DOE/MT/95011--T1

Scale-Up of Advanced Hot-Gas Desulfurization Sorbents

CONTRACT INFORMATION

Contract Number:	DE-FG22-95MT95011
Contractor	Hampton University Department of Chemical Engineering Hampton, Virginia 23668
Principal Investigators	K. Jothimurugesan Adeyinka A. Adeyiga Santosh K. Gangwal (RTI)
DOE Project Officer	Kamalendu Das
Reporting Period	October 1, 1995 - March 31, 1996

OBJECTIVES

The overall objective of this project is to develop regenerable sorbents for hot gas desulfurization in IGCC systems. The specific objective of the project is to develop durable advanced sorbents that demonstrate a strong resistance to attrition and chemical deactivation, and high activity at temperatures as low as 343°C(650°F). A number of formulations will be prepared and screened in a ½-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 to 650° C. After initial screening, at least 3 promising formulations will be tested for 25-30 cycles of absorption and regeneration. One of the superior formulations with the best cyclic performance will be selected for investigating scale up parameters. The scaled-up formulation will be tested for long term durability and chemical reactivity.

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. In these advanced systems, coal is gasified to produce a gas at high temperature and high pressure (HTHP) conditions. The hot gas is cleaned

DISCLAIMER

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 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 25-30 cycles. Stability of the hot-gas desulfurization step over 100s of cycles is essential for improved IGCC economics over conventional power plants. Thus a pressing need exists for developing durable second generation sorbents with much improved and stable reactivity during cyclic operation.

The overall objective of this project is to develop regenerable sorbents for hot gas desulfurization in IGCC systems. The specific objective of the project is to develop durable advanced sorbents that demonstrate a strong resistance to attrition and chemical deactivation, and high activity at temperatures as low as 343°C(650°F). With UCI's and RTI's assistance, a promising sorbent preparation technique likely to lead stable sorbents has been identified. Using this technique, a number of formulations will be prepared and screened in a ½-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 to 650°C. After initial screening, at least 3 promising formulations will be tested for 25-30 cycles of absorption and regeneration. One of the superior formulations with the best cyclic performance will be selected for investigating scale up parameters. The scaled-up formulation will be tested for long term durability and chemical reactivity.

PROJECT DESCRIPTION/RESULTS AND ACCOMPLISHMENTS

The project consists of three major experimental tasks (Tasks 1-3) addressing the contract objectives described above.

Task 1: Optimization of Preparation

Task 2: Investigation of Scale-Up

Task 3: Preparation of 100 lb Batch

Task 1: Optimization of Preparation

A highly promising method was recently developed to prepare suitable sorbents. Various sorbents were prepared by our proprietary method. The main parameters we have varied was various concentrations of starting materials and ageing conditions. The starting compounds was chosen based on water solubility, commercial availability and low costs and that avoid introducing elements that may be deleterious in the final sorbent or that cause difficulties in subsequent processing. These prepared sorbents will be tested soon in the fixed bed reactor.

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.

Since MCRH-10 (which has no catalyst additives) sorbent showed excellent sulfidation and regeneration behavior in the short cycles, it was decided to investigate the feasibility of low temperature regeneration, at about 500°C. The low temperature regeneration capability of the sorbent is required for Kellogg's transport reactor application. The MCRH-10 sorbent was evaluated in a bubbling fluidized-bed mode. The following paragraphs will provide the detailed description of the experimental system and procedure.

The MCRH-10 sorbent was evaluated in an atmospheric quartz fludized-bed bench-scale unit. The fludized-bed reactor is a quartz tube (26 mm I.D. and 100 cm long) separated by a coarse quartz frit located midway in the tube. The sorbent powder is supported on the quartz frit. The section below the frit (lower section of the reactor which is 50 cm long) is packed with quartz rings (approximately 0.5 cm diameter and 0.7 cm long). The reactor is heated by an electric furnace.

During sulfidation, the coal gas source is a tank consisting of premixed gases, namely, 49.8% H_2, 23.4% CO_2, 13.4% CO, 12% N_2 and 1.4% H_2S. Steam is generated by feeding water at the

reactor bottom through a syringe pump. Desired composition of coal gas (44.3% H_2, 20.8% CO_2, 11.9% CO, 11.05% H_2O, 10.7% N_2, and 1.25% H_2S) is obtained by feeding metered quantity of dry coal gas and water at the reactor bottom. During regeneration, desired concentration of O_2 is obtained by feeding metered quantities of N_2 and air.

The effluent gas from the sorbent bed is passed through a condenser, where the steam is condensed and collected in a catch pot. The coolant in the condenser is maintained at 5°C using a chiller. During sulfidation, the effluent gas after the condenser catch pot is directly vented to the hood without measuring the reactor outlet H_2S concentration. However, during regeneration, the effluent gas after the catch pot is analyzed using a Western Research SO_2 Analyzer (Model 721-AT) and the O_2 concentration by using a Teledyne Trace O_2 Analyzer. The dead volume is minimized by directly piping reactor effluent to the analyzers.

The reactor was loaded with 20.1 g of MCRH-10 sorbent and heated in 800 sccm of N_2. After the bed reached 427°C, the sorbent was exposed to 900 sccm of the simulated coal gas (of composition as given above) was passed for 4 h. After sulfidation, the reactor was purged with N_2 for about 10 minutes before initiating sorbent regeneration.

Sorbent regeneration was performed with 500 sccm of approximately 3 vol.% O_2 in N_2. Regeneration was started at 475°C. The sorbent bed temperature was increased 25°C when the SO_2 concentration in the effluent had peaked and was decreasing. The bed temperature was increased to sustain/restart the regeneration and/or to decompose the sulfates formed.This increase in bed temperature by 25°C at the onset of decrease in SO_2 concentration was continued till the bed temperature reached 625°C. At 625 C, the regeneration was continued until O_2 breakthrough occurred, following which the bed was cooled under N_2 flow.

Regeneration was started at 475°C. Figure 1 shows SO_2 and temperature profiles obtained during regeneration. Oxygen breakthrough was observed almost immediately. Oxygen concentration remained high until the bed temperature reached 570° C. As the bed temperature increased from 570°C, oxygen content of the effluent dropped to zero and SO_2 concentration of the effluent increased to 2 vol%, which is roughly the stoichiometric amount expected with 3 Vol% O_2 in N_2. Table 1 provides SO_2 and O_2 concentrations in the reactor effluent during regeneration. The results clearly show that the sulfided sorbent can be ignited as low as 575°C.

Task 2. Investigation of Scale-Up

Forming operations to making particles for both fluidized-bed and moving bed was investigated by a balance among several factors, including rheological properties of the mixture, and the necessity to achieve satisfactory strength, an open-pore structure, and high activity for hydrogen sulfide removal. Suitable rheological properties was obtained by incorporating certain organic (e.g. methocel) and inorganic binders (e.g. kaolin and bentonite) and micropore formers.

Hampton, RTI and UCI team so far worked on the forming operations of MCRH-25 material to improve the strength of the material. Following list will provide what we have done so far.

PP-3488 3000 g oxides dried at 302°F overnight, 2.5% bentonite, 5% kaolin, pelletize .11-.12

PP-3488-1 3000 g oxides dried at 302°F overnight, 2.5% bentonite, 5% kaolin, 3% starch, pelletize .11-.12

PP-3512 2500 g oxides calcined at 537°C for 1 hour, 2.5% bentonite, 5% kaolin, pelletize .12

PP-3563-1 3000 g oxides calcined at 537°C for 1 hour, 5% bentonite, pelletize .11-.12

PP-3563-2 3000 g oxides calcined at 537°C for 1 hour, 5% bentonite, 0.25 methocel, pelletize .11-.12

PP-3588 3000 g oxides (5% bentonite in ppt) calcined at 315°C overnight, 5% bentonite

PP-3589 3000 g ball-milled oxides (5% bentonite in ppt) calcined at 315°C overnight, 5% bentonite

All of the samples have <5 lb crush strength when calcined at 700-750°C. Additional work is underway to further improve the crush strength of the materials.

Further a 5890-Hewlett Packard gas chromatography (with Flame Photometric Detector and Thermal Conductivity Detector)has been purchased and installed.

FUTURE WORK

Various formulations of sorbents with and without catalyst additives will be prepared, formed, and then it will be investigated for its ability to remove hydrogen sulfide.

TIME SCHEDULE FOR YEAR 1

TASK	Semiannual	
	1	2
Sorbent Preparation		
Sorbent Characterization		
Sorbent Evaluation		
Investigation of Scale-Up		
Semiannual Reports	✍	✍

PUBLICATION/PRESENTATION

1. K. Jothimurugesan, A.A. Adeyiga and S.K. Gangwal "Regenerable Sorbents for Desulfurization of Coal Gas", Fourth Annual HBCUs/Private Sector Energy Research and Development Technology Transfer symposium, Greensboro, NC, April 2-4, 1996.

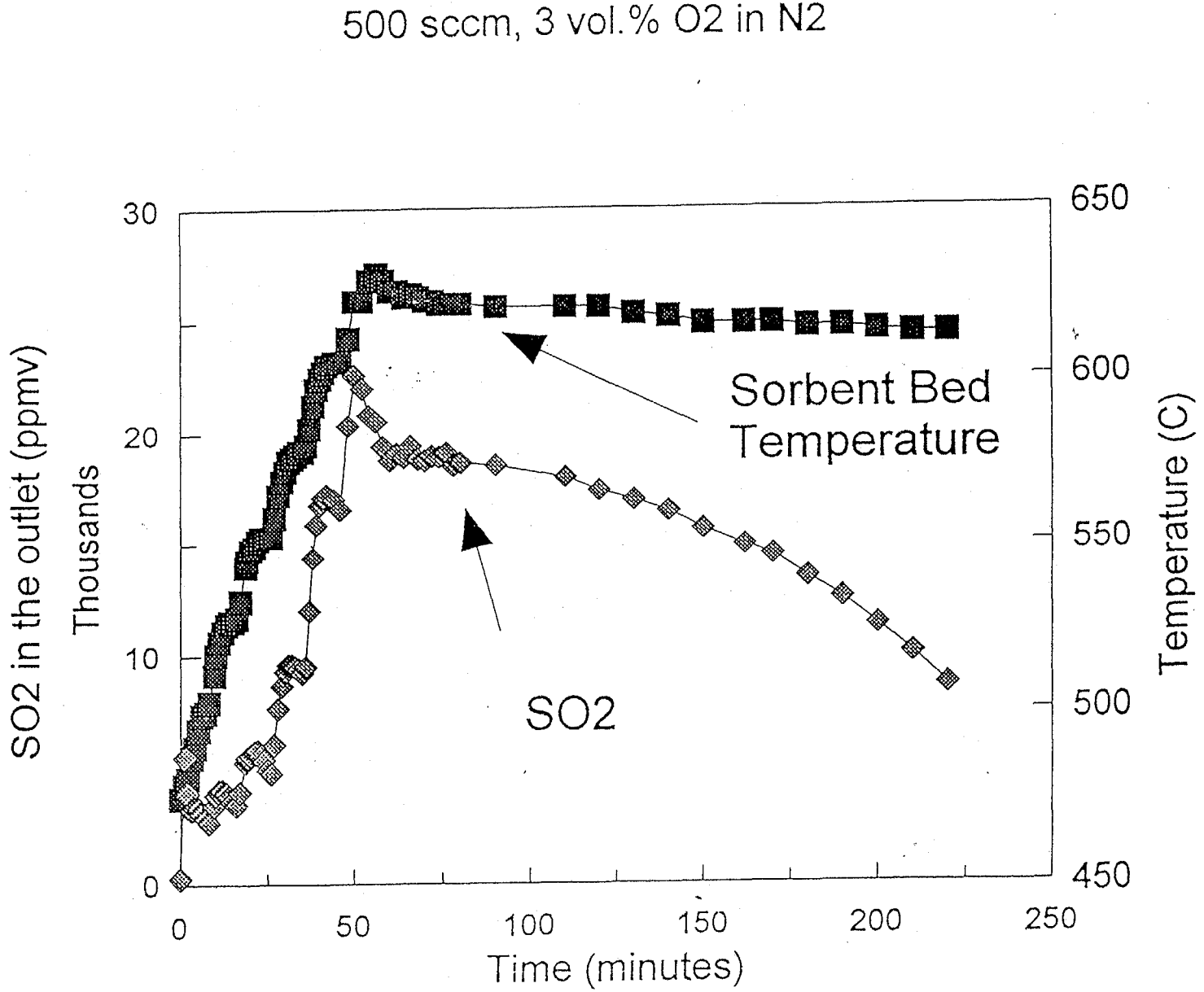
Regeneration using MCRH-10 Sorbent
500 sccm, 3 vol.% O2 in N2
SO2 in the outlet (ppmv)
Thousands
30
20
10
0
650
600
550
500
450
Temperature (C)
0
50
100
150
200
250
Time (minutes)
Sorbent Bed Temperature
SO2

Figure 1

Table 1. Time Variation of the Bed Temperature, SO_2 Concentration and O_2 Concentration During Regeneration.

Time (minutes)	Event	Bed Temperature (°C)	SO_2 Concentration (ppmv)	O_2 Concentration (%)
0	Regeneration started	475	260	0
1	-	479	5600	0
2	Temperature increased	481	3980	2
4	-	490	3360	2
6	-	499	3120	2
7	Temperature increased	500	2890	2
12	-	524	4130	2
14	-	527	3840	2
15	Temperature increased	566	3630	2
22	-	551	5840	2
25	-	552	5000	2
26	Temperature increased	552	4820	2
31	-	575	9610	1.4
34	-	578	9410	1.3
35	Temperature increased	578	9220	1.3
42	-	604	17280	0.3
44	-	605	17000	0.35
46	Temperature increased	605	16520	0.4
50	-	623	22660	0
162	O_2 Breakthrough	616	14890	0.7