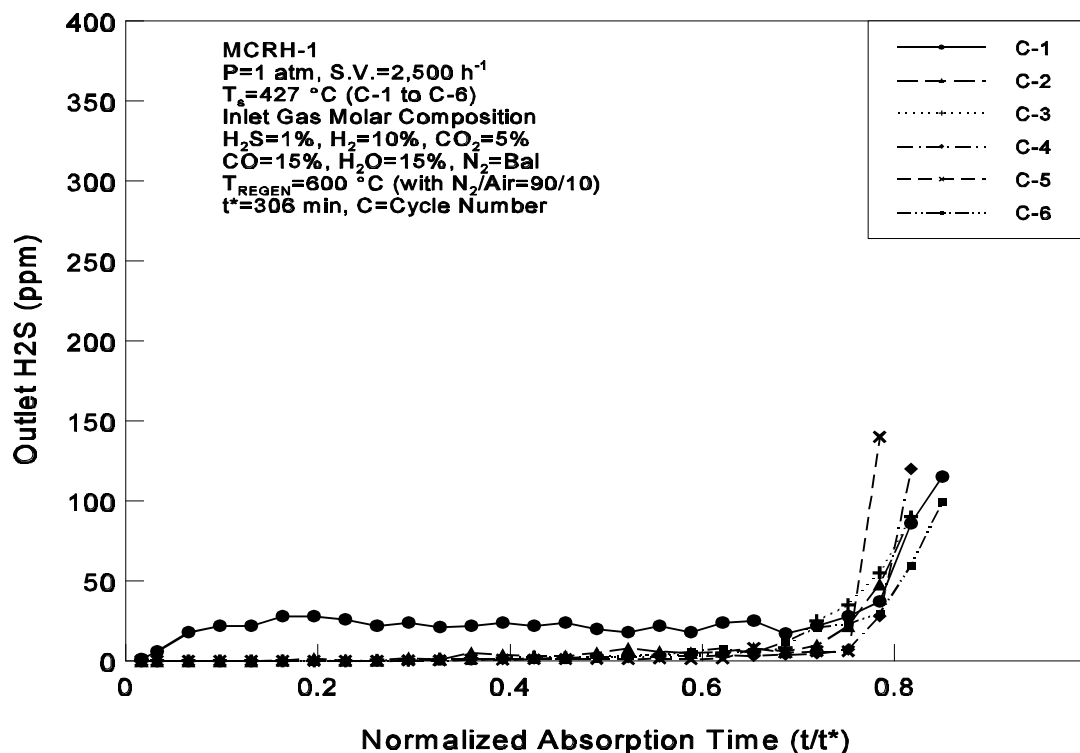

Figure 1. H_2S Breakthrough Curves in Successive Sulfidation Cycles of Sorbent MCRH-1

level remained at 0 ppm until 17 percent sorbent conversion and then gradually increased to ~5 ppm when conversion reached 80%. The sorbent conversions at 343 and 538 °C were 60 and 100%, respectively.

Figure 2 shows the H_2S breakthrough profiles for a another ZnO-based sorbent (MCRH-10) as a function of normalized time. Complete (>95%) sorbent conversion was observed at breakthrough at 800 °F, and the pre-breakthrough H_2S level was below 50 ppm.

Figure 3 shows the breakthrough profiles for a superior zinc-based sorbent (MCRH-25). This sorbent was modified to regenerate at temperataures as low as 475 to 525 °C. It was tested for 100 cycles of sulfidation in the laboratory-scale reactor. Regeneration between cycles was conducted with 10 mol% air-90 mol% with N_2 at 579 °C. However, in independent tests at Research Triangle Insititute, the sorbent was found to be fully regenerable at temperatures as low as 475 °C with 2% O_2. The gas hourly space velocity for the 100-cycle test was about 2,500 h^1 (STP) both in sulfidation and in regeneration. Sulfidation tests were carried out with a sulfidation gas containing 10 mol% H_2, 15 mol% CO, 5 mol% CO_2, 1 mol% H_2S, 15 mol% H_2O, and balance N_2. At 427 °C sulfidation, for cycles 1 to 20 the pre-breakthrough conversion was between 80 and 90%. For cycles 21 to 30 the conversion increased from 90 to 100% and remained constant at 100% conversion up to the 100 cycles.
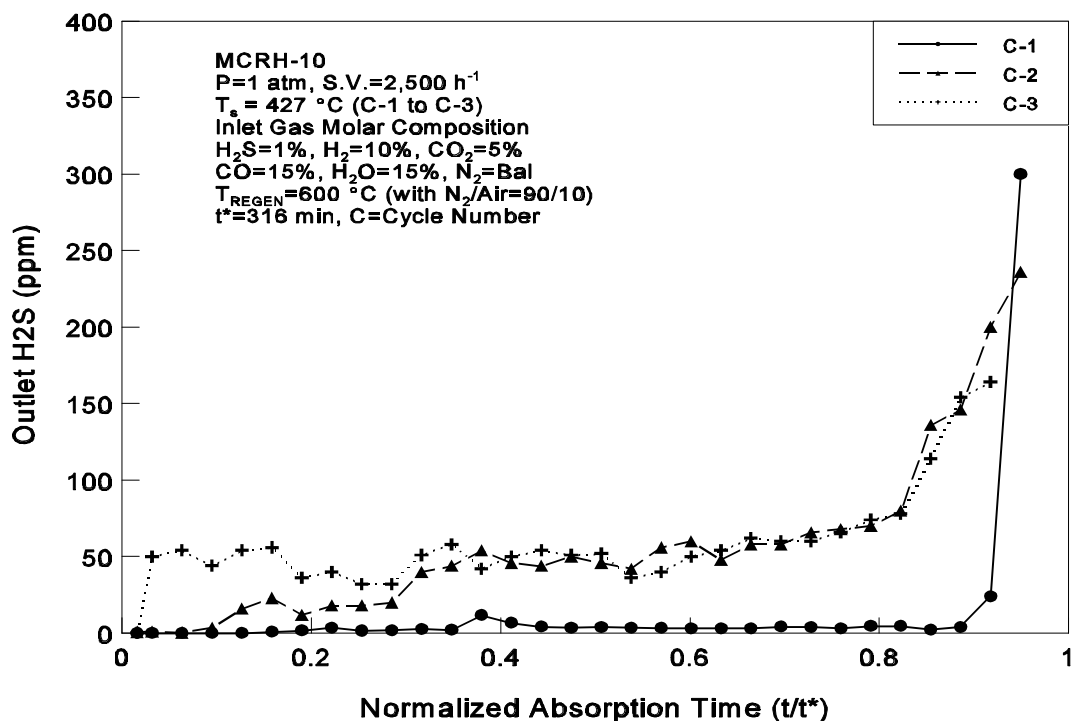

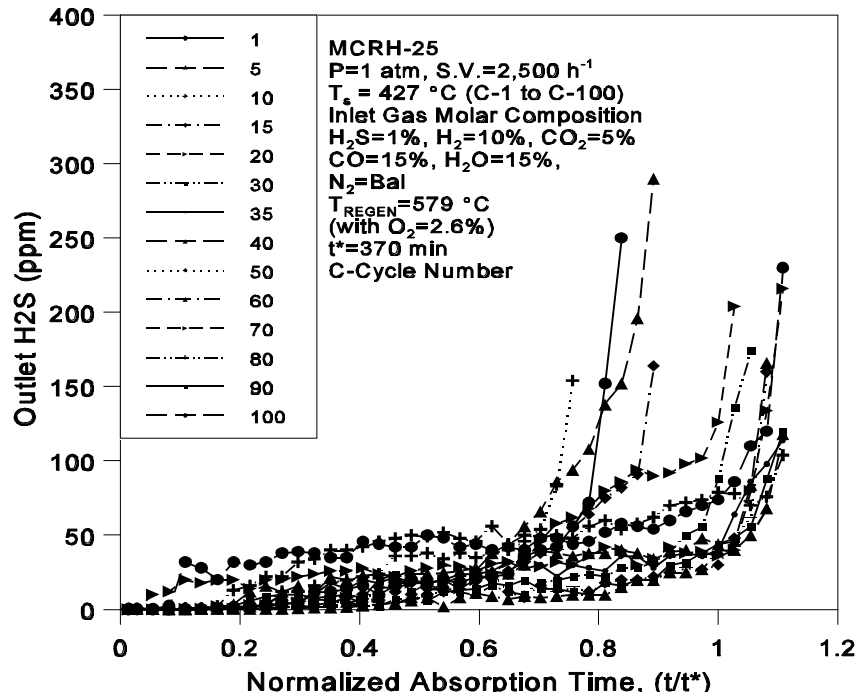Figure 2. H_2S Breakthrough Curves in Successive Sulfidation Cycles of Sorbent MCRH-10

Figure 3. H$_2$S Breakthrough Curves in Successive Sulfidation Cycles of Sorbent MCRH-25

There was no deactivation in 100 cycles in this fixed-bed study. The sulfur capacities of the MCRH-25 sorbent during cycles 1, 25, 50, 75, and 100 were 22.5, 27.7, 27.7, 27.7, and 27.7 gS/100 g of sorbent, respectively, again indicating a 100 percent capacity utilization even after 100 cycles. Sulfur capacity was calculated using the concentration of hydrogen sulfide in the feed, the breakthrough time, and the amount of sorbent used. The chemical reactivity was measured by using TGA for fresh, and 100-cycle used sorbent. The TGA results indicated that the rate of sulfur pickup for the fresh and the 100-cycle used sorbent remained relatively constant. An interesting observation was that the reactivity of the 100-cycle used sorbent was higher than that of the fresh sorbent in the TGA results. This result agreed with the observed increase in breakthrough time in the 100-cycle fixed-bed study.

Application

The 100-cycle test clearly demonstrated that the MCRH-25 sorbent does not chemically deactivate. This is in contrast to existing leading sorbents such as Z-sorb and ZT-4 that deactiviated significantly, as much as 50% in 50 to 100 cycles. Furethermore, the sorbent regenerated at temperatures as low as 475 °C, in conrast to current zinc-based sorbents taht require 600 °C or higher. As the current scale of tests is with powders only, the sorbent needs to

be made attrition resistant for moving-bed and fluidized-bed reactors. This research is currently ongoing.

Future Activities

The future activity will include development and testing of attrition resistant zinc-oxide-based sorbents for fluidized bed applications suitable for the Sierra-Pacific plant.

Acknowledgments

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