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FLUIDIZED-BED SORBENTS

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Fluidized-Bed Sorbents

CONTRACT INFORMATION

Contract Number	DE-AC21-88MC25006
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Period of Performance	September 21, 1988 to November 20, 1994

Schedule and Milestones

FY94 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A
Scaleup of Granulation	—	—	—	—	—	—						
Z-SORB Sorbent Testing		—	—	—	—	—	—					
Topical Report							—	—	—	—		
Life-Cycle Test with ZT-4										—	—	—
Large Sorbent Batch									—	—	—	—
Technology Transfer	—	—	—	—	—	—	—	—	—	—	—	—

OBJECTIVES

The objectives of this project are to identify and demonstrate methods for enhancing long-term chemical reactivity and attrition resistance of zinc oxide-based mixed metal-oxide sorbents for desulfurization of hot coal-derived gases in a high-temperature, high-pressure (HTHP) fluidized-bed reactor. Specific objectives of this study are the following:

- Investigating various manufacturing methods to produce zinc ferrite and zinc titanate sorbents in a particle size range of 50 to 400 μm;

- Characterizating and screening the formulations for chemical reactivity, attrition resistance, and structural properties;

- Testing selected formulations in an HTHP bench-scale fluidized-bed reactor to obtain an unbiased ranking of the promising sorbents;

- Investigating the effect of various process variables, such as temperature, nature of coal gas, gas velocity, and chemical composition of the sorbent, on the performance of the sorbent;

- Life-cycle testing of the superior zinc ferrite and zinc titanate formulations under HTHP conditions to determine their long-term chemical reactivity and mechanical strength;

- Addressing various reactor design issues;

- Generating a database on sorbent properties and performance (e.g., rates of reaction, attrition rate) to be used in the design and scaleup of future commercial hot-gas desulfurization systems.

- Transferring sorbent manufacturing technology to the private sector; and

- Producing a large batch (in tonnage quantities) of the sorbent to demonstrate commercial feasibility of the preparation method.

BACKGROUND INFORMATION

Research Triangle Institute (RTI) is assisting the U.S. Department of Energy/Morgantown Energy Technology Center (DOE/METC) in the development of a fluidized-bed hot-gas desulfurization system employing ZnO-based mixed metal-oxide sorbents for removal of sulfurous compounds (e.g., H_2S, COS, CS_2) at high-temperature (500 to 750 °C [932 to 1,382 °F]), high-pressure (15 to 20 atm) conditions. Desulfurization of hot coal gas in a fluidized-bed reactor offers a number of potential advantages over fixed beds. Although fixed-bed reactors are operationally simple and provide high sorbent sulfur capacity and zinc utilization and low sulfur breakthrough, they suffer from some serious problems including the need to use hot valves and poor ability to control the temperature during highly exothermic regeneration. Recently, severe spalling and decrepitation of zinc titanate sorbent pellets in fixed beds surfaced as a serious problem owing to the formation of zinc sulfate and subsequent expansion in molar volume during regeneration (Mei et al., 1993). In contrast, fluidizable zinc titanate particles became stronger with cycling and do not suffer from sulfate formation problems (Gupta and Gangwal, 1993). Additionally, fluidized-bed reactors have a number of advantages including easier control of temperature during regeneration, use of small particles leading to faster overall kinetics, and nearly continuous steady-state operation. However, a highly reactive and attrition-resistant sorbent is required, and scaleup and turndown limitations exist for fluidized-bed systems.

PROJECT DESCRIPTION

In this program, regenerable ZnO-based mixed metal-oxide sorbents are being developed and tested. These include zinc ferrite, zinc titanate and Z-SORB sorbents. The Z-SORB sorbent is a proprietary sorbent developed by Phillips Petroleum Company (PPCo).

Design and Construction of an HTHP Bench-Scale Sorbent Test Facility

During the first phase (1989) of this program, a 3-in. ID bench-scale HTHP semi-batch fluidized-bed reactor system was designed and constructed. This reactor operates in a semi-batch mode because the flow of gas phase is continuous while sorbent particles remain in the reactor. This system is capable of operation at up to 871 °C

(1,600 °F) at 20 atm. Any simulated coal gas can be generated in this system using a battery of eight mass flow controllers and three positive displacement pumps (for pumping liquid water to generate steam). This system is equipped with a state-of-the-art computer controlled data acquisition system. A series of gas chromatographs (GCs) and continuous on-line analyzer measure the concentrations of various species in the reactor exit gas such as H_2S, COS, SO_2, CO_2, H_2, CH_4, N_2, CO, O_2. A complete description of this test facility is given elsewhere (Gupta and Gangwal, 1992; 1993).

Development and Testing of Zinc Ferrite Sorbents

Earlier work in this program was focused on preparing fluidizable zinc ferrite particles in 50- to 300-µm particle diameter range. A number of sorbent preparation techniques were investigated including spray drying, impregnation, crushing the durable extrudates and screening, and granulation.

Of these techniques investigated, granulation proved to be the most successful and a number of zinc ferrite sorbent formulations were prepared using this technique. Testing of these sorbents in the HTHP bench reactor demonstrated that these sorbents possess sulfur capacity and attrition resistance as good as or better than sorbents prepared by crushing and screening. Results of bench-scale testing of selected sorbent formulations are described elsewhere (Gupta and Gangwal, 1991).

With zinc ferrite sorbents, excessive sorbent loss was observed at a sulfidation temperature of 625 °C (1,157 °F). It is thought that attrition of the sorbent in the reactor is primarily due to chemical transformations rather than mechanical forces. Possible chemical transformations responsible for attrition are excessive reduction of $ZnFe_2O_4$ and iron carbide formation (Gupta and Gangwal, 1991; Gupta et al., 1992).

The applicability of zinc ferrite as a hot-gas desulfurization sorbent, therefore, is conservatively limited to below 550 °C (1,022 °F) and to moderately reducing coal gases, such as low-Btu gas from an air-blown gasifier containing at least 15 percent water vapor. Higher temperatures, as shown in the study, led to excessive sorbent weakening.

Development and Testing of Zinc Titanate Sorbents

To extend the operating temperature and desulfurize highly reducing coal gases, zinc titanate sorbent was developed for fluidized-bed reactors. Following the success of the granulation technique with zinc ferrite sorbents, it was used to prepare a series of zinc titanate formulations in the 50- to 400-µm particle diameter range. A number of sorbent formulations prepared using the granulation technique exhibited excellent durability, attrition resistance, and sulfur capacity during multicycle testing as described in an RTI topical report to METC (Gupta and Gangwal, 1992).

Based on screening tests, a series of promising sorbent formulations were identified. Further testing of these formulations indicated that ZT-4 sorbent had the best overall performance tested in terms of attrition resistance, chemical reactivity, regenerability, sulfur capacity, and other physical and structural properties. RTI was granted a U.S. Patent on manufacture of fluidizable zinc titanate sorbent (Gupta et al., 1993).

Ten HTHP runs were carried out, each involving 10 sulfidation-regeneration cycles in the bench unit. Bench-scale testing variables included sorbent type, temperature (550 to 750 °C [1,022 to 1,382 °F]), gas type (KRW or Texaco gasifier gas), steam content of coal gas, and fluidizing gas velocity (6 to 15 cm/sec). In all 10 multicycle tests, unlike zinc ferrite sorbents, the sulfur capacity utilization for zinc titanate sorbents at breakthrough was consistently between 40 and 60 percent with very little decline with cycling. The attrition resistance of 10-cycle regenerated sorbent was significantly better than the fresh sorbent in all the runs. The detailed test results are described in an RTI topical report to METC (Gupta and Gangwal, 1992).

Reactor Design Issues

During bench-scale testing, it was demonstrated that sulfided sorbent can be completely regenerated with 1 to 5 percent O_2 in N_2. Sulfate formation was not found to occur at 760 °C (1,400 °F) and 15 atm (220 psia). The inlet temperature could be controlled to reach the required 760 °C (1,400 °F) with any of the oxygen contents tested. Also, regeneration of the zinc titanate sorbent demonstrated stoichiometric formation of an essentially O_2-free, SO_2-containing off-gas according to $ZnS + (3/2) O_2 \rightarrow ZnO + SO_2$. A quasi-steady-state generation of SO_2-containing off-gas was demonstrated indicating that a nearly constant steady-state SO_2 content in the regeneration off-gas of a commercial fluidized-bed system can be obtained. The constancy of SO_2 concentration in the regeneration tail-gas is believed to be essential for economical downstream processing to elemental sulfur or sulfuric acid.

The sulfidation reaction was found to be controlled by intrinsic chemical reaction rather than external or pore diffusion. The apparent activation energy for the sulfidation reaction ranged from 15 to 20 kcal/mol depending on the sorbent composition, indicating that significant reduction in size of the desulfurization reactor can be achieved by increasing the operating temperature. A simple single-parameter mathematical model that assumed well-mixed solid phase and plug flow of gas made a reasonable prediction of the breakthrough behavior in the semi-batch HTHP reactor. Effects of addition of HCl and NH_3 were also investigated on the sorbent performance (Gupta and Gangwal, 1992).

100-Cycle Test with ZT-4

Following the successful multicycle parametric testing of various zinc titanate formulations in the bench-scale fluidized-bed reactor, a life-cycle test consisting of 100 sulfidation-regeneration cycles was carried out to determine the long-term reactivity and mechanical strength of ZT-4 sorbent. This life-cycle test was carried out at 750 °C (1,382 °F) sulfidation temperature, 15 atm (220 psia) pressure with a medium Btu Texaco O_2-blown gasifier gas containing 11,400 ppmv of H_2S. These highly severe sulfidation conditions were purposely selected to provide possible worst-case results of long-term sorbent durability. Regeneration of the sulfided sorbent was performed using 2 to 2.5 percent O_2 in N_2 in a temperature range of 720 to 760 °C (1,328 to 1,400 °F). The amount of sorbent in the reactor was 500 g and a relatively high superficial gas velocity of 15 cm/s was used to ensure good fluidization and to more closely simulate commercial operation. This resulted in a superficial gas residence time of only about 1.24 seconds.

This life cycle test conducted under extremely severe operating conditions, and highly reducing nature of coal gas, demonstrated superior performance of the ZT-4 sorbent. The following were the pertinent findings of this life-cycle test:

- The ZT-4 sorbent consistently reduced the H_2S content of coal gas from 11,400 ppmv to <20 ppmv in a semi-batch bench-scale fluidized-bed at 750 °C (1,382 °F) and 15 atm.
- The sorbent was found to be fully regenerable, with negligible residual sulfate remaining. An oxygen concentration of 2 to 3 percent with N_2 diluent was found to result in adequate regeneration rates with no temperature control problems due to the exothermicity of the regeneration reaction.

- The sulfur capacity of the sorbent at breakthrough of 500 ppmv H_2S ranged from 12.6 wt% in Cycle 1 to 5.8 wt% in Cycle 100 with an average of about 9 percent. Most of the decline in the sulfur capacity occurred during the first 50 cycles.

- The decline in sulfur capture capacity was found to correlate with a decrease in the BET surface area, pore volume, and internal porosity. The best correlation, as expected with small particles, was with the BET surface area.

- X-ray diffraction (XRD) analysis indicated the presence of zinc silicate in the sorbent, which is believed to result from the reaction of ZnO with free SiO_2 released from the distributor material. Zinc silicate is believed to be a potential cause of some of the reactivity loss.

- Attrition resistance measurements carried out in our 3-hole airjet attrition tester indicated that the attrition resistance of the sorbent after 100 cycles of testing was significantly higher (<3% 5-h loss) over that of the fresh sorbent (about 40% 5-h loss).

- No significant sorbent loss (<2%) from the reactor was detected over 100 cycles. The total zinc loss determined by chemical analysis was negligible.

Complete details of the test conditions and experimental results are reported in RTI's recent topical report to METC (Gupta and Gangwal, 1993).

Z-SORB Sorbent Testing

PPCo developed a fluidizable version of its Z-SORB sorbent for testing in RTI's HTHP fluidized-bed bench-scale test facility as discussed previously. A life-cycle test consisting of 50 cycles of sulfidation and regeneration was carried out with PPCo's involvement and guidance throughout the test to demonstrate long-term durability and mechanical strength. The details of this test and experimental findings are described in a separate paper entitled "Fluidization Studies Using Phillips Z-SORB Sorbent," included in this proceedings volume. A topical report jointly prepared by RTI and PPCo is currently being reviewed and will be submitted to METC by June 30, 1994.

Scaleup of the Granulation Technique

As discussed previously, the fluidizable zinc titanate sorbents (e.g., ZT-4) prepared by granulation technique exhibited superior performance during long-term testing. These sorbents were prepared in a laboratory-scale granulator of 2-L capacity. In order to prepare large sorbent batches for clean coal demonstration plants, the lab-scale granulator was replaced by a 35-L machine. A number of zinc titanate batches were prepared in this machine with the recipe used in preparation of ZT-4.

The physical and chemical properties of the sorbent designated as ZT-4L ('L' refers to the large machine) were compared with those of the original ZT-4. Table 1 shows a comparison of these properties. Figure 1 shows a comparison of the thermogravimetric analyzer (TGA) reactivities of ZT-4 and ZT-4L measured using the standard 1.5-cycle TGA test described in Gupta and Gangwal (1992). It is noteworthy in Figure 1 that at saturation the weight gain is identical for both the sorbents as would be expected owing to their exact chemical composition. The slope of the sulfidation curve in Figure 1, which represents the rate of H_2S absorption, is somewhat greater for ZT-4L compared to ZT-4, indicating a degree of superior chemical reactivity. Examination of physical property data listed in Table 1 for both the sorbents clearly indicates superior attrition resistance of ZT-4L over ZT-4. The difference in the surface areas and the pore size distribution is insignificant.

Table 1. Physical Properties of ZT-4 and ZT-4L

	ZT-4	ZT-4L
ZnO-to-TiO_2 molar ratio	1.5	1.5
Binder content	5 wt%	5 wt%
Particle size range	100 to 300 μm	100 to 300 μm
Mean particle size[a]	174.6 μm	179.9 μm
Surface area	3.53 m^2/g	3.4 m^2/g
Mercury pore volume	0.2229 cc/g	0.1968 cc/g
Median pore diameter	2,175 Å	1,734 Å
Attrition resistance		
5-h loss	39.7%	17.0%
20-h loss	89.0%	71.0%

[a]Harmonic mean.

Other structural properties such as XRD phases and chemical analyses for Zn and Ti were almost identical for both formulations. These data clearly show that the scaleup of the manufacturing process by a factor of 17.5 was highly successful. The sorbent prepared using the 35-L machine possessed better chemical reactivity and attrition resistance. A large sorbent batch (3,000 kg) employing the 35-L machine is currently being produced.

Technology Transfer

RTI and DOE were granted a U.S. Patent (No. 5,254,516) on October 19, 1993 on the manufacture of the fluidizable zinc titanate sorbents by the granulation technique. Discussions were held with a number of U.S. catalyst manufacturers to commercialize the technology. These discussions culminated in identification of a catalyst manufacturer, Contract Materials Processing, Inc. (CMP), in Baltimore, MD. A contract was executed between RTI and CMP. CMP has extensive experience and facilities for manufacturing large quantities of custom (toll) catalysts and adsorbents for a variety of applications.

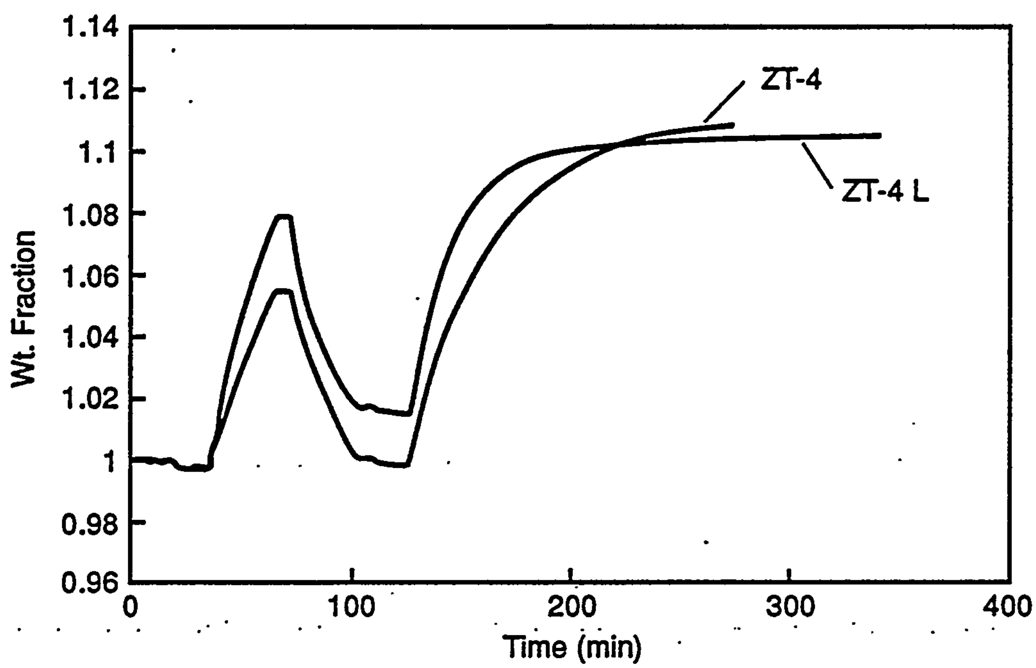

Figure 1. A Comparison of TGA Chemical Reactivities of ZT-4 and ZT-4L

Table 2 shows the cost projections for manufacture of ZT-4 sorbent by granulation independently provided by CMP. Anticipated demand figures were provided by DOE. As can be seen, the current price is $7.91 based on a relatively small demand and, as demand increases, the price will be reduced to about $3.20/lb. This price is close to that contemplated by DOE/METC in their projections for future IGCC plants (Schmidt, 1993).

It may be mentioned here that the ZT-4 sorbent was independently tested by the Institute of Gas Technology (IGT) under a contract with Enviropower to confirm the data obtained at RTI. IGT confirmed the RTI performance data on the sorbent.

Plans are under way to test the ZT-4 sorbent with real coal gas at DOE/METC in the fall of 1994 (Portzer and Gangwal, 1994). This test with real coal gas will demonstrate the applicability of the sorbent with other gas contaminants such as NH_3, HCl, heavy metals, and fine particles.

RTI is working closely or having discussions with a number of private companies in the United States and abroad to promote commercialization of the zinc titanate technology. These include PPCo, Tampella Power/Enviropower, M.W. Kellogg, Texaco and a number of companies in Europe and the Far East.

Table 2. Cost Projections for Manufacture of ZT-4 by Granulation[a]

Year	Quantity (tonnes)[b]	Cost ($/lb) (1994$)
1994	3	7.91
1995	3	7.91
1996	10	7.91
1997	60	5.80
1998	60	5.80
1999	60	5.80
2000	60	3.20
2001 to 2005	60 to 180	<3.20

[a] Independently provided by CMP.
[b] Tonnes = 1,000 kg.

Production of Large Sorbent Batches

RTI arranged a shipment of 2,000 kg of T-2551 zinc titanate sorbent from United Catalysts, Inc. (UCI) of Louisville, KY, to Enviropower in Finland for testing in the pilot plant. UCI produced this sorbent batch on a "best-efforts basis." Table 3 compares the properties of T-2551 with ZT-4L. Clearly, both the TGA reactivity and the attrition resistance of the ZT-4L sorbent is better than the T-2551 formulation. UCI did not disclose the details of the manufacturing method.

Following successful scaleup of the granulation technique and execution of a business agreement between CMP and RTI as discussed previously, commercialization of this technology depends on the success of upcoming pilot-scale demonstration tests and subsequent large-scale demonstration under the DOE Clean Coal Technology Projects. Under a Cooperative Research and Development Agreement (CRADA) between DOE/METC and Enviropower, CMP is currently manufacturing a

Table 3. Comparison of T-2551 and ZT-4L

	T-2551	ZT-4L
Chemical composition		
ZnO/TiO_2 (molar)	1.5	1.5
% S-capacity at saturation[a]	14	22
Attrition resistance (%)		
5-h loss	39.4	17.0
20-h loss	67.8	71.0
Median pore diameter (Å)	8,887	1,734
Mercury pore volume (cc/g)	0.21	0.20
BET surface area (m^2/g)	0.93	3.4

[a] Measured in the TGA.

3,000-kg batch of ZT-4L using the 35-L machine. Out of the 3,000 kg, 2,000 kg of the sorbent will be shipped to Enviropower in Finland for pilot-plant testing and the remaining 1,000 kg will be delivered to DOE/METC for testing in their process developmental Unit (PDU). The expected date of delivery of the sorbent is about August 15, 1994.

FUTURE WORK

Preliminary investigation of preparing zinc titanate particles by spray drying indicates that highly reactive and attrition-resistant (better than a fluid catalytic cracking [FCC] catalyst used in petroleum refineries) particles can be prepared at a price of about $3/lb. Further development of this technique is continuing.

Currently, the 3,000-kg batch of the ZT-4 sorbent is being produced by CMP. A life-cycle test consisting of 50 cycles of sulfidation and regeneration will be performed with this sorbent to provide long-term reactivity and attrition data to Enviropower prior to their pilot-scale tests.

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