

Development of Advanced Hot-Gas Desulfurization Processes

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Introduction

Advanced integrated gasification combined cycle (IGCC) power plants nearing completion, such as Sierra-pacific, employ a circulating fluidized-bed (transport) reactor hot-gas desulfurization (HGD) process that uses 70-80 μm average particle size (aps) zinc-based mixed-metal oxide sorbent for removing H_2S from coal gas down to less than 20 ppmv. The sorbent undergoes cycles of absorption (sulfidation) and air regeneration. The key barrier issues associated with a fluidized-bed HGD process are chemical degradation, physical attrition, high regeneration light-off temperature, and high cost of the sorbent. Another inherent complication in all air-regeneration-based HGD processes is the disposal of the problematic dilute SO_2 containing regeneration tail gas. Direct Sulfur Recovery Process (DSRP), a leading first generation technology, efficiently reduces this SO_2 to desirable elemental sulfur, but requires the use of 1-3 % of the coal gas, thus resulting in an energy penalty to the plant. Advanced second-generation processes are under development that can reduce this energy penalty by modifying the sorbent so that it could be directly regenerated to elemental sulfur.

Objectives

The objective of this study is to develop (i) optimized low-cost sorbent materials with 70-80 μm average aps meeting all Sierra specs and (ii) modified fluidizable sorbent materials that can be regenerated to produce elemental sulfur directly with minimal or no use of coal gas.

Approach

A highly promising method was recently developed under this contract to prepare suitable sorbents. Based on fixed-bed microreactor screening of numerous sorbents, an attrition-resistant fluidizable sorbent designated MCRH-67 was selected for high temperature, high pressure (HTHP) testing. MCRH-67 sorbent formulation scaled up to 100 lb, by United catalysts, Inc. was extensively tested. The sorbent lost capacity during pure air regeneration. Effect of calcination temperature on sorbent capacity was evaluated. The sorbent surface is being modified to prevent

sintering during pure air regeneration.

Project Description

Sorbent Preparation

A highly promising method was developed under this project in cooperation 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 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 determination; and (4) atomic absorption (AA) spectrometry for elemental composition analysis.

Experimental Setup

The sorbent materials prepared were tested in a laboratory scale, HTHP 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 the 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 acted 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 (vol %) 10 H₂, 15 CO, 5 CO₂, 1 H₂S, 15 H₂O, and balance N₂. The outlet H₂S and SO₂ concentrations were monitored using a HP5890 gas chromatograph.

A typical run consists of loading the sorbent and heating the reactor to a desired temperature of 300-500°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 H₂S was measured continuously in the effluent gas. When the H₂S concentration in the effluent gas reached 500 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 400-550°C with pure air. In all the runs, space velocity used was in the range of 2000-3000 h⁻¹. The regeneration of the sulfided material was carried out until the SO₂ concentration in the reactor effluent dropped below 50 ppm. These sulfidation-regeneration cycles were repeated as many times as desired. Typically each material was tested for 5-10 cycles to obtain meaningful data on material durability. At the end of a 5-10 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 reaction.

Results

Table 1 shows that the attrition resistance of the sorbents prepared with our proprietary method is extremely high compared to first generation sorbents and it satisfies the target set by Kellogg for their transport reactor at the Sierra-Pacific Clean Coal Technology IGCC demonstration plant

Table 1. Attrition of Fresh and Used MCRH-67 Sorbent

Sorbent	<u>3-hole attrition loss (wt %)</u>	
	<i>1 hour</i>	<i>5 hour</i>
Fresh	1.2	1.9
Used, 3 cycles	1.0	1.6

The H₂S breakthrough results indicated essentially complete removal of H₂S until breakthrough in the 3 cycles. However, the pre-breakthrough level increased with cycling. Modifications were made to the sorbent to increase its ability to withstand high temperature and prevent loss of capacity due to sintering.

Figure 1 shows the breakthrough profiles for a recently prepared zinc-based sorbent FHR-23. Regeneration between cycles was conducted with pure air at 700°C. The gas hourly space velocity for the test was about 2500 h⁻¹ both in sulfidation and in regeneration. Sulfidation tests were carried out with a sulfidation gas containing (vol%): H₂=10%, CO=15%, CO₂=5%, H₂S=1.0%, H₂O=15% and bal N₂. FHR-23 sorbent showed excellent sulfidation behavior. The pre-breakthrough H₂S level was less than 100 ppm

Figure 2 show the H₂S breakthrough profiles for a another ZnO-based sorbent (FHR-32) as a function of time. The pre-breakthrough H₂S level was below 50 ppm.

Future Activities

Various formulations of sorbents with catalyst additives will be prepared and investigated for their ability to produce elemental sulfur during regeneration.

Contract Information

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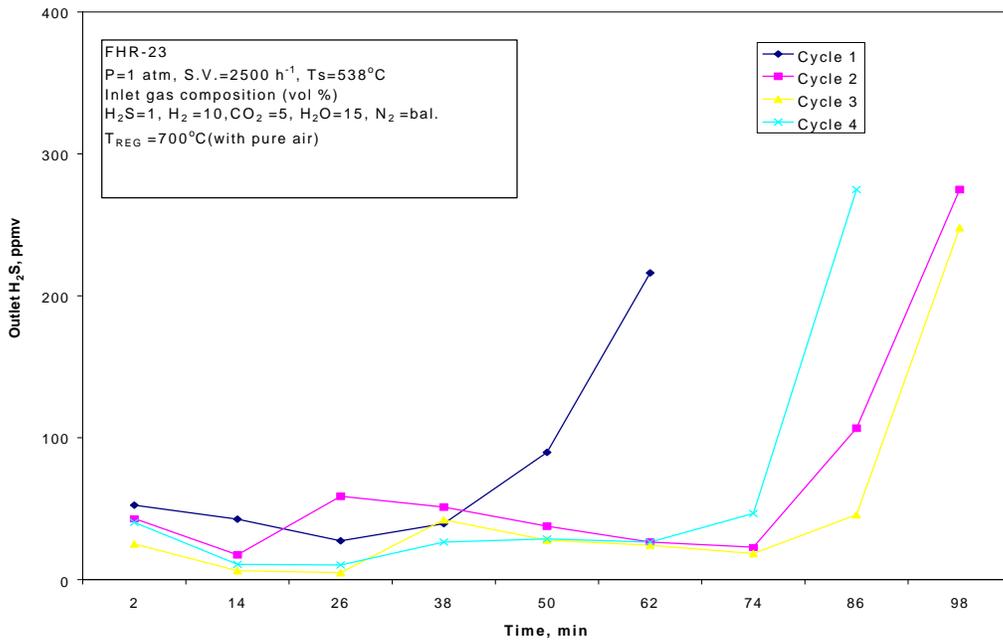


Figure 1. H₂S Breakthrough Curves in Successive Sulfidation Cycles of FHR-23

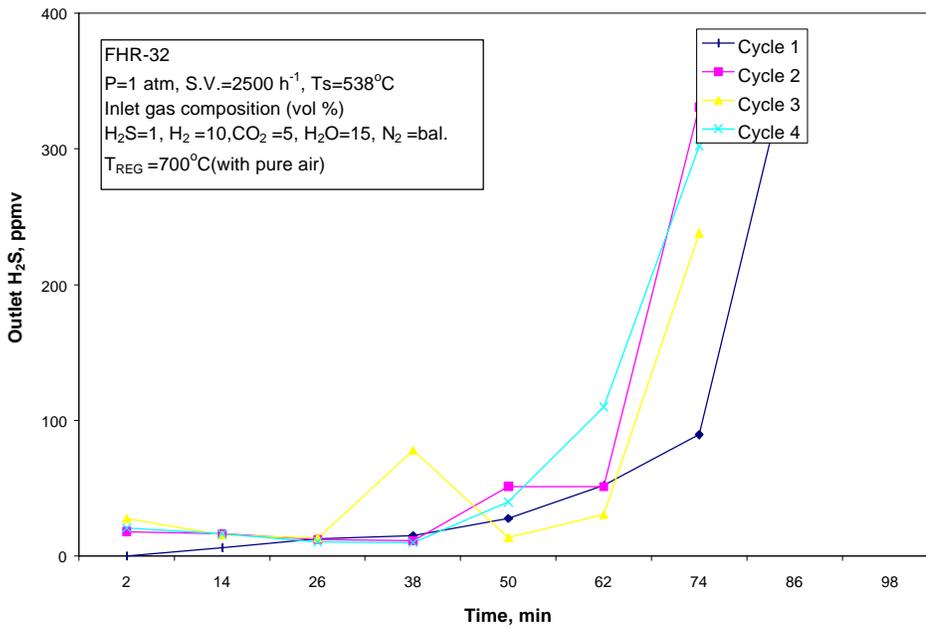


Figure 2. Breakthrough Behavior of FHR-32

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