

**FLUIDIZATION STUDIES USING PHILLIPS Z-SORB SORBENT**

**Authors:**

S. K. Gangwal  
R. P. Gupta  
G. P. Khare  
G. A. Delzer  
D. H. Kubicek

**Contractor:**

Research Triangle Institute  
P. O. Box 12194  
Research Triangle Park, North Carolina 27709-2194

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**CONTRACT INFORMATION**

**Contract Number** DE-AC21-88MC25006

**Contractor** Research Triangle Institute  
P. O. Box 12194  
Research Triangle Park, NC 27709-2194  
(919) 541-8023

**Contractor Project Manager** Santosh K. Gangwal

**Investigators** Raghubir P. Gupta  
Gyanesh P. Khare, Phillips Petroleum Company  
Gary A. Delzer, Phillips Petroleum Company  
Don H. Kubicek, Phillips Petroleum Company

**METC Project Managers** Suresh C. Jain  
Daniel C. Cicero

**Period of Performance** October 1, 1993 to June 30, 1994

**Schedule and Milestones****FY94 Program Schedule**

	S	O	N	D	J	F	M	A	M	J	J	A
Z-SORB Sorbent Testing												
Data Analysis												
Topical Report												

**OBJECTIVES**

The objectives of this project are to determine the long-term chemical reactivity and mechanical durability of a fluidized version of Phillips Petroleum Company's (PPCo's) proprietary Z-SORB sorbent for the desulfurization of coal-derived gases in a high-pressure (20 atm) fluidized-bed reactor under simulated U-Gas

conditions and at a moderate operating temperature of 538 °C (1,000 °F).

**BACKGROUND INFORMATION**

Z-SORB sorbent is a regenerable sorbent for hydrogen sulfide. It is based on zinc oxide supported in a porous matrix and contains a nickel

oxide promoter. Originally, it was developed for tail-gas cleanup (Brinkmeyer and Delzer, 1990), but recently it has been tested for removal of hydrogen sulfide from hot simulated fuel gas that is representative of a coal gasification process. For the latter technology, previous fixed-bed sorbents have shown poor mechanical stability due to spalling when absorbing hydrogen sulfide in reducing gas atmospheres or when being regenerated over many cycles (Mei et al., 1993). Recent tests have shown that Z-SORB sorbent had excellent chemical reactivity and mechanical stability for application in fixed-bed reactors (Campbell et al., 1993).

In an ongoing sorbent research and development program, PPCo has developed a fluidized version of the Z-SORB III sorbent that is the subject of investigation in this paper.

## PROJECT DESCRIPTION

Project participants in this study were PPCo and Research Triangle Institute (RTI). This work was part of the project entitled "Enhanced Durability of Desulfurization Sorbents for Fluidized Bed Applications." Sorbents developed for fluidized-bed operation must demonstrate high chemical reactivity, as measured by the rate of sulfur absorption and the sulfur loading capacity, as well as good fluidizing characteristics and mechanical strength characterized by low attrition losses. A fluidized version of PPCo's proprietary Z-SORB III sorbent was prepared by Phillips Research and Development. The sorbent used in this study had an average particle size of 175  $\mu\text{m}$ , a particle size range of 50 to 300  $\mu\text{m}$  and an apparent bulk density of 0.9 to 1.0 g/cc. The sorbent manufacturing process has been demonstrated for 100-lb batch sizes and is believed to be easily scaleable to commercial quantities.

After the initial chemical activity testing at PPCo, the sorbent was provided to RTI for testing

in their bench-scale high-temperature, high-pressure (HTHP) semi-batch fluidized-bed reactor system. The reactor unit, shown in Figure 1, is described in detail elsewhere (Gupta and Gangwal, 1992). From initial thermogravimetric analyzer (TGA) tests, it was evident that this sorbent had high chemical reactivity for sulfur capture at operating temperatures of 482 to 538 °C (900 to 1,000 °F). Consequently, for the 50-cycle (sulfidation and regeneration) long-term testing of this sorbent, an absorption temperature of 538 °C (1,000 °F) was selected. Other test conditions are listed in Table 1, and the composition of simulated air-blown U-gasifier gas is included in Table 2. Testing was done in a 2-in. diameter reactor with 500 g of sorbent. Feed gases entered at the bottom of the reactor vessel and exited at the top. The detailed test procedure is described elsewhere (Gupta and Gangwal, 1993). The sorbent was subjected to alternating periods of sulfidation and regeneration. Sulfidation was accomplished by feeding simulated U-Gas composition produced by mixing of individual metered components upstream of the reactor. For regeneration, air was diluted with nitrogen. Initially, regeneration was initiated at 649 °C (1,200 °F) and 2.5 mol% oxygen in nitrogen.

Online analysis of the exiting gas was performed using a series of gas chromatographs (GCs). Concentrations of sulfurous gases ( $\text{H}_2\text{S}$ ,  $\text{COS}$ , and  $\text{SO}_2$ ) were measured every 5 minutes using a Varian flame photometric detector (FPD), while  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{O}_2$ , and  $\text{CH}_4$  concentrations were measured every 25 minutes using a Carle thermal conductivity detector (TCD). During regeneration, the  $\text{SO}_2$  concentration was monitored using a continuous  $\text{SO}_2$  analyzer (Model 721AT2 from Western Research).

After 25 cycles of sulfidation (24 cycles of regeneration) the run was stopped, reactor unloaded, and 100 g (20 percent of total inventory) of sorbent was removed from the reactor for analysis and characterization. The

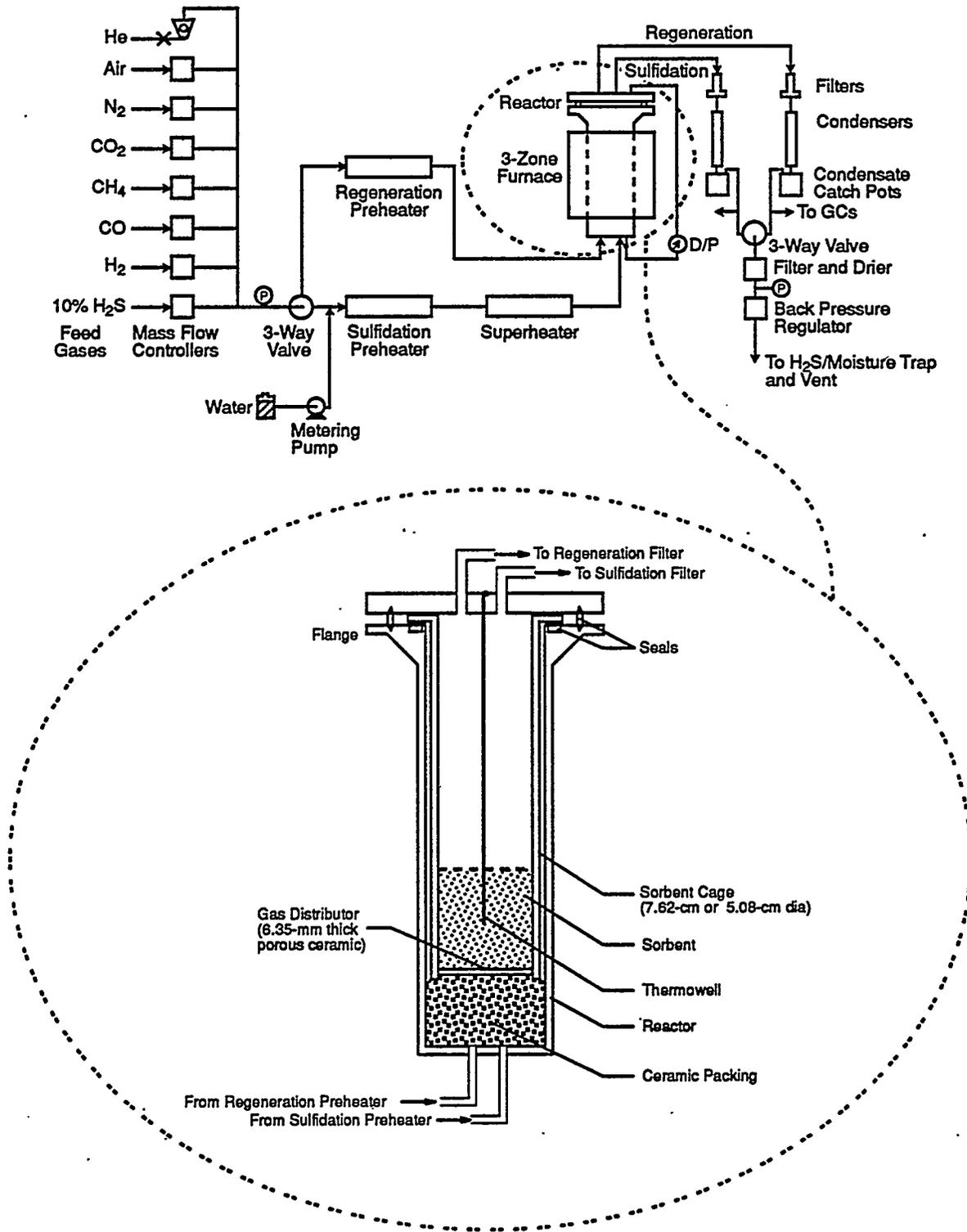


Figure 1. Bench-Scale Fluidized-Bed Sorbent Test Facility

**Table 1. Nominal Test Conditions  
Used in 50-Cycle Test**

Sulfidation	
Sorbent	Z-SORB III
Temperature	538 °C (1,000 °F)
Pressure	20 atm (294 psia)
Sorbent particle size	100 to 300 µm ( $d_{50} \approx 174.3 \mu\text{m}$ ) <sup>a</sup>
Sorbent inventory	500 g (Cycles 1 to 25) <sup>b</sup> 400 g (Cycles 26 to 51) <sup>c</sup>
Total gas flow rate	75 slpm (Cycles 1 to 25) 60 slpm (Cycles 26 to 35) 75 slpm (Cycles 36 to 51)
Sulfidation gas	Simulated U-Gas Gasifier Gas <sup>d</sup>
H <sub>2</sub> S content of coal gas	5,000 ppmv (0.5 mol%)
Reactor tube diameter	5.08-cm (2 in.-ID)
Regeneration	
Initial temperature	580 to 650 °C (1,076 to 1,200 °F)
Maximum temperature	690 to 780 °C (1,274 to 1,436 °F)
Pressure	20 atm (294 psia)
Gas flow	Same as sulfidation <sup>e</sup>
Regeneration gas	2 to 2.5% O <sub>2</sub> in N <sub>2</sub>

<sup>a</sup>  $d_{50}$  is the harmonic mean.

<sup>b</sup> Weight of uncalcined sorbent. On heating, sorbent lost 35 g weight due to evolution of 7 percent bound moisture.

<sup>c</sup> Weight of the sorbent in sulfided state containing 12.15 wt% S. The weight of regenerated sorbent would be 375.7 g.

<sup>d</sup> Complete gas composition is specified in Table 2.

<sup>e</sup> The same flow rates were used during regeneration as sulfidation (i.e., 75, 60, 75 slpm).

remaining 400 g of sorbent was reloaded to the reactor and regenerated before continuing to Sulfidation Cycles 26 to 50. The test program ended after the 50th sulfidation cycle. The reacted sorbent was subjected to a high-temperature exposure after the normal 50th regeneration cycle in an attempt to determine if excessive sulfates

**Table 2. Gas Composition**

Component	Vol%
H <sub>2</sub>	14.2
H <sub>2</sub> S	0.5 (5,000 ppmv)
CO	23.1
CO <sub>2</sub>	5.8
N <sub>2</sub>	49.8
H <sub>2</sub> O	6.6
Total	100.0

had been accumulated on the sorbent. Monitoring of SO<sub>2</sub> in the regenerator off-gas indicated minimum residual sulfate.

## RESULTS

The sulfidation runs as indicated in Table 1 were carried out at 20 atm (294 psia) 538 °C (1,000 °F) using 5,000 ppmv (0.5 mol%) H<sub>2</sub>S in the feed. The superficial gas velocity of about 9 cm/s was selected based on prior experimental and theoretical information to ensure complete fluidization of the sorbent. This resulted in a superficial gas residence time of 2.38 s based on a slumped bed of density at 72 lb/ft<sup>3</sup>. Figure 2 shows the hydrogen sulfide breakthrough curves for selected cycles. The sulfur loadings were constant for the first ten cycles with breakthrough (500 ppm H<sub>2</sub>S in effluent) occurring in 175 minutes. Estimation of sorbent utilization indicated that nearly 100 percent of the sorbent theoretical loading capacity was utilized over the first 10 cycles. Another interesting feature for this sorbent was its high efficiency for sulfur removal manifested in complete removal of H<sub>2</sub>S (to nearly zero ppm) for the first 70 percent of each cycle prior to breakthrough.

During the first 10 cycles, the regenerations were very smooth, completing in about 60 minutes. Typically the regenerations were initiated at

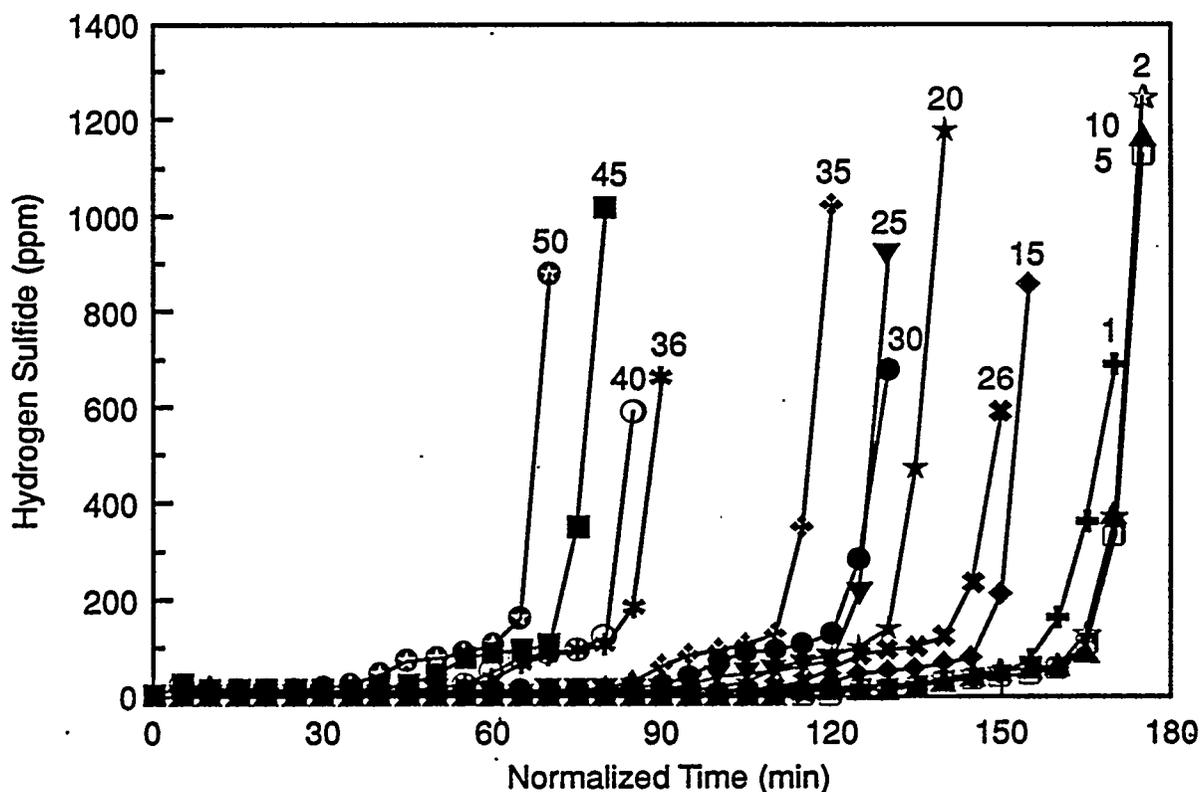


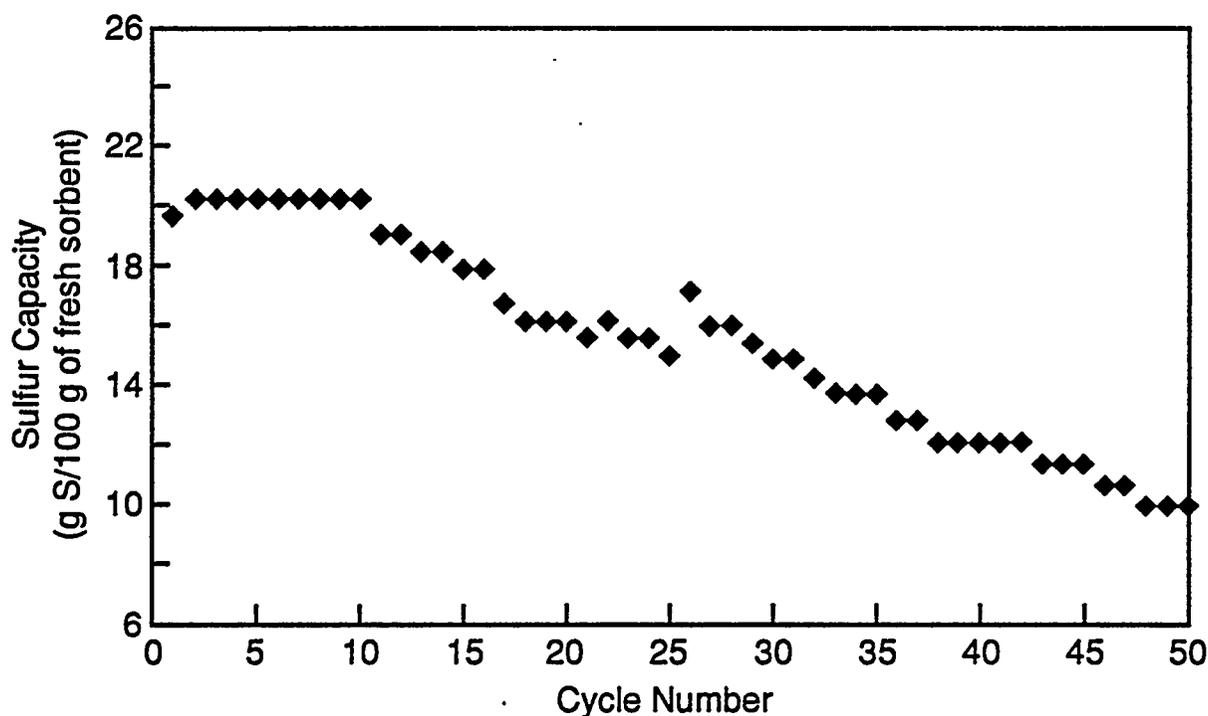
Figure 2. Breakthrough Behavior of Z-SORB III Sorbent U-Gas; 20 atm; 538 °C (1,000 °F)

649 °C (1,200 °F) leading to a peak temperature in the vicinity of 690 °C (1,275 °F). After the first ten cycles of operation, the sorbent suffered, as yet unexplained, exotherms during the start of regenerations resulting in undesired, uncontrolled temperature excursions up to 760 °C (1,400 °F). Breakthrough time declined by 30 percent in the first 25 cycles.

The sulfided sorbent removed from the reactor after 25 cycles was reloaded in the reactor after being stored for about 6 to 7 weeks to complete necessary analyses. The amount of sorbent reloaded was 20 percent less than the initial start-of-the-run loading; therefore, the feed gas flow rate was reduced by 20 percent for cycles 26 to 35, i.e., from 75.0 to 60.0 slpm to maintain the same gas residence time. The initial regeneration (No. 25) was successful and the sorbent reactivity in the 26th cycle was actually higher than what was observed prior to reactor unloading. After the

next several cycles of operation, it became evident that the gas flow rate of 60 slpm was not quite enough to achieve a good quality fluidization of the sorbent; therefore, starting at Cycle 36 the gas flow rate was restored to 75 slpm. This change resulted in more smooth cycling.

The breakthrough curves presented in Figure 2 exhibit the sorbent performance for the entire test. It is quite noteworthy that the sorbent performance remained quite high after 50 cycles of operation. The sulfur capacities of the sorbent during Cycles 1 and 50 were 20.16 and 9.98 g S/100 g of sorbent, respectively, indicating about a 50 percent capacity utilization even after 50 cycles. In Figure 3, the sulfur capacity (g of S pickup per 100 g of sorbent) is plotted as a function of cycle number. Sulfur capacity is calculated using the concentration of H<sub>2</sub>S in feed, breakthrough time of 500 ppmv H<sub>2</sub>S in the effluent and the amount of sorbent used. Actual sulfur chemical analyses



**Figure 3. Sulfur Capacity of Z-SORB III Sorbent U-Gas; 538 °C (1,000 °F); 20 atm; 500 ppm Breakthrough.**

after 25 and 50 cycles closely corroborated the calculated sulfur capacity.

As mentioned previously, the sorbent for the desulfurization application must have high chemical reactivity. The chemical reactivity is measured by the total sulfur loading capacity as well as the rate of sulfur absorption. In order to measure the latter, standard 1.5-cycle TGA reactivity tests described in Gupta and Gangwal (1992) were carried out for fresh and 25- and 50-cycle reacted sorbents. Figure 4 depicts both the saturation (indicated by the maximum weight gain during the second cycle) and the rate of sulfur pickup (indicated by the slope of the sulfidation curve). While this figure shows that saturation sulfur pickup decreases with increasing number of cycles as expected and observed for conventional desulfurization sorbents, it is important to note that the rate of sulfur pickup for 25- and 50-cycle reacted sorbent remained relatively constant even though the capacity had dropped.

Other notable findings of this test were that in the fluidized-bed reactor there was no evidence of the absorption exotherm that was previously observed in the fixed-bed reactor tests conducted at METC (Campbell et al., 1993) and attributed to methanation reaction promoted by nickel present in Z-SORB sorbent. GC analysis of the absorption effluent gas did indicate an occurrence of water gas shift reaction leading to higher concentration of hydrogen.

#### **Sorbent Loss from the Reactor**

The net sorbent loss during the entire 50 cycles was 0.5 percent of the original charge based on the weights of sorbent removed from the reactor and the material deposited on filters and lines. This is indicative of low attrition and high mechanical stability of Z-SORB sorbent. The total sorbent loss from the reactor itself was 2.5 percent.

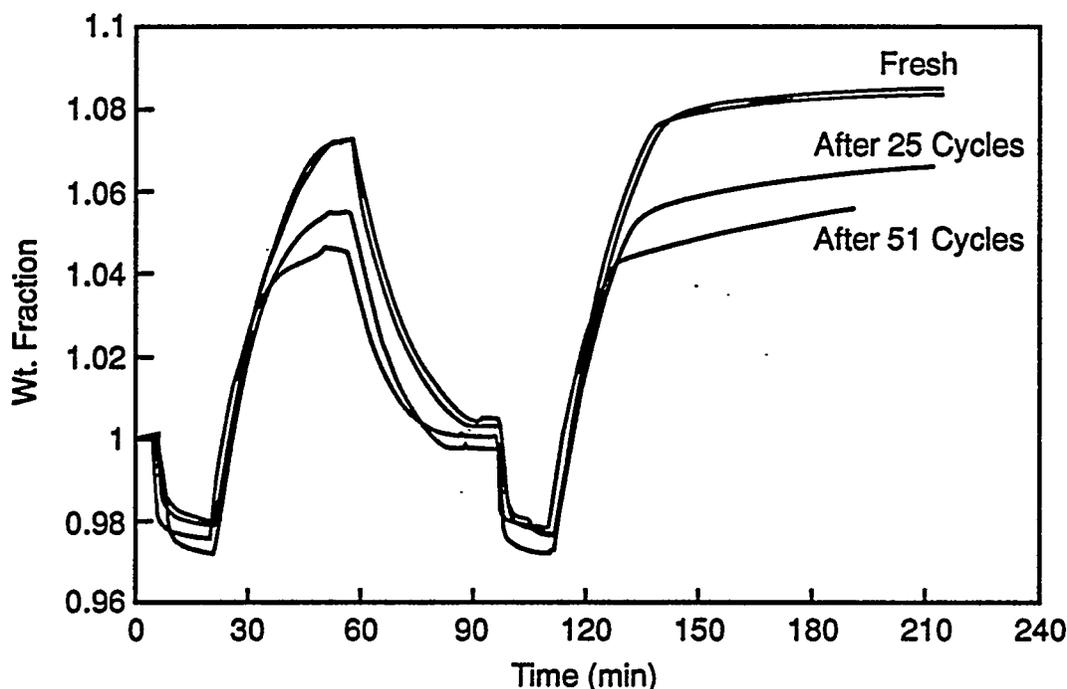


Figure 4. TGA Reactivity of Fresh and Reacted Z-SORB Sorbent

#### Selected Physical Properties of Fresh and Reacted Sorbents

Selected physical properties of the fresh and reacted sorbents were measured and are presented in Table 3. The average particle size of the sulfided sorbent after 25 and 50 sulfidations remained essentially the same within experimental error. These results corroborate the relatively small sorbent loss observed from the reactor, indicating good mechanical stability of the sorbent. The compacted bulk density of Z-SORB sorbent ( $66.5 \text{ lb/ft}^3$ ) increased about 8 percent after 25 cycles of operation, but then it remained essentially the same through the 50 cycles. This indicates that sorbent undergoes some sintering/shrinking at the beginning, but then the density does not change further and remains relatively constant through the life-cycle test. Attrition tests performed in RTI's 3-hole airjet attrition tester indicated that the attrition resistance of the 25-cycle sulfided sorbent was lower than the fresh material. However, very little change in the attri-

Table 3. Physical Properties of Fresh and Spent Sorbent

	Fresh	After 25th sulfidation	After 51st sulfidation
Average particle size ( $\mu\text{m}$ )	174.3	170.8	173.7
Compacted bulk density ( $\text{lb/ft}^3$ )	66.54	72.12	72.58

tion resistance was found between the 25-cycle sulfided and 51-cycle sulfided materials. It is realized that attrition data from an actual reactor environment is preferable to simulation using a 3-hole attrition test.

#### CONCLUSIONS

The 50-cycle data show that the fluidizable Z-SORB sorbent has high chemical reactivity and

mechanical durability for hot-gas desulfurization at 538 °C (1,000 °F). Z-SORB sorbent has very high efficiency for H<sub>2</sub>S removal to essentially zero levels for a major portion of absorption cycle and a nearly constant rate of sulfur absorption whether fresh or reacted. The sulfur capacity of the sorbent at breakthrough (500 ppm H<sub>2</sub>S in the reactor effluent) was 20.16 g S/100 g sorbent in Cycle 1 and 9.98 g S/100 g sorbent in Cycle 50. This sorbent can be easily regenerated at 649 to 704 °C (1,200 to 1,300 °F) with little evidence of sulfate accumulation. During the 50-cycle test only small changes were observed for such important sorbent physical properties as bulk density and particle size. Delineation of the capacity declines observed following Cycle 10 suggests additional research in this area. Definition of the required experiments is currently under assessment.

## ACKNOWLEDGMENTS

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