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Development of Advanced Hot-Gas Desulfurization Sorbents

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Hampton University
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PB.15 Development of Advanced Hot-Gas Desulfurization Sorbents

CONTRACT INFORMATION

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DOE Project Officer	Kamalendu Das
Period of Performance	October 1, 1994 to September 30, 1995
Schedule and Milestones	

FY 1994 Program Schedule

	O	N	D	J	F	M	A	M	J	J	A	S
Test Plan	———	———										
Sorbent Preparation			———	———	———	———	———	———				
Sorbent Screening				———	———	———	———	———	———	———	———	

OBJECTIVES

The objective of this study is to develop hot-gas cleanup sorbents for relatively lower temperature application, with emphasis on the temperature range from 343-538°C (650-1000°F). A number of formulations will be prepared and screened for testing in a 1/2-inch fixed bed reactor at high pressure (1 to 20 atm) and high temperatures using simulated coal-derived fuel-gases. Screening criteria will include, chemical reactivity, stability, and regenerability over the temperature range of 343°C (650°F) to 538°C (1000°F). Each formulation will be tested for up to 5 cycles of absorption and regeneration. To prevent sulfation, catalyst additives will be investigated, which would promote a lower ignition of the regeneration. Selected superior formulation will be tested for long term (up to least 30 cycles) durability and chemical reactivity in the reactor.

BACKGROUND INFORMATION

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 higher thermal efficiency and lower gaseous, liquid, and solid discharges than conventional pulverized-coal-fired power plants. Hot gas cleanup offers the potentially key advantages of higher plant thermal efficiencies and lower costs due to the elimination of fuel gas cooling and associated heat exchangers.

Sorbents based on zinc oxide are currently the leading candidates and are being developed for moving-, and fluidized-bed reactor applications. Zinc oxide based sorbents can effectively reduce the H_2S in coal gas to 10 ppm levels. Most of the hot-gas desulfurization research has focused on the development of mixed-metal oxide sorbents for application at 538°C (1000°F) to 760 °C (1400°F).

This project aims to develop hot-gas cleanup sorbents for relatively lower temperature applications, 343°C (650°F) to 538°C (1000°F) with emphasis on the temperature range from 400 to 500°C. There are a number of reasons for development of sorbents suitable for this temperature range. 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. Another important reason to reduce hot-gas cleanup severity is to reduce the operating temperatures and temperature swings of on-off valves and vessels for cyclic fixed-bed desulfurization/regeneration systems, lock-hopper valves for moving-bed applications, and the turbine load control valves. Finally, the current plans in Europe call for hot-gas desulfurization system operation at 350-600 °C. Also iron-oxide process development studies in Japan have concentrated on a temperature range of 400-600 °C. Thus development of suitable advanced sorbents in this temperature range is necessary to remain in the forefront in hot-gas cleanup technology.

PROJECT DESCRIPTION

Sorbent Preparation and Characterization

A highly promising method was recently developed under this contract to prepare suitable sorbents. Zinc oxide based sorbents was prepared using this proprietary technique. The following analytical techniques was used to characterize the fresh, sulfided and regenerated sorbents

1. X-ray Diffraction (XRD) for crystalline phase.
2. Surface area measurement will be based on the standard BET method.
3. Hg-porosimetry for pore volume, bulk density, average pore diameter and pore size distribution determination.
4. Atomic Absorption (AA) Spectrometry for elemental composition analysis.

Experimental Setup

The sorbents were evaluated with respect to their sulfidation-regeneration performance, in a packed-bed microreactor. The set-up is shown schematically in Figure 1.

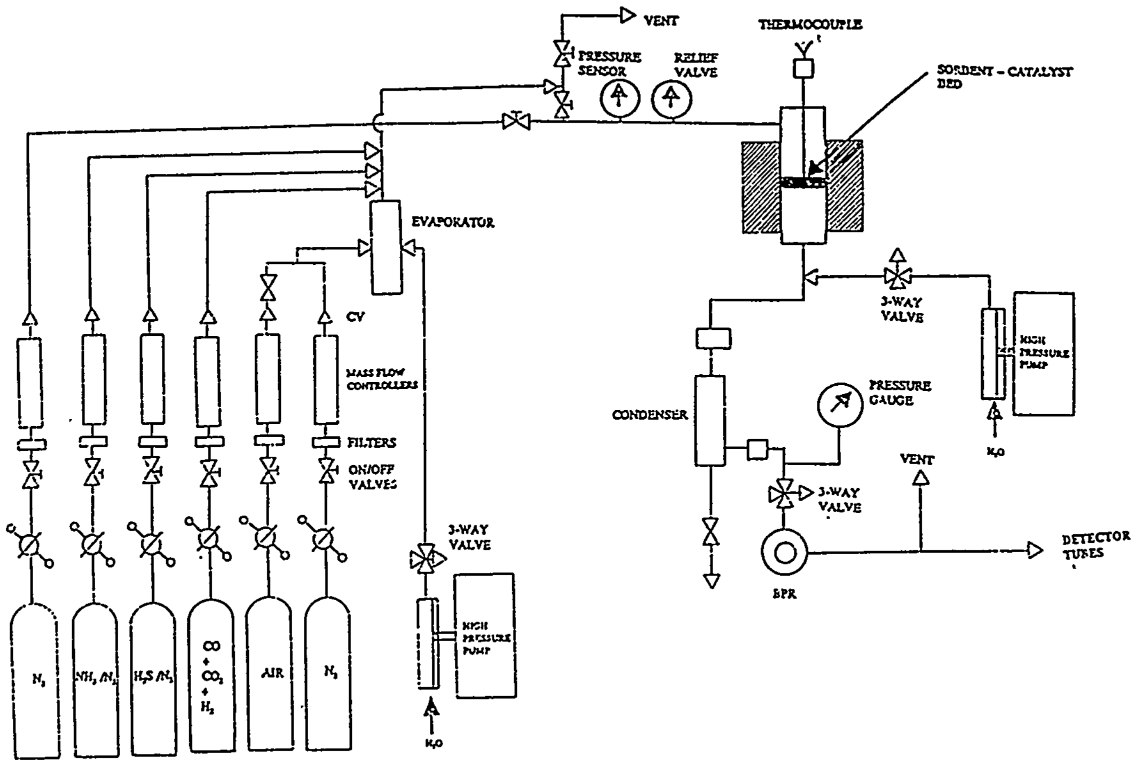

Figure 1. Schematic of the Reactor System for Sulfidation and Regeneration Studies

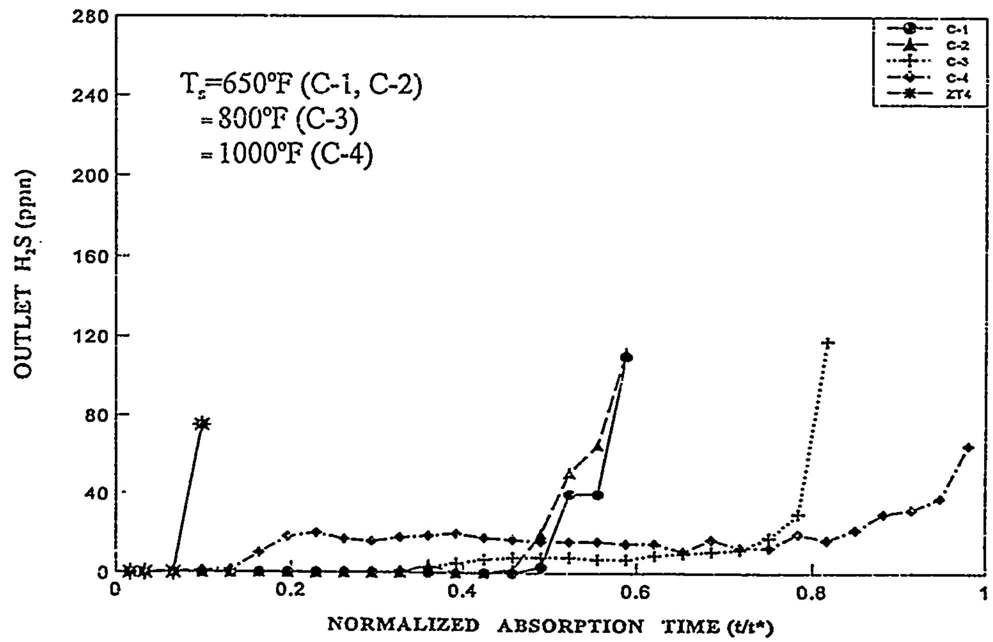

Figure 2. H_2S Breakthrough Curves in Successive Sulfidation Cycles of Sorbent MCRH-1

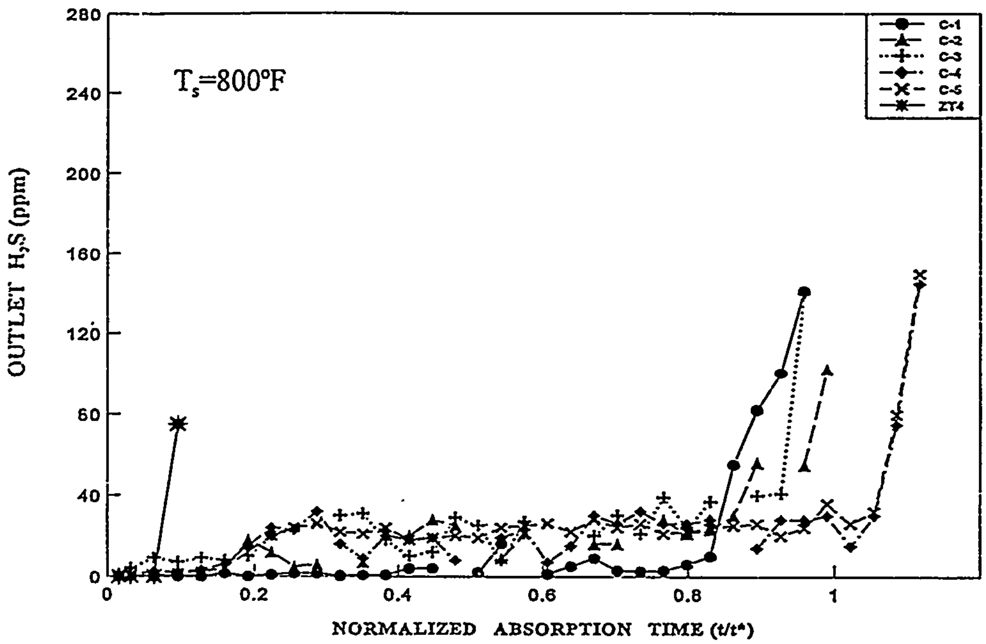

Figure 3. H_2S Breakthrough Curves in Successive Sulfidation Cycles of Sorbent MCRH-10

This system includes a feed gas supply section in which the simulated coal gas components, supplied from standard high-pressure cylinders equipped with pressure regulators, are mixed and metered by a battery of electronic mass flow controllers. Steam is added to the mixed dry gas by vaporizing liquid water injected into the gas stream at a controlled rate by a high pressure metering pump. The pressure inside the reactor is controlled by a back pressure regulator and measured by an electronic pressure sensor. The bed temperature is measured by a chromel-alumel thermocouple. The product gas is passed through ice traps to condense water, and then analyzed for H_2S, and SO_2 by Matheson gas detector tubes.

TEST 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 bal N_2. Figure 2 show the H_2S breakthrough profiles as a function of normalized time. In tests with the MCRH-1 sorbent conducted at 800°F , the sorbent conversion at breakthrough was 80 percent. In fact, the H_2S level remained at 0 ppm until 17 percent sorbent conversion and then gradually increased to ~5 ppm when conversion reached 80 percent. The sorbent conversion at 650 and 1000°F was 60 and 100 percent respectively. Under the same conditions, at 800°F ZT-4 (currently the leading sorbent) conversion was less than 10%.

Figure 3 show the H_2S breakthrough profiles for a another ZnO-based sorbent(MCRH-10) as a function of normalized time. Complete (100%) sorbent conversion was observed at breakthrough at 800°F and the pre-breakthrough H_2S level was below 35 ppm.

FUTURE WORK

Various formulations of sorbents with

catalyst additives will be prepared and investigated for their ability to be regenerated at lower temperature.

PUBLICATION/PRESENTATION

K. Jothimurugesan, A.A. Adeyiga and S.K. Gangwal "Development of Advanced Hot-Gas Desulfurization Sorbents" Project Review Meeting, DOE/METC, February 24, 1994

K. Jothimurugesan, A.A. Adeyiga and S.K. Gangwal "Development of Advanced Hot-Gas Desulfurization Sorbents" 1995 Annual AIChE Meeting, November-17,Miami Beach, FL. Abstract submitted

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