

**SIMULTANEOUS REMOVAL OF H<sub>2</sub>S AND NH<sub>3</sub> IN COAL GASIFICATION PROCESSES**

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**Contract Number:**

DE-FG22-93MT93005

**Conference Title:**

Coal-Fired Power Systems 94 -- Advances in IGCC and PFBC  
Review Meeting

**Conference Location:**

Morgantown, West Virginia

**Conference Dates:**

June 21-23, 1994

**Conference Sponsor:**

U.S. Department of Energy, Office of Fossil Energy, Morgantown Energy  
Technology Center

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## Simultaneous Removal of H<sub>2</sub>S and NH<sub>3</sub> in Coal Gasification Processes

### CONTRACT INFORMATION

Contact Number DE-FG22-93MT93005

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Period of Performance September 2, 1993 to September 1, 1996

### Schedule and Milestones

#### FY 1993 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A
Test Plan	_____											
Fabrication		_____										
Sorbent-Catalyst Preparation					_____							
Sorbent-Catalyst Screening										_____		

### OBJECTIVES

The objective of this study is to develop advanced high-temperature coal gas desulfurization mixed-metal oxide sorbents with stable ammonia decomposition materials at 550-800° C (1022-1472° F). The specific objectives of the project are to: (i) Develop a combined sorbent-catalyst materials shall be capable of removing hydrogen sulfide to less than 20 ppmv and

ammonia by at least 90 percent. (ii) Carry out comparative fixed-bed studies of absorption and regeneration with various formulations of sorbent-catalyst systems and select most promising sorbent-catalyst type. (iii) Conduct long-term (at least 30 cycles) durability and chemical reactivity in the fixed-bed with the superior sorbent-catalyst.

## BACKGROUND INFORMATION

Nitrogen ( $N_2$ ) occurs in coal in the form of tightly bound organic ring compounds, typically at levels of 1 to 2 wt% on a dry-ash-free basis. During coal gasification, this fuel-bound nitrogen is released principally as ammonia and nitrogen, with smaller levels of HCN. The formation of  $NH_3$  in a coal gasification process is a function of the fuel gas composition and the gasifier operating conditions. During the use of coal gas to generate electricity in gas-fired turbines, fuel bound ( $N_2$ ) is converted to nitrogen oxides ( $NO_x$ ), which are difficult to remove and are highly undesirable as atmospheric pollutants. Recent results indicate that while the efficiency of molten carbonate fuel cell (MCFC) anodes is not effected by exposure to  $NH_3$ ,  $NO_x$  is generated during combustion of the anode exhaust gas. Thus,  $NH_3$  must be removed from the coal gas before it is used in IGCC or MCFC applications.

The product stream from a high temperature, oxygen-blown gasifier, such as Texaco, contains about 2000 ppmv of  $NH_3$ , where higher concentrations (about 5000 ppmv) occur when the gasification is conducted at lower temperatures, such as in the Lurgi or GE air-blown gasifier. A range of 1500 to 3000 ppmv is considered for this study.

Removal of  $H_2S$  using zinc-based sorbents, particularly zinc titanate, to < 20 ppmv levels has been well established (Lew et al., 1989; Jothimurugesan and Harrison, 1990; Woods et al., 1990; Gupta and Gangwal, 1993). Previous literature study indicated that catalysts have high activities for  $NH_3$  decomposition (Krishnan et al., 1988). If desulfurization sorbents such as zinc titanate could be used along with the  $NH_3$  decomposition catalysts to decompose

ammonia present in hot coal gas, then the number of unit processes necessary to clean hot coal gas could be reduced by one.

The objective of this project is to develop successful combination of an  $NH_3$  decomposition catalyst with the mixed-metal oxide sorbent so that the sorbent-catalyst activity remains stable for  $NH_3$  decomposition in addition to  $H_2S$  removal under cyclic sulfidation-regeneration conditions in the temperature range of 550–800° C (1022–1472° F) and pressures up to 20 atm.

## PROJECT DESCRIPTION

### Sorbent-Catalyst Preparation

The mixed metal-oxide sorbent (Zinc Titanate) was prepared by the coprecipitation method in order to generate as high a surface area as possible. In order to investigate the effect of calcination temperature, three zinc titanates were calcined at 600, 700 and 800°C. The surface area variations with temperature is shown in Figure 1. As the calcination temperature increases from 600 to 800° C, the surface area decreases from 89 to 19 m<sup>2</sup>/g. The ammonia decomposition catalyst was added to zinc-titanium oxide by impregnation technique. After the impregnation, the material was dried at 110° C (230° F), followed by calcination in air at 800° C (1472° F) for 1 hour.

### Experimental Setup

The laboratory-scale fixed-bed reactor system constructed is shown schematically in Figure 2 to determine the activity of the sorbent-catalyst formulations for their ammonia decomposition activity and  $H_2S$  removal ability using a simulated coal gas. The simulated coal gas will be

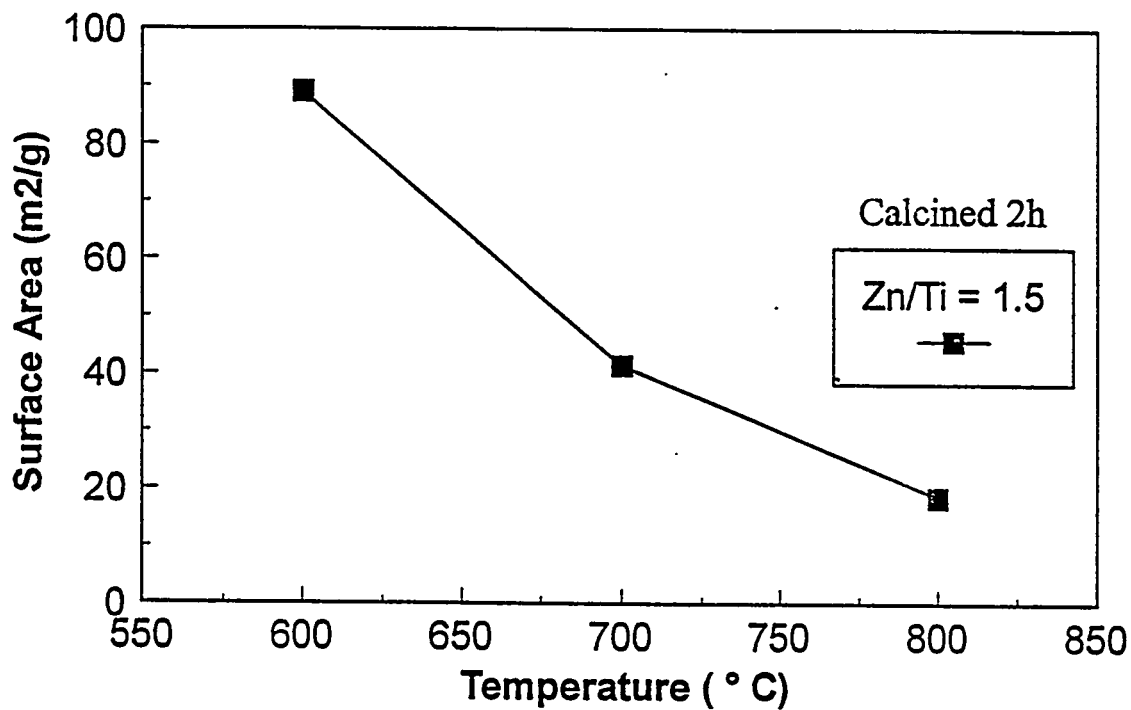


Figure 1. Effect of Calcination Temperature on the Zn-Ti-O Surface Area

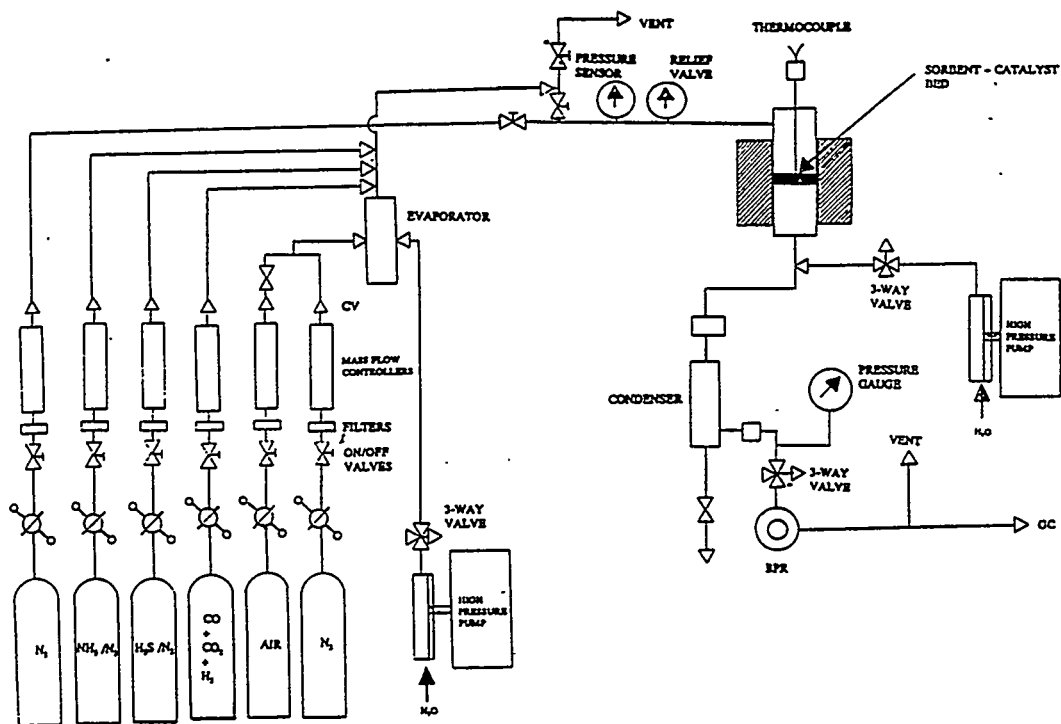
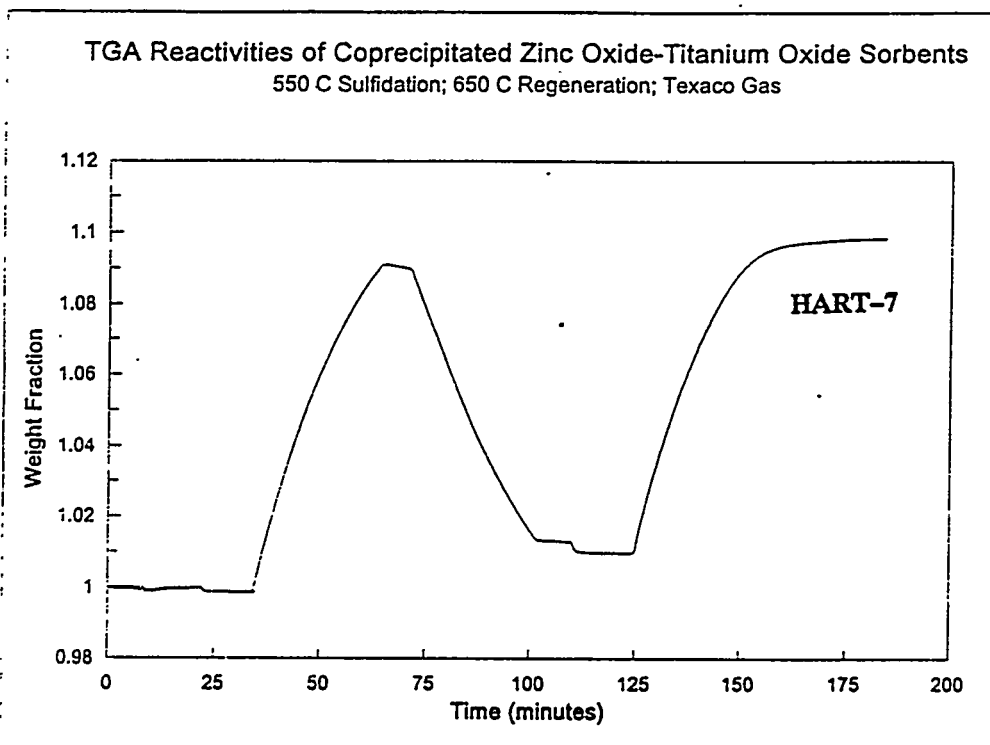


Figure 2. Schematic Diagram of Fixed-Bed Reactor System



**Figure 3. TGA Reactivities of Coprecipitated Zinc Oxide-Titanium Oxide Sorbents**

prepared by blending the pure and pre-mixed gases. The flow rates of these gases will be controlled and monitored by high pressure mass flow controllers. Steam will be added to the mixed dry gas by vaporizing liquid water injected into the gas stream at a controlled rate by a high pressure syringe pump. The pressure inside the reactor will be controlled by a back pressure regulator and will be measured using an electronic pressure sensor. The thermocouples are positioned to measure the temperatures of the preheated feed gas, reactor bed temperature and the temperature of the product gas. The product gases will be analyzed for  $H_2S$  and  $NH_3$  by using Detector Tubes and Ion-Selective Electrodes.

### TEST RESULTS

The TGA reactivity of the sorbents was measured in simulated Texaco gas (with about 1%  $H_2S$ ) at 550° C (Figure 3) using the RTI, TGA facilities. TGA runs consisted of a 550° C sulfidation, 650°C regeneration with 2%  $O_2$ , 18%  $H_2O$ , balance

$N_2$ , followed by a second sulfidation. As seen from Figure 3, the HART-7 sample showed excellent reactivity.

### FUTURE WORK

Various formulations of sorbent-catalyst will be prepared and then it will be tested in the fixed bed reactor system.

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