**High-Temperature, High-Pressure
Testing of Zinc Titanate in a Bench-Scale
Fluidized-Bed Reactor for 100 Cycles**

Topical Report

**R. P. Gupta
S. K. Gangwal**

June 1993

Work Performed Under Contract No.: DE-AC21-88MC25006

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

By
Research Triangle Institute
Research Triangle Park, North Carolina

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June 1993

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ABSTRACT

Research Triangle Institute (RTI), under contract to the U.S. Department of Energy/Morgantown Energy Technology Center (DOE/METC), performed a life-cycle test consisting of 100 sulfidation-regeneration cycles on a zinc titanate material. This zinc titanate formulation (designated as ZT-4 and having a Zn-to-Ti molar ratio of 1.5) had exhibited the best overall performance in terms of chemical reactivity, sulfur capacity, regenerability, structural properties, and, most important, the attrition resistance based on multicycle testing of a number of sorbent formulations in a bench-scale fluidized-bed reactor. Test conditions in this life-cycle test were

- Desulfurization temperature: 750 °C (1,382 °F);
- Pressure: 15 atm (220 psia);
- Coal gas: simulated Texaco entrained-bed oxygen-blown gasifier gas containing 11,400 ppm of H₂S; and
- Superficial gas velocity: 15.64 cm/sec (0.51 ft/sec).

The ZT-4 sorbent used in this test was prepared using a granulation technique. Five hundred grams of the sorbent in the 100- to 300- μ m particle diameter range was tested in a 2-in.-ID stainless steel reactor.

Even at the relatively high temperature of 750 °C, the sorbent consistently reduced the H₂S content of coal gas from 11,400 ppm to <20 ppmv before breakthrough. The sulfur capacity of the sorbent at a breakthrough of 500 ppm H₂S in reactor exit gas (defined arbitrarily) ranged from 12.6 wt percent in Cycle 1 to 5.8 wt percent in Cycle 100 with an average of about 9 wt percent. Most of the decline in the sulfur capacity occurred during the first 50 cycles and stabilized somewhat thereafter. The drop in sulfur capacity was found to correlate with a decrease in surface area and pore volume. No significant sorbent loss (<2%) from the reactor was observed. The attrition resistance of the sorbent after 100 cycles of testing was more than an order of magnitude better than that of fresh material. Analysis of Zn and Ti contents did not show any zinc loss, which might be expected over the 100 cycles at 750 °C.

X-ray diffraction (XRD) analysis of reacted sorbent indicated the presence of zinc silicate in the sorbent whose formation is believed to be via the reaction of ZnO with free SiO₂ released from the distributor material (which contained about 85 percent alumina and 15 percent silica). Zinc silicate, which may have led to the surface area loss, is believed to be responsible for some of the reactivity loss. Overall, this life cycle test carried out under extremely severe test conditions clearly demonstrated the feasibility of zinc titanate sorbent in a fluidized-bed reactor.

ACKNOWLEDGMENTS

This work was sponsored by the Morgantown Energy Technology Center (METC) of the U.S. Department of Energy (DOE) under Contract No. DE-AC21-88MC25006. Valuable guidance and suggestions provided by Mr. Suresh C. Jain of METC as Contracting Officer's Representative (COR) are deeply appreciated. Helpful discussions were also held with Drs. Tom Grindley, Tom Dorchak, and L.D. Gasper-Galvin of METC. Dr. Ranjani Siriwardane of METC performed Fourier transform infrared spectroscopy (FTIR) studies on fresh and reacted sorbent samples. Dr. John J. Renton of West Virginia University (WVU) conducted all the X-ray diffraction (XRD) and scanning electron microscope (SEM) analyses. Dr. Wahab Mojtahedi and Mr. Kari Salo of Enviropower, Inc., arranged the independent testing of ZT-4 at the Institute of Gas Technology (IGT). Dr. Javad Abbasian tested the ZT-4 at IGT and supplied the reacted material to the Research Triangle Institute (RTI). Dr. Ted M. Knowlton of Particulate Solids Research, Inc. (PSRI), supplied the US 260 fluid-catalytic cracking (FCC) catalyst sample for attrition testing. Messrs. D.A. Ward, E.W. Johnson, and G.B. Howe carried out the experimental work. Dr. David Binstock analyzed the samples for Zn, Ti, and Si contents. Technical assistance from Dr. William J. McMichael, Mike Taylor, Gary Folsom, and Jan Shirley is gratefully acknowledged.

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EXECUTIVE SUMMARY

Integrated gasification combined cycle (IGCC) power plants are being advanced worldwide to produce electricity from coal owing to their potential for superior environmental performance, economics, and efficiency in comparison to conventional coal-based power plants. A key component of these plants is a hot-gas desulfurization system employing efficient regenerable mixed-metal oxide sorbents. Leading sorbent candidates include zinc ferrite and zinc titanate. These sorbents can remove hydrogen sulfide (H_2S) in the fuel gas down to very low levels (typically <20 ppmv) at 500 to 750 °C and can be readily regenerated for multicycle operation with air. The desulfurization and regeneration reactions can be carried out in fixed-, moving-, or fluidized-bed reactors. Fluidized-bed reactors are perhaps most suited for hot-gas desulfurization owing to their ability to better control the temperature during the highly exothermic regeneration typically carried out using an air-diluent (typically nitrogen or steam) mixture.

Other potential advantages of a fluidized-bed reactor include excellent gas-solid contact, the ability to continuously add or remove sorbent, the use of small particles leading to faster overall kinetics, and nearly continuous steady-state operation. However, highly attrition-resistant sorbents with good sulfur capacity that are capable of withstanding stresses induced by rapid temperature swings, chemical transformations, and fluidization and transport are required before fluidized beds can be employed successfully.

To this end, the Research Triangle Institute (RTI) has formulated and tested a series of zinc titanate sorbents in a high-temperature, high-pressure (HTHP) fluidized-bed bench-scale reactor. These sorbent formulations were prepared using a granulation technique (which had been successfully used previously for zinc ferrite). Multi-cycle HTHP bench-scale testing of these sorbents under a variety of conditions (temperature: 550 to 750 °C; Zn-to-Ti ratio: 0.8 to 1.5; sulfidation gas: KRW, Texaco; steam content of coal gas: 5 to 20 percent; fluidizing gas velocity: 0.25 to 0.5 ft/sec) culminated in the development of a ZT-4 sorbent (see Table E-1 for its properties) that exhibited the best overall performance in terms of chemical reactivity, sulfur capacity, regenerability, structural properties, and attrition resistance. Following this parametric study, a life-cycle test consisting of 100 sulfidation-regeneration cycles was carried out with ZT-4 in the bench unit under conditions shown in Table E-2.

Table E-1. Properties of ZT-4

ZnO-to- TiO_2 molar ratio	1.5 (nominal)
Calcination conditions	2 hr @ 850 °C
Binder content	5 wt % bentonite
Particle size range	100 to 300 μm
Compacted bulk density	95.0 lb/ft ³
BET surface area	3.53 m ² /g
Median pore diameter (MPD)	2157 Å
Mercury pore volume (MPV)	0.2229 cm ³ /g
Attrition rate ^a	
5-hr loss	39.55%
20-hr loss	89.00%
X-ray diffraction (XRD) phases	Zn_2TiO_4 , TiO_2 (rutile phase), traces of $\text{Zn}_2\text{Ti}_3\text{O}_8$ and ZnTiO_3

^aMeasured in an air-jet three-hole attrition tester.

Table E-2. Nominal Test Conditions for 100-Cycle Test

<u>Sulfidation</u>	
Sorbent	ZT-4 ^a
Temperature	750 °C (1382 °F)
Pressure	15 atm (220 psia)
Particle size	100 to 300 µm ($d_{50} \approx 175 \mu\text{m}$) ^b
Sorbent inventory	500 g
Total gas flow rate	76 slpm (161.5 scfh)
Superficial gas velocity	15.64 cm/sec (0.51 ft/sec)
Sulfidation gas	Simulated Texaco gas
H ₂ S content of coal gas	11,400 ppmv (1.14%)
<u>Regeneration</u>	
Temperature	760 to 785 °C (1400 to 1445 °F)
Pressure	15 atm (220 psia)
Total gas flow rate	76 slpm (161.5 scfh)
O ₂ content of regeneration gas	2.3 to 2.5%
Diluent	Nitrogen

^aSorbent properties are listed in Table E-1.

^b d_{50} indicates 50% below 175 µm.

The sorbent consistently reduced the H₂S content of coal gas from 11,400 ppm to <20 ppmv before breakthrough as shown in Figure E-1. The sulfur capacity of the sorbent at the breakthrough point of 500-ppmv H₂S ranged from 12.6 wt percent in Cycle 1 to 5.8 wt percent in Cycle 100 with an average of about 9 wt percent as depicted in Figure E-2. Most of the decline in the sulfur capacity occurred during the first 50 cycles and stabilized somewhat thereafter. The decline in sulfur capacity was found to directly correlate with a decrease in the BET surface area and pore volume as shown in Figure E-3. Indeed, the correlation coefficient was greater than 0.95 in both cases. The correlation was better with BET surface area which is perhaps expected for the small particles in a fluidized-bed reactor.

The sorbent was found to be fully regenerable, with negligible residual sulfate remaining. An oxygen concentration of 2 to 3 percent with N₂ diluent was found to result in adequate regeneration rates and posed no temperature control problems (due to the exothermicity of the regeneration reaction).

XRD analysis indicated the presence of zinc silicate in the sorbent, which is believed to result from the reaction of ZnO with free SiO₂ released from the distributor (used in the reactor for the coal gas) introducing material that contained about 85 percent alumina and 15 percent silica. Zinc silicate, which may have led to the surface area loss, is believed to be a potential cause of some, if not all, reactivity loss. Therefore, use of a metal distributor is preferable in

Figure E-1. H₂S breakthrough curves for selected cycles.

Figure E-2. Sorbent sulfur capacity for Cycles 1 to 100.

Figure E-3. Change in BET and MPV as a function of change in sulfur pickup.

future bench runs and a distributor material not containing silica is recommended for commercial application.

The attrition rate (defined in terms of percent weight loss) of the 100-cycle reacted sorbent (measured in a three-hole attrition tester) decreased by more than an order of magnitude compared to that of the fresh sorbent as illustrated in Figure E-4. Also included for comparison in this figure is the attrition rate of used US 260 fluid-catalytic cracking (FCC) catalyst.

No significant sorbent loss (<2%) from the reactor was detected over the 100 cycles, including the loss in handling the sorbent. The zinc loss, determined by chemical analysis, was negligible. In fact, the Zn-to-Ti ratio increased from 1.45 in the fresh sorbent to 1.48 in the 100-cycle reacted sorbent.

Overall, this life-cycle test, carried out under extremely severe conditions, clearly demonstrated the feasibility of zinc titanate sorbent in a fluidized-bed reactor.

Based on the results of this study, the following major recommendations are made for future work:

- As a result of good performance with simulated coal gas, ZT-4 should be tested with actual coal-derived gases to study the effect of other coal gas contaminants such as NH_3 , HCl , alkali, and trace metals.

Figure E-4. Attrition behavior of fresh and reacted ZT-4 measured in a three-hole air-jet attrition tester.

- Because the bench-scale data gathered in this life-cycle test only address the sorbent's reactivity and mechanical strength over 100 cycles, they provide limited information for design of a commercial fluidized-bed reactor that would operate in a continuous mode. Therefore, a continuous bench-scale absorber-regenerator system with a sorbent circulation arrangement should be designed, built, and tested to serve as a prototype of a commercial system.
- A long-term run should be conducted with a distributor plate that does not contain silica.
- The production of ZT-4 should be scaled up to semicommercial (pilot-scale) quantities.

1.0 INTRODUCTION

The U.S. Department of Energy/Morgantown Energy Technology Center (DOE/METC) has been actively pursuing the development of various hot-gas desulfurization processes for the last two decades. The primary motivation for this development is to generate a more economical, environmentally superior, and reliable process to purify the product gas of coal gasifiers for use in gas turbines and fuel cells. Earlier METC efforts (since 1980) were focused on developing regenerable desulfurization sorbents in the form of extrudates for use in cyclical fixed- or moving-bed reactors. Considerable efforts were expended on the development of a zinc ferrite sorbent identified as possessing desirable properties of good regenerability, a high degree of desulfurization, and a high sulfur loading (Grindley and Steinfeld, 1981). Sub-pilot-scale testing of zinc ferrite at KRW (Haldipur et al., 1987) and Texaco (Wu et al., 1989) demonstrated its ability to remove H_2S up to 98.9 percent; however, considerable sorbent decrepitation was observed under adverse conditions with highly reducing coal gas. Testing of zinc ferrite in a fluidized-bed reactor at the Research Triangle Institute (RTI) (Gupta and Gangwal, 1991) and at DOE/METC (Grindley, 1991) showed some sorbent attrition, but not severe decrepitation.

In view of the above-mentioned problem with zinc ferrite, zinc titanate sorbents started receiving serious attention. Recent tests conducted at Texaco (Robin et al., 1992) and at DOE/METC (Gasper-Galvin, 1993) resulted in severe spalling of zinc titanate pellets in fixed-bed reactor tests. The primary cause of the spalling is believed to be the formation of zinc sulfate during regeneration. Zinc sulfate formation leads to a large expansion in molar volume (the molar volume of zinc sulfate is $41.57 \text{ cm}^3/\text{mol}$, compared to 23.85 for ZnS and 14.34 for ZnO).

In addition to their simplicity of operation, a number of other advantages are associated with fixed-bed reactors, such as high sorbent sulfur capacity, zinc utilization, and low sulfur breakthrough. However, sorbent spalling and decrepitation remain serious problems with fixed-bed systems. Also the highly exothermic regeneration and the need to use hot valves impose serious limitations on the use of fixed-bed reactors. These problems are not as serious in fluidized-bed reactors, which are currently being investigated.

Fluidized-bed reactors (conceptually shown in Figure 1) 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 attrition-resistant sorbent is required, and scaleup and turndown limitations exist for fluidized-bed systems. Recent work at RTI has indicated that attrition-resistant zinc titanate formulations with good chemical reactivity, sulfur capacity, and regenerability can be prepared in a particle size range of 50- to 400- μm dia using an easily scalable granulation technique. Evaluation of a series of zinc titanate formulations prepared using this technique indicated that a zinc titanate formulation designated as ZT-4 with a 1.5 Zn-to-Ti atomic ratio exhibited the best overall performance in terms of attrition resistance and sulfur capacity (Gupta and Gangwal, 1992).

To determine the long-term chemical reactivity and mechanical durability of this formulation, RTI performed a life-cycle test consisting of 100 cycles of sulfidation and regeneration. This topical report describes the experimental details and results of this test along with a detailed data analysis followed by pertinent conclusions.

Source: Grindley, 1991.

Figure 1. Schematic illustration of removal of H_2S from hot coal gas in a fluidized-bed reactor.

2.0 EXPERIMENTAL APPARATUS

The bench-scale test facility employed in this test has been described in detail previously in two of RTI's topical reports to DOE/METC (Gupta and Gangwal, 1991, 1992). However, for the sake of completeness, it is briefly described here. Figure 2 shows a schematic of this test facility. It is a skid-mounted system capable of operation at up to 870 °C at 20 atm pressure.

The reactor is constructed using a 4-in., schedule-160, 316 stainless steel (SS) pipe. Most of the other system components are constructed with either 316 or 304 SS. All hot H₂S-wetted parts are Alon-processed (a high-temperature aluminum vapor treatment) to prevent corrosion of SS by sulfur gases in the presence of steam. The main components of the reactor facility are (1) gas delivery system, (2) reactor assembly, (3) data acquisition and process control, (4) gas analysis system, and (5) reactor offgas venting system. Each is briefly described below.

A battery of seven mass flow controllers (MFCs) capable of operation at pressures up to 100 atm controls the flow rate and composition of simulated coal gas using bottled gases for CO, H₂, CO₂, N₂, H₂S, O₂, and air. A positive displacement pump feeds deionized water to a boiler and superheater to generate steam. The delivery system can generate simulated coal gasifier gases representative of all types of gasifiers.

The fluidized-bed desulfurization reactor is also shown in Figure 2. The unique feature of this reactor is a removable cage for easy loading and unloading of the sorbent. The reactor can accommodate both 7.62-cm (3-in.) and 5.1-cm (2-in.) dia sorbent cages. A removable α -alumina distributor plate is positioned at the bottom of each cage to introduce hot coal gas into the reactor. The reactor is housed inside a three-zone furnace equipped with separate temperature controllers for each zone and the furnace can heat the reactor up to 850 °C. Ceramic thimble filters downstream of the reactor capture particles from the sulfidation and regeneration exit lines upstream of the condensers. The reactor exit gas, after passing through the thimble filters, is cooled using heat exchangers.

The reactor temperature is monitored at the bed inlet below the distributor, halfway in the bed, and at the bed outlet in the freeboard using Type-K thermocouples. The thermocouples, equipped with a digital display, are connected to a data acquisition system described later. Pressure is controlled precisely by two back pressure regulators (BPRs) in series. A differential pressure indicator across the reactor provides an indication of fluidization behavior of the hot sorbent in the reactor.

A small slipstream of steam-free gas from the reactor is diverted to an online gas analysis system, which consists of two gas chromatographs (GCs): a Carle series 400 AGC with a thermal conductivity detector (TCD), and a Varian 3300 with a flame photometric detector (FPD). Both FPD and TCD are connected to Spectra Physics SP4270 integrators to intermittently measure the gas composition. Multiple GC sampling valves and dual loops in the Varian FPD measure H₂S and COS from 1,500 ppmv to <0.1 ppmv every 6 min. High concentrations of H₂S, SO₂, and other bulk gases (H₂, CO₂, N₂, O₂, CH₄, and CO) are measured every 25 min with the Carle TCD to evaluate mass balance. An online continuous SO₂ analyzer, Model 721 AT2 from Western Research, is used to measure the SO₂ evolution during sorbent regeneration.

Figure 2. Bench-scale fluidized-bed sorbent test facility.

In previous bench runs, described in RTI's earlier topical report (Gupta and Gangwal, 1992), an analog data acquisition system was used. This system was not very user friendly and data analysis required manual entry of data from a strip-chart recorder output to a spreadsheet file. As a result, only limited analyses on the data could be performed. Therefore, this analog data acquisition system was replaced by a digital OM-480 Modular Data Logging System from Omega Instruments (Model No. 163568-96A). Installation of this new data system facilitated continuous data acquisition via a LabTech Note-Book Software using an IBM personal computer. Moreover, audible alarms for low and high limits on various gas flow rates and temperatures were programmed, allowing efficient and uninterrupted operation of the test facility.

The new data logging module has 16 separate channels. Each channel accepts one input. The input can be a voltage signal (0 to 5 V), a direct thermocouple input (no transducer required), or a current signal (mA). This allows connection of the output signal from the MFCs and thermocouples directly into the module without introducing any system noise. Out of 16 channels, eight channels are used for monitoring the flow rates from MFCs (N_2 , H_2 , CO, CO_2 , air, H_2S/H_2 , CH_4 , and an additional N_2). Six channels are used for monitoring temperatures. Temperature is monitored in the sorbent bed, reactor freeboard, superheater, sulfidation condenser, and sulfidation and regeneration filters. One channel is used to gather SO_2 concentration data from the online SO_2 analyzer. The remaining channel is currently not being used and is available to monitor any other desired process parameter.

The output from the OM-480 module is connected to an IBM personal computer via an RS232 serial cable. The LabTech Note-Book software is a real-time data acquisition program that controls inflow and outflow of information from the various channels. It is an integrated software package for data acquisition, process control, monitoring, and data analysis. Using this software, collected data can be processed in real time through an extensive list of mathematical functions, displayed to the screen, and logged to a disk in a format directly compatible with most spreadsheet programs.

The typical frequency of data collection in the bench run was 30 sec. Various temperatures and flow rates were digitally and graphically displayed on the computer screen during the entire run. Any system disturbances were instantly displayed on the screen in addition to activation of an audible alarm.

The foregoing description of the data acquisition system is included to indicate the care with which run data were collected. The entire system worked very effectively and provided a number of valuable insights into the reactor operation, especially during regeneration.

Another major modification that was made in the reactor system was the installation of a new sulfidation condenser. The previous condenser did not have adequate capacity to condense approximately 15 slpm steam from 750 °C to room temperature. The new Parker Dual Heat Transfer Coil condenser with American Society for Mechanical Engineers (ASME) code was manufactured by the Parker Hannifin Corporation of Huntsville, Alabama. Essentially, it is a double-pipe heat exchanger made of copper with an external tube of 1-in.- and 1/2-in.-OD internal tube. The coil diameter is approximately 8 in. and it contains 10 coils with a total surface area for heat transfer of 1.93 ft². Tap water was used as a cooling medium with a flow rate of about 2 gal/min. This heat exchanger condensed the steam from hot coal gas very efficiently. The steam flow rate was about 1.5 lb/hr (14 slpm).

3.0 SORBENT CHARACTERISTICS

The zinc titanate sorbent that was selected for this test was ZT-4. This formulation had exhibited the best overall performance among all the formulations tested as described in RTI's previous topical report (Gupta and Gangwal, 1992). Table 1 lists various physical and chemical properties of this sorbent.

Table 1. Various Physical and Chemical Properties of ZT-4 Formulation

ZnO-to-TiO ₂ molar ratio	1.5 (nominal)
Calcination conditions	2 hr @ 850 °C
Binder content	5 wt % bentonite
Particle size range	100 to 300 µm
Compacted bulk density	95.0 lb/ft ³
BET surface area	3.53 m ² /g
Median pore diameter (MPD)	2157 Å
Mercury pore volume (MPV)	0.2229 cm ³ /g
Attrition rate ^a	
5-hr loss	39.55%
20-hr loss	89.00%
X-ray diffraction (XRD) phases	Zn ₂ TiO ₄ , TiO ₂ (rutile phase), traces of Zn ₂ Ti ₃ O ₈ and ZnTiO ₃

^aMeasured in an air-jet three-hole attrition tester.

4.0 EXPERIMENTAL APPROACH

Table 2 lists the nominal test conditions for the 100-cycle test. The composition of the simulated Texaco gas is specified in Table 3.

Test Procedure

Based on the series of 10-cycle high-temperature, high-pressure (HTHP) bench runs as described in a previous RTI topical report (Gupta and Gangwal, 1992), the test procedure followed is described below:

Table 2. Nominal Test Conditions Used In 100-Cycle Test

<u>Sulfidation</u>	
Sorbent	ZT-4 ^a
Temperature	750 °C (1382 °F)
Pressure	15 atm (220 psia)
Particle size	100 to 300 µm ($d_{50} \approx 175 \mu\text{m}$) ^b
Sorbent inventory	500 g
Total gas flow rate	76 slpm (161.5 scfh)
Superficial gas velocity	15.64 cm/sec (0.51 ft/sec)
Sulfidation gas	Simulated Texaco gas ^c
H ₂ S content of coal gas	11,400 ppmv (1.14%)
<u>Regeneration</u>	
Temperature	760 to 785 °C (1400 to 1445 °F)
Pressure	15 atm (220 psia)
Total gas flow rate	76 slpm (161.5 scfh)
O ₂ content of regeneration gas	2.3 to 2.5%
Diluent	Nitrogen

^aSorbent properties are listed in Table 1.

^b d_{50} indicates 50% below 175 µm.

^cComplete gas composition is given in Table 3.

Startup

1. Five hundred grams of prescreened sorbent in the particle diameter range of 100 to 300 μm was loaded into the sorbent cage. The cage was then placed in the reactor shell and the entire reactor system (described previously) was assembled. New thimble filters were mounted on sulfidation and regeneration lines. Following this assembly, the reactor was leak-tested.
2. The reactor was pressurized to 220 psia and heated to 750 $^{\circ}\text{C}$ with a continuous flow of nitrogen through the reactor.

Table 3. Nominal Gas Composition of the Simulated Texaco Gas

Component	Vol %
H_2	29.94
CO_2	12.51
H_2O	18.25
H_2S	1.14
N_2	0.00
CO	<u>38.16</u>
Total	100.00

Run Procedure

1. Once the sorbent bed attained the desired temperature (750 $^{\circ}\text{C}$), it was sulfided by flowing the simulated coal gas through it. The composition of the gas exiting the reactor was measured continuously using the series of GCs described previously. Sulfidation of the sorbent was continued until the H_2S concentration in the reactor exit gas reached 500 ppmv, defined as the breakthrough point. At this point, the flow of coal gas was stopped and switched to nitrogen to purge the reactor. Purging of the reactor was continued for about 60 min. The reactor temperature was lowered to about 720 $^{\circ}\text{C}$, allowing for a 50 to 60 $^{\circ}\text{C}$ rise during regeneration.
2. Once the sorbent bed attained a temperature in the vicinity of 720 $^{\circ}\text{C}$, the sulfided sorbent was regenerated using a gas mixture containing air and nitrogen. The flow rates of air and nitrogen were adjusted to obtain an oxygen concentration of about 2.3 to 2.5 volume percent. This oxygen concentration had been found to be optimum from previous experience (Gupta and Gangwal, 1992). A higher oxygen concentration caused some difficulties in controlling the reactor bed temperature in the window of 750 to 780 $^{\circ}\text{C}$. Oxygen contents lower than 2.3 percent resulted in slower regeneration kinetics.

Sorbent regeneration was continued until the SO_2 concentration in the regeneration tail gas fell below 250 ppmv. At this point, the regeneration gas flow was switched to N_2 purge.

3. Steps 1 and 2 were repeated for subsequent cycles.

Shutdown

In this long-duration run, the reactor was kept hot with a continuous nitrogen purge during weekdays, and it was shut down during weekends. The shutdown procedure consisted of the following steps:

1. The main reactor furnace, preheater, superheater, and variacs controlling various heat tapes were switched off.
2. Nitrogen purge was continued for the entire duration of reactor cooling.
3. The reactor was depressurized by opening the BPR to the fully open position.
4. The sorbent bed temperature was continuously monitored during the cooling process.
5. When the sorbent bed temperature reached nearly ambient, the reactor was dismantled if sorbent examination and characterization were desired; otherwise, the unit was heated on Monday using the startup and test procedure previously described.

Shakedown Test

In previous HTHP multicycle bench-scale runs (Runs 1 to 9) described in an earlier RTI topical report (Gupta and Gangwal, 1992), a velocity of about 0.25 ft/sec (7.6 cm/sec) was used. Because most commercial bubbling fluidized-bed reactors are operated at higher velocities, it was thought that the velocity should be doubled to get a higher U/U_{mf} . Doubling the velocity necessitated a total gas flow rate of about 76 slpm. To handle these high flows, a number of modifications in the bench-scale test facility were made. These modifications are discussed in Section 2.0 of this report.

A sulfidation temperature of 750 °C for zinc titanate had not been tested before in a fluidized-bed reactor. Because zinc vaporization by reduction might be excessive at 750 °C, a shakedown test consisting of three sulfidation-regeneration cycles was performed using the test conditions in Table 2. This test demonstrated that the modifications made in the reactor system were adequate to carry out the actual test at the prescribed conditions.

Intermediate Shutdown and Startup of Reactor

Sorbent samples were withdrawn from the reactor after various cycles to track the correlation of sorbent reactivity with its physical and chemical properties. Typically, two sulfidation-regeneration cycles were carried out in an 8-hr day. One day per week was devoted to regular reactor maintenance. The sorbent samples were withdrawn after 10, 18, 26, 34, 42, 50, 59, 75, 81, and 85 cycles for characterization. Characterization results are reported in Section 6.0.

5.0 EXPERIMENTAL MEASUREMENTS

As discussed previously, most of the experimental measurements were performed using a computerized data acquisition system. Nonetheless, the furnace temperature settings, GC calibration, and ΔP data were recorded in the operator data sheets.

Online analysis of the gas exiting the reactor was performed using two GCs. Concentrations of sulfurous gases (H_2S , COS, CS_2 , and SO_2) were measured every 6 min, while CO, H_2 , N_2 , CO_2 , O_2 and higher H_2S and SO_2 concentrations were measured every 25 min using the automated system previously described.

The amount of aqueous condensate knocked out by the condenser was recorded. Selected condensate samples were analyzed for Zn, Ti, and S.

After a predetermined number of cycles, the sorbent was removed from the reactor and weighed to determine any weight loss due to elutriation. A representative sample weighing about 2 to 3 g was withdrawn from the removed sorbent batch for characterization. The representative sample was withdrawn after removing all the sorbent in a tray and homogenizing it. The sample used for characterization was never withdrawn from the reactor directly because it would come from the top part of the bed and would not be representative of actual sorbent.

A series of characterizations were performed on the representative sample including particle size analysis, pore size distribution, BET surface area, thermogravimetric analyzer (TGA) reactivity, Zn and Ti contents, XRD, and scanning electron microscopy (SEM).

The amounts of particles captured by the sulfidation and regeneration filters were also measured. In some cases, these collected particles were analyzed for zinc and titanium contents.

6.0 EXPERIMENTAL RESULTS

6.1 MINIMUM FLUIDIZATION VELOCITY

Before actual testing began, the sorbent was subjected to a cold flow test to determine its fluidization characteristics. A description of RTI's cold flow test facility appeared in a previous RTI topical report (Gupta and Gangwal, 1992). Also, a small number of fluidization tests were carried out in the actual HTHP reactor using nitrogen. Figure 3(a) shows typical fluidization curves at 1 and 15 atm pressures plotted using the data collected in the 3-in.-ID cold flow unit. These curves show the relationship between superficial gas velocity and pressure drop. At minimum fluidization, the pressure drop is equal to the weight of the bed. At this point, the entire bed is in motion and a further increase in gas velocity is accompanied by a minimal increase in differential pressure due to increased pressure drop across the distributor.

From this plot, the minimum fluidization velocity (U_{mf}) is estimated to be about 18 cm/sec at 15 atm. Estimation of U_{mf} using the literature correlations is highly subjective because of uncertainties associated with the measurement of Φ_s (sphericity of the particle), ϵ_{mf} (bed voidage at minimum fluidization), and d_p (particle diameter), particularly when the bed contains particles of wide size distribution. Extrapolation of this value (determined at 25 °C) to high temperature would lead to a significantly lower U_{mf} at 750 °C because of the decrease in gas density and the increase in gas viscosity with increase in temperature. Furthermore, ϵ_{mf} will increase with increase in temperature.

A series of measurements were made in the bench unit itself with the 2-in.-ID sorbent cage to determine the minimum fluidization velocity at HTHP conditions. Pressure drop across the bed was measured as a function of superficial gas velocity. Figure 3(b) shows the fluidization behavior of the sorbent at 650 °C and 15 atm.

From Figure 3(b), the minimum fluidization velocity at 650 °C and 15 atm is estimated to be 6.37 cm/sec. From the available correlation for U_{mf} in the literature, it is estimated to be about 1.87 cm/sec using an average particle size of 175 μm . Thus, the actual U_{mf} is about 3.4 times that of the predicted value based on an average particle size. If U_{mf} is estimated for the largest particle in the bed, it will be 5.5 cm/sec. This value is much closer to the experimentally observed value.

In the life-cycle test, a superficial gas velocity of 15.64 cm/sec was used (see Table 2), which translated into a U/U_{mf} ratio of about 2.45 using the value of U_{mf} determined experimentally. Because of a relatively small diameter of the reactor tube (2-in. ID), the possibility of slugging existed at these velocities. Unfortunately, no correlations are available in the literature that can predict slugging at high pressures. The well-known Stewart-Davidson correlation (whose validity at high pressures is not known) was used to check if slugging would occur in the reactor. According to this correlation (Stewart and Davidson, 1967), slugging will set in at a velocity higher than U_o where U_o is given by

$$U_o = U_{mf} + 0.07\sqrt{gd_t}.$$

Figure 3. Determination of minimum fluidization velocity in (a) cold flow unit and (b) bench unit.

Here d_t is the diameter of the reactor tube in centimeters and g is the acceleration due to gravity in cm/sec^2 .

$$\begin{aligned}U_o &= 6.37 + 0.07 \sqrt{(980) \cdot (2 \times 2.54)} \\&= 11.3 \text{ cm/sec}\end{aligned}$$

Thus, according to this value of U_o , the bed will slug under the test conditions.

The Stewart-Davidson correlation is merely a **sufficient** condition for slugging, not the **necessary** condition. The necessary condition is given by Baeyens and Geldart (1974), according to which a minimum bed height, Z_s , is needed for slugging to set in, where Z_s is given by

$$Z_s = 60d_t^{0.175} \text{ [cm]} .$$

For the 2-in.-ID bed used, $Z_s = 79.74$ cm. The bed height used in the 100-cycle test was about 20 cm ($L/D = 4$). As this height is too low for slugging to set in, it is very likely that the reactor was not operated in a slugging mode.

6.2 BREAKTHROUGH BEHAVIOR

Hydrogen sulfide (H_2S) and carbonyl sulfide (COS) concentrations in reactor outlet gases were measured every 6 minutes to determine the sorbent's desulfurization efficiency. Appendix A shows the breakthrough data for both H_2S and COS for Cycles 1 to 100. It should be noted that data reported in Appendix A are on a dry basis—the gas sample is sent to the GC system after steam is condensed. Therefore, the actual H_2S and COS concentrations will be approximately 84 percent of that shown in Appendix A.

Figure 4 shows the H_2S breakthrough curves for the first 10 cycles. As can be seen, essentially no change in H_2S breakthrough behavior is observed with cycling. The COS evolved during these 10 cycles was in the range of 0 to 10 ppmv as depicted in Figure 5.

Because it is difficult to combine 100 curves on a single plot, H_2S breakthrough behavior during a few selected cycles (Cycles 1, 10, 20, 30, 50, 60, 70, 80, 90, and 100) is shown in Figure 6. The H_2S concentration data for all the cycles are listed in Appendix A, as previously mentioned. As can be seen, the prebreakthrough H_2S level in all the cycles was consistently below 20 ppmv. It should be noted that the equilibrium H_2S concentration at 750 °C in Texaco gas is about 12 ppmv as computed from thermodynamic data (Gupta and Gangwal, 1992).

A gradual decline in breakthrough time (needed to reach an H_2S concentration of 500 ppmv from the inlet value of about 11,400 ppmv) is observed over the 100 cycles with about 80 percent decline in the first 50 cycles. This indicates a loss of sorbent reactivity with cycling and is discussed later in greater detail.

6.3 SORBENT SULFUR CAPACITY AT BREAKTHROUGH

Based on the breakthrough behavior discussed in Section 6.2, the sulfur capture by the sorbent was calculated for Cycles 1 to 100. Figure 7 shows the actual sulfur absorbed by the

Figure 4. H₂S breakthrough curves for Cycles 1 to 10.

Figure 5. COS breakthrough curves for Cycles 1 to 10.

Figure 6. H₂S breakthrough curves for selected cycles.

Figure 7. Sorbent sulfur capacity for Cycles 1 to 100.

sorbent as a function of cycle number at breakthrough—500 ppmv of H₂S in reactor outlet gas. During the first 18 cycles, the sulfur capacity remained nearly constant at 13.4 g S/100 g of fresh sorbent, indicating about 60 percent capacity utilization. The theoretical saturation sulfur absorption capacity of ZT-4 is about 22.5 g S/100 g of fresh sorbent based on ZnO + H₂S → ZnS + H₂O stoichiometry. Only ZnO in zinc titanate absorbs sulfur; TiO₂ only provides stability to ZnO and does not participate in the desulfurization reaction. The sulfur capacities of the sorbent during the 50th and 100th cycles were 7.45 and 5.96 g S/100 g fresh sorbent, respectively, further corroborating the fact that most of the deactivation occurred during the first 50 cycles.

The decline in breakthrough time with cycling, as stated in Section 6.2, manifests itself in a decline in sulfur absorption. In fact, the S-capacity shown in Figure 7 is directly proportional to breakthrough time. It appears from Figure 7 that the sulfur capacity evinces a step profile. This is due to the 6-min frequency of collecting breakthrough data (see Appendix A). A 6-min decrease (one less data point) in breakthrough time will reduce the sulfur capacity by 1.49 g S/100 g sorbent, as illustrated in Table 4.

The following example shows a typical calculation of sulfur capacity:

$$\begin{aligned} \text{Sulfur Capacity} &= \frac{\left(\begin{array}{c} \text{Mole Fraction} \\ \text{of H}_2\text{S in} \\ \text{Coal Gas} \end{array} \right) \left(\begin{array}{c} \text{Molar Flow} \\ \text{Rate of Coal Gas} \\ \text{(mol/min)} \end{array} \right) \left(\begin{array}{c} \text{MW of Sulfur} \end{array} \right) \left(\begin{array}{c} \text{Breakthrough} \\ \text{Time} \\ \text{(min)} \end{array} \right)}{\text{g of Fresh Sorbent Loaded in the Reactor/100}} \\ &= \frac{\left(11,400 \times 10^{-6} \right) \left(\frac{76.22}{22.4} \right) (32) (54)}{500/100} = 13.42 . \end{aligned}$$

The above calculation procedure assumes that all the sulfur is picked up by the sorbent and no sulfur escapes with the gas exiting the reactor. Because, on an average, the sorbent picks up 99 percent of the sulfur at breakthrough, this assumption is fairly good.

If the frequency of data collection is increased, for instance, from 6 min to 2 min, the decline in sulfur capacity with cycling as illustrated in Figure 7 will show a more gradual change. Nonetheless, it is evident that the sorbent exhibits about a 55 percent drop in sulfur capacity in Cycle 100 compared to Cycle 1. The principal causes for this drop are discussed below.

Table 4. Sulfur Capacity at Various Breakthrough Times

Breakthrough time (min)	54	48	42	36	30	24
Sulfur capacity (g S/100 g fresh sorbent)	13.42	11.93	10.44	8.95	7.45	5.96

6.4 SORBENT LOSS FROM THE REACTOR

Because the test conditions used during this run were extremely severe and no previous data are available for zinc titanate at 750 °C in a fluidized-bed reactor, sorbent loss from the reactor was a major concern. To determine the sorbent loss during this 100-cycle testing, the run was stopped at various cycles in between, as previously discussed. Table 5 shows the weights of sorbent recovered during each segment of the run. Also included in this table are the weights of sorbent deposits found on sulfidation and regeneration filters.

According to the data reported in Table 5, very little sorbent was lost from the reactor. The net total sorbent loss during the entire 100 cycles was 1.64 percent based on the weights of sorbent removed from the reactor and the material deposited on filters and lines. The total sorbent loss from the reactor itself was 4.51 percent. On the other hand, the total sorbent loss from the 100-cycle test with T-2465M zinc ferrite in the same reactor was 42 percent despite significantly milder operating conditions—KRW gas containing 20 percent steam at 625 °C.

It is to be noted here that a sorbent inventory of 500 g (of regenerated material) in the reactor was maintained nearly all the time. The reactor was always opened after the regeneration. No samples of sulfided material were removed. Whenever the reactor was opened, about 2 to 3 g of material was removed for characterization. This material and the

Table 5. Sorbent Loss During 100 Cycles

Cycles	Sorbent Inventory (g)	Sorbent Recovery (g)			Loss (%)
		Reactor	Filters and lines	Total	
1-10	500	497.81	1.79	499.60	0.08
11-18	500	497.27	2.30	499.57	0.09
19-26	500	497.41	2.00	499.41	0.12
27-34	500	498.22	1.20	499.42	0.12
35-42	500	498.41	1.00	499.41	0.12
43-50	500	498.35	1.20	499.55	0.09
51-59	500	497.61	0.78	498.39	0.32
60-75	500	497.50	1.84	499.34	0.13
76-81	500	498.65	NA	498.65	0.27
82-85	500	499.00	0.70	499.70	0.06
86-100	500	497.20	1.70	498.90	0.22
Total sorbent loss during 100 cycles = 1.64%					

amount lost, as discussed above, were replenished by adding 4 to 5 g of fresh material to make up 500 g of sorbent. After Cycles 10 and 50, attrition tests on the reacted sorbents were performed. The attrition test required 50 g of the sample; therefore, in both instances 50 g of fresh material was added to make up to 500 g. Addition of these small amounts of fresh material was not expected to alter the breakthrough behavior significantly.

The sorbent deposits that were found on sulfidation and regeneration filters and reactor lines were believed to be due predominantly to particle elutriation and not zinc vaporization. Based on RTI's experience, deposits due to zinc vaporization and condensation are generally in the form of a white shiny material; these types of deposit were not evident in this run. Therefore, no significant zinc vaporization is suspected, which is further confirmed by zinc and titanium analyses discussed in Section 6.5.

6.5 ZINC VAPORIZATION

Because the possibility of zinc oxide reduction followed by zinc vaporization was a major concern at the sulfidation temperature of 750 °C, sorbent samples at the end of each block-set were analyzed for zinc and titanium using the inductively coupled plasma (ICP) technique. A description of this analytical technique was reported in Gupta and Gangwal (1992). Table 6 shows the Zn and Ti analysis results together with the precision of measurement. It should be noted that the accuracy of the ICP technique for this analysis is within ± 5 percent.

Table 6. Zinc and Titanium Analysis Results

Sample	Zn (wt %)	Ti (wt %)
Fresh	45.6 $\pm$ 0.48	23.0 $\pm$ 0.21
After 10 cycles	46.2 $\pm$ 0.46	21.5 $\pm$ 0.33
18	44.2 $\pm$ 0.50	21.1 $\pm$ 0.51
26	45.7 $\pm$ 0.86	22.2 $\pm$ 0.84
34	43.8 $\pm$ 0.19	21.6 $\pm$ 0.30
42	44.0 $\pm$ 0.50	22.1 $\pm$ 0.20
50	43.0 $\pm$ 0.44	21.8 $\pm$ 0.55
59	44.7 $\pm$ 0.38	21.8 $\pm$ 0.30
75	45.4 $\pm$ 0.39	21.9 $\pm$ 0.54
81	43.9 $\pm$ 0.35	21.7 $\pm$ 0.15
85	44.5 $\pm$ 0.24	21.5 $\pm$ 0.34
100	43.4 $\pm$ 0.28	21.6 $\pm$ 0.38

Figure 8 shows the Zn and Ti contents of the sorbent after various cycles with appropriate error bars. As can be seen from these data, zinc content varies between 43 and 46 percent with no particular trend. Similarly, the data for Ti analysis are also scattered between 21 and 23 percent. However, the variation in Ti values is not significant after 25 cycles.

Due to the scatter in individual zinc and titanium values, it is believed that a better number to look at is the Zn-to-Ti ratio. This is because the zinc and titanium are analyzed from the same sample which has not been normalized in size. Based on the data reported in Table 6, the values of Zn-to-Ti ratio were calculated. The top graph in Figure 8 shows this plot. It appears that initially, during Cycles 1 to 10, the Zn-to-Ti ratio increased, and thereafter it steadily declined up to 50 cycles. After 50 cycles, scatter in the Zn-to-Ti ratio is observed.

The Zn-to-Ti ratio increased from 1.45 in the fresh sorbent to 1.48 in the sorbent removed from the reactor at the end of 100 cycles. In fact, it remained above the initial 1.45 throughout the 100 cycles. Thus, based on the data reported here, it cannot be said with certainty that any zinc loss occurred from the sorbent over the 100 cycles.

6.6 PARTICLE SIZE DISTRIBUTION

The particle size distribution of the sorbent was measured in the fresh state and after 10, 50, and 100 cycles. Unlike other characterizations, particle size and attrition were not measured after each block-set to preserve the mechanical integrity of the sorbent.

Figure 9 shows the particle size distribution of fresh, 10-, 50-, and 100-cycle reacted sorbent. No significant generation of fines (below 140 mesh) is observed as would be expected if the

Figure 8. Zn and Ti contents of sorbent at the end of selected cycles (also shown is the Zn/Ti ratio with appropriate error bars).

Figure 9. Particle size distribution of ZT-4 after Cycles 0, 10, 50, and 100.

sorbent were to undergo significant attrition. The particle size distribution does not appear to change significantly with sorbent cycling. The average particle sizes based on arithmetic as well as harmonic means were calculated and are shown in Table 7.

The average sorbent particle size decreased consistently over Cycles 1 to 100 from a value of 174.6 to 160.4 μm . At the end of Cycle 50, about 75 g of the reacted sorbent was removed to carry out the attrition test. This amount was replenished by adding 75 g of the fresh sorbent with an average particle size of 174.6 μm . As a result, the particle size distribution of the sorbent in Cycle 51 was different than the one after Cycle 50. Simple calculations indicated that the harmonic mean of the sorbent at the start of the 51st cycle was 163.6 μm , as shown in Table 7. A relatively small decrease in particle size was observed during Cycles 51 to 100 from 163.6 to 160.4 μm compared to the decrease between Cycles 1 to 50. This observation further corroborates that most of the decline in the sorbent reactivity occurred in the first 50 cycles.

6.7 ATTRITION RESISTANCE

Sorbent durability is perhaps the biggest concern in the design of a commercial hot-gas desulfurization system. One of the main objectives of this long-duration life-cycle test was to determine whether the sorbent would maintain its mechanical strength over the 100 sulfidation-regeneration cycles.

Table 7. Average Sorbent Particle Size after Various Cycles

	Harmonic mean (μm)	Arithmetic mean (μm)
Fresh	174.6	189.5
After 10 cycles	170.1	185.1
After 50 cycles	161.8	176.4
Start 51st cycle	163.6	178.4
After 100 cycles	160.4	177.2

Similarly to particle size distribution, the sorbent was subjected to attrition testing at four points during the entire 100-cycle run, namely, in the fresh state and after 10, 50, and 100 cycles. Unlike the other characterizations, more frequent attrition measurements were not made because the sorbent used in the attrition tester had to be discarded. Removal of sorbent from the reactor after each block-set for attrition testing and its subsequent replenishment by fresh sorbent would have posed serious problems in interpreting the sorbent reactivity data.

Figure 10 shows the weight loss data collected using a three-hole attrition tester after various cycles. Also included in this figure are the attrition data for a benchmark used US 260 fluid-catalytic cracking (FCC) catalyst obtained from Particulate Solids Research, Inc. (PSRI), for

Figure 10. Attrition behavior of fresh and reacted ZT-4 measured in a three-hole air-jet attrition tester.

comparison purposes. It should be noted that the particle size range of zinc titanate sorbent samples was 100 to 300 μm , while FCC catalyst particles were in the size range of 75 to 150 μm . It is well known that the weight loss in this type of attrition device is roughly proportional to the square of particle diameter. This means that, if the FCC catalyst particles were in the 100- to 300- μm range, the weight loss would be approximately three times more than what was measured.

As discussed in a previous RTI topical report (Gupta and Gangwal, 1992), unlike a single-hole tester, the attrition resistance measured using a three-hole tester cannot be defined in terms of a percent value. It is qualitatively expressed in terms of percent sorbent loss in 5 and 20 hr. The 5-hr loss represents initial sorbent loss due to carryover of fines and rounding of edges, while the 20-hr loss represents the fines generated and elutriated due to shearing of particles owing to a high-velocity impact by air at nearly sonic velocities. If these 5- and 20-hr losses are compared for two sorbents having similar particle size distributions, the sorbent with the higher loss would be more prone to attrition as compared to the sorbent with lower 5- and 20-hr losses.

It is evident from the data in Figure 10 that the sorbent gradually becomes more attrition-resistant with cycling and appears to stabilize in attrition resistance after 50 cycles. This is consistent with some earlier findings (Gupta and Gangwal, 1992). The increase in attrition resistance can be due to a number of factors including rounding of edges with cycling, decrease in sorbent internal porosity (discussed in Section 6.10), and increase in particle density. After 100 cycles, the sorbent is at least as good as the equilibrium FCC catalyst (if particle size is taken into account). Thus, it is not anticipated that continuous operation of a fluidized-bed hot-gas desulfurization system would present any serious problems in terms of particle attrition while employing a sorbent similar to ZT-4.

It should be borne in mind that the weight loss data depicted in Figure 10 are strictly relative and should not be used to estimate sorbent replenishment rates. The attrition test employed here is extremely severe (because of nearly sonic velocities) and is used merely to establish a relative ranking of various sorbents as discussed in a previous RTI topical report (Gupta and Gangwal, 1992).

6.8 BET SURFACE AREA

The BET surface area of the sorbent was measured after each block-set to correlate it with change in sulfur capacity. Figure 11 shows the BET surface area measured using N_2 adsorption (Quantasorb Surface Area Analyzer) as a function of cycle number. The detailed measurement procedure for surface area was described in Gupta and Gangwal (1992).

It is clear from Figure 11 that the surface area progressively decreases with cycling. The surface area of the fresh sorbent was about 3.5 m^2/g , falling to about 0.8 m^2/g after 100 cycles. Most of this decrease in the BET surface area occurs during the first 50 cycles and the surface area stabilizes somewhat thereafter. This decrease in surface area correlates with the drop in sorbent reactivity. However, the surface area is not the only factor responsible for the sorbent's reactivity decline. Other factors such as silicate formation and loss of porosity are also responsible, as discussed later.

The drop in surface area can be attributed primarily to two factors: (1) prolonged exposure of the sorbent to 750 $^\circ\text{C}$ or higher for at least 2,000 hours and (2) cyclic sulfidation-regeneration

Figure 11. BET surface area of ZT-4 sorbent during the 100-cycle test.

with the accompanying solid structural changes. Another potential factor, as discussed in Section 9.0, could be the formation of zinc silicate in the sorbent structure.

6.9 TGA CHEMICAL REACTIVITY

After each block-set, sorbent samples were subjected to the standard 1.5-cycle TGA reactivity test described in Gupta and Gangwal (1992). Figure 12 shows the TGA reactivity profiles for the sorbent after various cycles. As can be seen, both the saturation sulfur pickup (indicated by the maximum weight gain during the second cycle) and the rate of sulfur pickup (indicated by the slope of the sulfidation curve) decrease with cycling. Estimates of saturation sulfur pickup were made and are plotted against cycle number in Figure 13. This figure shows that, similar to drop in BET surface area, the saturation sulfur pickup decreases progressively with cycling with most of the drop (80%) occurring during the first 50 cycles. After 50 cycles, the rate of decrease is fairly small. This small rate can be attributed to the deactivation of the fresh sorbent added after 50 cycles to make up for the sorbent used in attrition testing as discussed in Section 6.6. Interestingly, computation of the correlation coefficient (R) between the BET

Figure 12. TGA reactivity profiles of ZT-4 after various cycles.

Figure 13. TGA saturation sulfur pickup as a function of cycle number.

surface area and saturation sulfur pickup gave a value of about 0.99, indicating nearly perfect correlation.

6.10 PORE SIZE DISTRIBUTION

The pore size distribution of the sorbent was measured after every block-set of experiments using a Micromeritics AutoPore 9220II mercury porosimeter. Figure 14 shows the plots of cumulative pore volume as a function of pore diameter. Pore diameter is directly proportional to the mercury filling pressure inside the pores. Examination of these pore size distribution plots reveals that the pore volume of the sorbent consistently decreases with cycling, while MPD (at 50 percent of the total cumulative pore volume) stays fairly constant. This behavior is further illustrated in Figure 15.

The consistent decrease in pore volume and fairly constant value of MPD with cycling indicates that some of the macropores are being closed during the course of the run. This observation is further corroborated by the porosity plot shown in Figure 16, which shows a progressive decline in sorbent internal porosity with cycling. It is believed that one of the potential causes of the decline in porosity, pore volume, and also in BET surface area is the formation of zinc silicate in the sorbent. Formation of zinc silicate is discussed further in Section 9.0.

Regression of porosity and pore volume data with the TGA sulfur pickup was performed and a very interesting trend was observed. The correlation coefficient between TGA sulfur pickup and MPV was 0.9624, while it was 0.9330 between TGA sulfur pickup and sorbent porosity. This

Figure 14. Cumulative pore volume as a function of pore diameter after selected cycles.

Figure 15. MPV volume and MPD for ZT-4 after selected cycles.

Figure 16. Particle density, skeletal density, and porosity of the sorbent after selected cycles.

indicates that the sulfur capture by the sorbent is directly related to its structural properties such as BET surface area, pore volume, and internal porosity.

6.11 SORBENT DENSITY

Various sorbent density measurements were performed including the following:

- Particle density (using mercury porosimetry),
- Skeletal density (using mercury porosimetry), and
- Compacted bulk density (using a graduated cylinder).

Figure 16 shows a series of plots of particle density, skeletal density, and porosity against cycle number. As expected, the particle density increases progressively with cycling, whereas the skeletal density values show a scatter between 4.6 and 5.2 with no particular trend. Increase in particle density is attributed to decrease in pore volume and porosity. Regression of particle density data with TGA sulfur pickup yields a correlation coefficient of -0.966. This indicates a good correlation between the two. The negative sign of correlation coefficient indicates that a decrease in TGA sulfur pickup correlates with an increase in particle density.

In addition to the above two measures, compacted bulk densities (CBDs) of the fresh and 100-cycle reacted sorbent were measured. This measurement was performed using a rather simple method in which 50 cc of the sorbent were tightly packed in a graduated cylinder by periodic tapping and the weight of the 50-cc volume was determined.

Efforts were made to keep the packing and voidage uniform to obtain reproducibility in the measurement. The CBD of the fresh material was 1.52 g/cc, whereas it was 2.10 g/cc for the 100-cycle reacted material. These values indicate a 38 percent increase in the CBD over 100 cycles.

6.12 XRD ANALYSIS

XRD analysis of the sorbent samples was performed at West Virginia University (WVU). A Phillips PW 1800 automatic XRD unit employing single-crystal monochromated copper $K\alpha$ radiation was used for XRD analysis. The analysis procedure is described in Gupta and Gangwal (1992).

Table 8 shows various crystalline phases detected in the sorbent samples extracted from the reactor after selected cycles. Detailed XRD results provided by WVU are provided in Appendix B. As noted in footnote (a) on Table 8, the reported value of Zn_2TiO_4 phase represents a total value of Zn_2TiO_4 and $Zn_2Ti_3O_8$ phases since lines for both phases appear in proximity to each other on an X-ray diffractogram. Therefore, the XRD composition cannot be used to close the zinc and titanium material balances. However, it should be possible to determine the relative amounts of Zn_2TiO_4 and $Zn_2Ti_3O_8$ by mass balance from the knowledge that Zn/Ti was approximately 1.5.

Table 8 shows that the predominant crystalline phase in the sorbent in fresh as well as in reacted state is Zn_2TiO_4 . Some free zinc oxide is detected in the fresh sorbent while none is detected in the reacted sorbent. The amount of $ZnTiO_3$ appears to correlate with the TiO_2 in the rutile form.

Table 8. XRD Phases Detected on Sorbent Samples

Phase	ZnO	ZnTiO ₃	Zn ₂ TiO ₄ ^a	TiO ₂ (rutile phase)	ZnSO ₄ · H ₂ O	2ZnO · SiO ₂	Total
Fresh ZT-4	1.2	2.6	94.2	2.0	0.0	0.0	100
10-cycle reacted	0.0	1.4	93.8	1.1	0.0	3.7	100
50-cycle reacted	0.0	0.0	95.8	0.6	0.1	3.5	100
85-cycle reacted	0.0	0.1	95.0	0.4	0.4	4.1	100
100-cycle reacted	0.0	0.2	95.0	0.3	0.4	4.1	100

^aRepresents a combination of Zn₂TiO₄ and Zn₂Ti₃O₈ phases.

The most important finding of this analysis was the presence of zinc silicate (2 ZnO · SiO₂) in the reacted sample. In addition to XRD, the presence of zinc silicate has been confirmed by the analysis of silica in the sorbent. No evidence of zinc silicate appears in the fresh sample, while zinc silicate increases to about 4 percent in the reacted material. Zinc silicate in the sorbent would be formed when ZnO and SiO₂ react at high temperature. This issue of zinc silicate, which is believed to be responsible for reactivity loss, is discussed further in Section 9.0.

6.13 SEM/EDS ANALYSIS

SEM/EDS analysis of the sorbent samples was performed at WVU after various cycles to examine the surface morphologies and homogeneity of zinc and titanium in the sorbent. Detailed results of SEM analysis are provided in Appendix C where SEMs of the fresh and 10-, 50-, 85-, and 100-cycle reacted material are shown along with Zn and Ti distribution and atomic composition maps determined by EDS. Examination of these micrographs indicates the following:

- The surface morphology of the sorbent becomes smoother as it is cycled. For example, the fresh sorbent sample has an irregular shape and this shape becomes more spherical after cycling. This may be one of the principal reasons of better attrition resistance of the reacted material.
- The Zn and Ti distribution, as indicated by the density of dots, appears to be fairly uniform in the fresh sample. This uniformity is not always maintained when sorbent is subjected to cyclic operation. For example, in the 50-cycle reacted material, a dense layer rich in Zn is observed near the surface, while a region of lean Zn concentration is detected near the center of the particle. This observation is similar to the data taken at METC using X-ray photoelectron spectroscopy (XPS) (Siriwardane and Poston, 1992). XPS analysis results are provided in Appendix D.

Based on the foregoing analyses, it is possible that zinc migration may occur during sulfidation with subsequent rearrangement of the structure during regeneration. Unlike sulfided samples, the regenerated samples do not exhibit unusually high Zn-to-Ti ratios at the surface. The Zn-to-Ti ratio of regenerated sample is close to the fresh material, indicating redistribution of migrated zinc and its subsequent reaction with TiO_2 during regeneration. The actual mechanism of this transformation, however, is not well understood.

7.0 OPERATIONAL PROBLEMS

Because this test run was of long duration, few operational problems were expected. The major problems encountered include the following:

- Rise in reactor pressure drop,
- Corrosion and failure of superheater,
- Corrosion of reactor lines, and
- Plugging of BPR.

The last three problems from the above list were minor. A new superheater was installed during Cycle 81. A line downstream of the reactor in the vent system (just before the BPR) developed a fine hole due to corrosion. As a result, the reactor became depressurized and this line had to be replaced. Plugging of the BPR by fine dust was observed only twice during the entire 100-cycle run, but it had to be cleaned frequently, even after a filter was installed upstream.

The major problem, not observed during previous multicycle bench runs, was a rise in pressure drop across the reactor. The total pressure drop, including the pressure drop through the alumina distributor, was about 20.5 in. of H₂O during the first 10 cycles. During Cycles 11 to 18, it increased steadily, rising to 51 in. during Cycle 18.

It was thought that perhaps the distributor (containing primarily alumina and some silica) was getting plugged due to deposition of carbon or other materials. When the reactor was opened after the 18th cycle, the distributor appeared in good shape from the outside with no visual deposits or color change. Therefore, the decision was made to continue with the same distributor; however, the Berl saddle-packing below the sorbent cage was replaced in the reactor shell. This provided an improvement—the ΔP dropped to about 34 in. of H₂O. However, during the subsequent block-set, the ΔP rose from 34 in. of H₂O during Cycle 19 to 53 in. of H₂O during Cycle 26. When the reactor was opened after the 26th cycle, the distributor was again removed from the sorbent cage. A yellow layer was found on the upper surface of the distributor, while the lower surface was covered with black spots. Specimens of the distributor, along with a piece of fresh distributor (for comparison purposes), were analyzed for C, S, Zn, and Ti contents; the results are shown in Table 9.

The carbon and sulfur analyses were performed at Galbraith Laboratories, and the Zn and Ti analyses were conducted at RTI. The data reported in Table 9 indicate no sulfur, but there is strong evidence of carbon and zinc in the used distributor. Perhaps the primary cause of carbon deposition may be due to the reaction: $\text{CO} + \text{H}_2 \rightleftharpoons \text{C} + \text{H}_2\text{O}$ or $2 \text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$, which might occur at the beginning of each sulfidation owing to the time lag between the start of steam flow

Table 9. C, S, Zn, and Ti Analyses of Alumina Distributor

	C	S	Zn	Ti
Fresh	<0.5%	<0.5%	<40 ppm	<80 ppm
After 26 cycles of use	1.37%	<0.5%	3.02 ± 0.05%	641 ± 30 ppm

and CO and H₂ flow. However, reasons for the zinc and titanium deposits in the distributor plate are not apparent.

After 26 cycles, the distributor was replaced and a ΔP ranging between 18 and 20 in. of H₂O was observed during Cycles 27 to 34. This value increased to 30 in. of H₂O after Cycle 50. A pressure drop of 10 in. of H₂O is needed to fluidize the bed at minimum fluidization conditions.

Similar problems occurred during operation of the reactor from Cycles 51 to 100. The distributor was replaced once more when the ΔP rose to almost 60 in. of water. During Cycle 100, the ΔP was 49 in. of H₂O.

The problem of ΔP rise may be avoided if a metal distributor is used in place of alumina. As discussed in Section 9.0, in addition to lessening the ΔP rise problem, use of a metal distributor also would, presumably, minimize the zinc silicate formation in the sorbent.

8.0 TEMPERATURE RISE AND SO₂ EVOLUTION DURING REGENERATION

As in the study reported in Gupta and Gangwal (1992) on analysis of temperature rise during regeneration, the temperature and the SO₂ content of the regeneration tail gas were continuously monitored. The SO₂ content of the regeneration tail gas was measured using a continuous SO₂ analyzer. Figure 17 shows the temperature and SO₂ evolution profiles during the 81st regeneration cycle. The noise in the temperature profile is due to interference of the temperature signal by the lead connecting the output of the SO₂ analyzer to the data acquisition system. This problem has now been corrected by replacing the lead connecting the output of the SO₂ analyzer to the data acquisition system.

As expected, both temperature and SO₂ evolution profiles exhibit the same trend. Both rise to a maximum value, stay at that point for a while, and then drop off rapidly, stabilizing at some point thereafter. The maximum SO₂ concentration is about 1.5 percent. The O₂ content of the regeneration inlet gas was about 2.45 percent. Stoichiometry dictates that maximum SO₂ concentration can be $\frac{2}{3} \times (2.45\%) = 1.63\%$. Thus, the observed value of SO₂ concentration is close to the predicted value because all the oxygen is consumed in the reactor as confirmed by the GC analysis of the regeneration tail gas.

Figure 17. Temperature and SO₂ evolution profiles during 81st regeneration.

9.0 FORMATION OF ZINC SILICATE IN THE SORBENT

The XRD data presented in Section 6.12 indicated the presence of zinc silicate in the reacted sample while no zinc silicate was observed in the original, unreacted sample. Formation of zinc silicate can occur by the following reaction:

The presence of silica (SiO_2) is required for the above reaction to proceed. SiO_2 is known to be present in two places: (1) in the bentonite binder of the sorbent, which contains about 63 percent silica, and (2) in the distributor material (ZAL-45 obtained from Zircar Company). Because, prior to testing, the sorbent was calcined at 850 °C for 2 hours in an oxidizing atmosphere, the silica present in bentonite is not expected to contribute to zinc silicate formation during the cyclic operation unless the reaction requires a reducing atmosphere. However, it is plausible that zinc silicate may form gradually over a long time. On the other hand, formation of zinc silicate via reaction of ZnO (present in the sorbent) and SiO_2 released from the distributor is more plausible. The manufacturer of the distributor plate material reported that up to 15 percent free silica can be present in this primarily alumina-containing material. Furthermore, according to Zircar (the supplier), this silica can potentially escape from alumina under reducing conditions, particularly in the presence of H_2 at temperatures above 1,200 °F (649 °C).

To confirm this hypothesis, the samples of original and used alumina (taken out from the reactor after 26 cycles) were analyzed for their silicon content along with samples of zinc titanate (fresh as well as 100-cycle reacted). Table 10 shows the results of chemical analysis for Si.

Table 10. Results of Chemical Analysis for Si

Sample	Si (wt %) ^a
Distributor - original	6.48 ± 0.28
Distributor - used	1.99 ± 0.03
ZT-4: fresh	0.590 ± 0.037
ZT-4: 100-cycle reacted	1.160 ± 0.330

^aAnalyzed using ICP spectroscopy.

These data clearly indicate that silica has escaped from the distributor. Furthermore, there is clear evidence of silica getting into the zinc titanate structure.

A material balance performed on the silicon leaving the alumina and then in the zinc titanate showed about 50 percent closure. This indicates that a major part of the silica released from the alumina had reacted with the sorbent forming zinc silicate.

The formation of zinc silicate via the above reaction is thermodynamically favorable with a ΔG of -34.085 kJ/mol of zinc silicate. Furthermore, this reaction is slightly exothermic with the (ΔH) of reaction being about -36.0 kJ/mol of zinc silicate formed.

Formation of zinc silicate inside the sorbent structure is believed to be a potential cause of the decline in the sorbent's sulfur capture capacity during the 100 cycles as discussed in this report. Zinc silicate is an inert compound and does not react with H_2S . A potential mechanism

by which zinc silicate could reduce the reactivity of the sorbent is by plugging some of the macropores, thus resulting in a decrease in pore volume and surface area.

The Institute of Gas Technology (IGT), on contract to Enviropower of Finland, tested RTI's ZT-4-T (a scaled-up batch of ZT-4) for 10 cycles in their HTHP bench reactor using a metal distributor plate. Over 10 cycles, the decline in the sorbent's sulfur capture capacity was much smaller than that observed at RTI using the silica-containing distributor (Abbasian, 1993).

Figure 18 shows the change in TGA reactivity in both cases—using an alumina distributor at RTI and a metal distributor at IGT. The decline in chemical reactivity for the sample tested at IGT is compared to the decline in the sample tested at RTI. The release of silica from the alumina distributor and its subsequent reaction with the sorbent forming zinc silicate appears to be responsible for at least some, if not all, reactivity loss.

Figure 18. TGA reactivity of ZT-4 and ZT-4-T before and after 10 cycles of testing at RTI and IGT using alumina and metal distributor plates, respectively.

10.0 CONCLUSIONS

The following conclusions can be made from the results of the life-cycle test:

- Zinc titanate (ZT-4) sorbent consistently reduced the H_2S content of coal gas from 11,400 ppmv to less than 20 ppmv in a semi-batch bench-scale fluidized-bed at 750 °C and 15 atm.
- The sorbent is 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 percent in Cycle 1 to 5.8 wt percent in Cycle 100 with an average of about 9 percent. Most of the decline in the sulfur capacity occurred during the first 50 cycles and stabilized somewhat thereafter.
- 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.
- 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.
- The attrition rate (defined in terms of percent weight loss) of the sorbent after 100 cycles of testing decreased by at least an order of magnitude over that of the fresh sorbent.
- No significant sorbent loss (<2%) from the reactor was detected over 100 cycles. The total zinc loss determined by chemical analysis was negligible. In fact, the Zn-to-Ti ratio increased from 1.45 in the fresh sorbent to 1.48 in the 100-cycle reacted material.
- In addition to zinc silicate formation, other possible mechanisms, by which the surface area and pore volume could decrease may be a change in the shape of the freshly granulated material due to cycling, as detected by SEM.

11.0 RECOMMENDATIONS FOR FUTURE WORK

Based on the testing results of this study, the major recommendations are made for future work:

- As a result of good performance with simulated coal gas, ZT-4 should be tested with actual coal-derived gases to study the effect of other coal gas contaminants such as NH_3 , HCl, alkali, and trace metals.
- Because the bench-scale data gathered in this life-cycle test only address the sorbent's reactivity and mechanical strength over 100 cycles, they provide limited information for design of a commercial fluidized-bed reactor that would operate in a continuous mode. Therefore, a continuous bench-scale absorber-regenerator system with a sorbent circulation arrangement should be designed, built, and tested to serve as a prototype of a commercial system.
- A long-term run should be conducted with a distributor plate that does not contain silica.
- The production of ZT-4 should be scaled up to semicommercial (pilot-scale) quantities.

12.0 REFERENCES

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LIST OF ACRONYMS AND ABBREVIATIONS

ASME	American Society for Mechanical Engineers
BPR	Back pressure regulator
CBD	Compacted bulk density
COR	Contracting Officer's Representative
DOE	U.S. Department of Energy
EDS	Energy dispersive spectroscopy
FCC	Fluid catalytic cracking
FPD	Flame photometric detector
FTIR	Fourier transform infrared
GC	Gas chromatograph
HTHP	High temperature, high pressure
ICP	Inductively coupled plasma
IGCC	Integrated gasification combined cycle
IGT	Institute of Gas Technology
METC	Morgantown Energy Technology Center
MFC	Mass flow controller
MPD	Median pore diameter
MPV	Mercury pore volume
PSRI	Particulate Solids Research, Inc.
RTI	Research Triangle Institute
scfh	standard cubic feet per hour (@ 0 °C and 1 atm)
SEM	Scanning electron microscopy
slpm	standard liters per minute (@ 0 °C and 1 atm)
SS	Stainless steel
TCD	Thermal conductivity detector
TGA	Thermogravimetric analyzer
WVU	West Virginia University
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

H₂S and COS Breakthrough Data for Cycles 1 to 100

Appendix A

100-CYCLE RUN

H₂S and COS Breakthrough Data

H₂S Breakthrough Data

Time(min)	Cycle									
	1	2	3	4	5	6	7	8	9	10
0	0	6.2	4.2	0	2.9	0	0	7.7	8.8	4.5
6	17.1	15.5	9.8	16.1	10.8	8.8	9.4	17.5	17.9	12.2
12	20.9	17.8	13.7	17.7	13.5	11.5	12.4	18	22	14.3
18	24.3	20.4	17.8	22.9	17.7	16.7	17.3	21.6	24.8	19.5
24	31.3	25.4	24.1	30.9	25.8	24.3	26.7	27.8	32.1	27
30	44.9	34.3	33.8	41.6	35.7	35.9	36.5	35.8	43.5	35.4
36	61.3	49.6	48	62.4	55.6	57.9	59.9	54.3	63.3	53.9
42	92.6	88.9	86.1	119.3	112.1	118.9	120.3	11.7	121.5	107
48	179.4	247	229.9	393.7	393.9	408	430.5	401	458.5	333.2
54	549.4	637.2	731.6	877.5	960.6	1022	969.7	1065.4		1071.5

A-2

COS Breakthrough Data

Time(min)	Cycle									
	1	2	3	4	5	6	7	8	9	10
0	0	4.9	7.5	0	0	0	0	3.4	29.7	0
6	0	0	0	0	0	0	0	0	9.9	0
12	0	0	0	0	0	0	0	0	4.3	0
18	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0	0
36	0	0	0	0	0	0	0	0	0	0
42	3.6	3.4	3.2	4.4		4.4	3.8	4.4	0	5.2
48	0	0	0	10.8	10.3	10.5	11.5	10.6	3	10.5
54	12.9	13.2	16.7	6	22	24.6	24.8	25.9		34.9

100-CYCLE RUN

H₂S and COS Breakthrough Data

H₂S Breakthrough Data

Time(min)	Cycle									
	11	12	13	14	15	16	17	18	19	20
0	0	14.9	11.6	0	0	0	0	0	7.4	0
6	11.3	23.1	24.1	25.1	25.1	10.9	16.15	0	18.6	14.8
12	13.5	30.5	25.9	25.2	22.1	12.8	17.74	10.2	23.2	19.9
18	18.5	35.8	29.2	30.1	27.2	17	23.06	15.1	33.8	28.8
24	24.1	42.6	34.2	34.1	34	25.3	32.18	20.9	45.2	38.2
30	32.5	52.1	42.5	43.5	42.3	34.8	41.23	28.5	64.5	58.8
36	47.9	73.4	62.2	60.8	58.8	46.4	58.8	43.6	134.6	123.6
42	89.8	139.4	119.3	113	120.8	74.9	104.6	93.2	514.4	519.1
48	267.1	462.5	381.2	357.5	393.6	165.8	357.4	368.4		
54	802.9	1125.7	966.9	1211.8	1217.5	561.5	1371.8	1282.5		

A-3

COS Breakthrough Data

Time(min)	Cycle									
	11	12	13	14	15	16	17	18	19	20
0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	0	0	0	0
36	0	0	0	0	0	0	0	0	0	0
42	0	5.8	4.2	17.2	0	0	0	0	4.4	0
48	8.9	15	11.8	37.9	0	6.5	0	11.2	0	14.1
54	22	27.9	24.1	30.2	27.2	17.7	33.1	30	0	0

100-CYCLE RUN

H₂S and COS Breakthrough Data

H₂S Breakthrough Data

Time(min)	Cycle									
	21	22	23	24	25	26	27	28	29	30
0	0	0	0	0	0	0	0	0	0	0
6	15.5	16.6	12.5	17.3	14.1	15.6	17.6	9.7	0	8.5
12	20.9	20.5	20.6	19	17.3	18.1	20.6	15	0	9.6
18	25.7	26.9	28.5	29.9	24.4	25.7	30	26.4	10.9	18.6
24	35.6	37.8	42.5	38.5	35.7	42.9	41.5	42.4	38.3	35.6
30	51.9	62.2	68	57.2	57.1	70.4	71	72.7	51.3	91.9
36	111.2	145.1	163.7	123.4	140	193.2	287.7	200.7	98.5	688.9
42	463.3	686.8	807.5	566.3	749.8	1160.5	1675	1156	528.3	0
48	1660.5									

COS Breakthrough Data

Time(min)	Cycle									
	21	22	23	24	25	26	27	28	29	30
0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	0	0	0	0	0	0
30	0	0	0	0	0	0	5.1	5.3	0	0
36	5.9	0	6.7	6.2	5.4	8.2	10.8	9.2	6.6	5.8
42	15.5	18.5	21.6	19.3	24	9.3	49.3	37.5	24.9	0
48	49.5	0	0	0	0	0				
54	0	0	0	0	0	0				

A-4

100-CYCLE RUN

H₂S and COS Breakthrough Data

H₂S Breakthrough Data

Time(min)	Cycle									
	31	32	33	34	35	36	37	38	39	40
0	0	0	8.8	0	8.3	0	15.2	0	0	0
6	21.7	6.5	19.4	13.5	14.5	10.8	23.6	6.1	21.6	12
12	22.1	12.4	21.2	23.9	17.8	17	25	10.8	26	14.8
18	31.5	23.1	24.7	32.2	25.2	25.3	34.6	13.7	30.9	20.8
24	44.6	37.5	34	45.7	36.1	36.6	46.5	24.2	43.9	25.9
30	70.7	64.1	52.4	94.6	50.1	62.6	94.4	53.7	85.5	41
36	219.2	302.3	104.2	716.5	131.8	275	452.9	502.9	695.2	126.8
42	1548.3	1926.4	1163.5	2294.9	1199.2	1981.2				2285.8

A-5

COS Breakthrough Data

Time(min)	Cycle									
	31	32	33	34	35	36	37	38	39	40
0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	7.9
12	0	0	0	0	0	0	0	0	0	7.4
18	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	0	0	0	0	0	0
30	0	0	4.1	0	0	0	6	0	7.2	0
36	9.8	13	0	21.7	9.6	12	20.2	22.1	29.5	9.7
42	51.9	70.6	45.6	117.9	51.4	76.2	99.1			138.6

100-CYCLE RUN

H₂S and COS Breakthrough Data

H₂S Breakthrough Data

Time(min)	Cycle									
	41	42	43	44	45	46	47	48	49	50
0	0	0	4.8	0	0	0	0	5	9	0
6	19.7	18.7	14.8	5.5	0	0	18.4	18.3	18.1	14.1
12	23.9	21.8	21.5	10.8	14.9	17.2	25.5	23.5	25.2	21.9
18	35	31.2	33.7	23.5	22.4	28.1	30.9	36.7	37.7	33.8
24	49.2	46.5	52.5	42.2	32.3	41.9	46.9	50.3	58	56.3
30	109.1	118.1	194	152.7	65	105.7	117.7	114.4	265.2	390.5
36	1153.6	1007	1867.5	1669	619.4	1243.5	1402.8	1231.1	2183.8	2372.6

A-6

COS Breakthrough Data

Time(min)	Cycle									
	41	42	43	44	45	46	47	48	49	50
0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	0	0	0	0	0	0
30	6.8	7.4	8.7	10.3	6.8	19.4	6	6.5	14.2	20.1
36	43.4	39.4	68.7	71.1	33.7	38.2	57.8	47.5	120	148.9

100-CYCLE RUN

H₂S and COS Breakthrough Data

H₂S Breakthrough Data

Time(min)	Cycle									
	51	52	53	54	55	56	57	58	59	60
0	10.5	0	10.5	0	0	0	0	11.7	0	0
6	8.4	13.9	23.3	41.8	19	15.4	18.2	18.4	31.1	21.5
12	29.9	23.6	28.2	48	23.3	22.2	26	22.5	35.6	25.8
18	44.9	39	40.7	55.3	35.2	36.9	42.4	38.7	52	43.1
24	71.3	63.3	60.1	82.2	36.3	64.9	77.1	76.3	113.4	113.7
30	299.1	169.4	158.9	226.3	66.4	347	448.2	564.8	1189.8	1128.9
36	885.2	1619.4	1427.6	1764	1766	2066.7	2113.9			

A-7

COS Breakthrough Data

Time(min)	Cycle									
	51	52	53	54	55	56	57	58	59	60
0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	0	0	0	5.5	6	4.7
30	11.7	6.1	11.1	9.4	11	13.9	16.3	27.2	38.3	32
36	69.7	44.7	49.5	17.2	63.6	94.6	101.2			

100-CYCLE RUN

H₂S and COS Breakthrough Data

H₂S Breakthrough Data

Time(min)	Cycle									
	61	62	63	64	65	66	67	68	69	70
0	0	0	0	0		12.7	0	25.1	0	0
6	16.3	8.3	17.1	13.2		25.5	12.3	24.1	16.3	17
12	24.5	14.3	24.9	22.5	30.3	25.3	24.4	31.3	27.3	27.5
18	38.8	28.2	40.4	33.9	47.2	34.9	39.5	44.5	50.5	45.7
24	73.4	51.1	70	51.9	100.9	54.4	70.8	81.7	110.3	89.3
30	315.3	257.5	354.3	211.4	895.1	227	510.7	389.6	797.5	624.2
36	1876.6	1898.2	1958.7	1756.5		1585.3		1796.6		

A-8

COS Breakthrough Data

Time(min)	Cycle									
	61	62	63	64	65	66	67	68	69	70
0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0
18	0	0	0	0	0	0	0	0	0	0
24	0	0	0	0	5.7	0	4.4	0	4.5	3.7
30	12.5	9.9	14.3	9.7	25	10	17.2	13.8	24.8	18.5
36	83.7	79.2	89.8	74.7		107.4		131.8		

100-CYCLE RUN

H₂S and COS Breakthrough Data

H₂S Breakthrough Data

Time(min)	Cycle									
	71	72	73	74	75	76	77	78	79	80
0	0	0	0	0	0	0	0	0	0	0
6	21.8	21.9	12.8	6.2	23.4	21.5	20.9	28.6	27.4	13.9
12	26	37.2	26.5	40.6	35.2	31.2	32.5	36	47.6	25.7
18	48.7	63.7	50.1	71	59.9	51.5	59.2	63	80.3	46.7
24	97.9	207.9	110	221.5	157.2	137.7	152.4	192.3	240.5	127.9
30	728.2	1601.5	922.2	1435.5	1272.3	1335.4	1335.9	1613.8	1684.2	1348

A-9

COS Breakthrough Data

Time(min)	Cycle									
	71	72	73	74	75	76	77	78	79	80
0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	5.1	0
12	0	0	0	0	0	0	0	0	0	0
18	0	4	4.4	4.4	4.7	0	0	0	6	0
24	5.3	9.6	4.7	9	10.5	7.2	8.6	8.4	10.6	0
30	23.6	83.8	29.8	50.7	56.9	55.9	54	62	77.6	45.9

100-CYCLE RUN

H₂S and COS Breakthrough Data

H₂S Breakthrough Data

Time(min)	Cycle									
	81	82	83	84	85	86	87	88	89	90
0	0	11.4	0	0	0	0	0	0	0	0
6	16.7	37.5	12.5	23.4	24.7	16	23.6	19.8	29.4	17
12	29.7	45.3	35.5	48.4	44.2	32.3	35.5	36.8	36.6	32.6
18	60.5	119.8	134.2	175.4	143.7	72.1	80.4	84.4	72.2	84.8
24	188.5	692.7	931.6	1165.9	934	362.4	450	507.7	524.4	756.8
30	736.2					1884.8	1954.8			

A-10

COS Breakthrough Data

Time(min)	Cycle									
	81	82	83	84	85	86	87	88	89	90
0	0	0	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0
18	0	8.2	8.9	9.4	7.5	0	0	4.8	6.6	0
24	7	27.6	39.2	47.1	38	12	17.1	20.1	23.8	19.5
30	59.4					99	103.7			

100-CYCLE RUN

H₂S and COS Breakthrough Data

H₂S Breakthrough Data

Time(min)	Cycle									
	91	92	93	94	95	96	97	98	99	100
0	0	0	0	0	0	21.8	0	0	0	0
6	0	26.5	22.4	16.7	16.2	56.4	21.7	18.7	32.7	22.7
12	0	44	41.1	33.3	32.3	43.1	38	29.7	56.7	39.3
18	0	110.6	113.3	97.4	88.3	101.9	105.9	87.7	80.8	92.4
24	634.5	1023	842.9	789	710	816.3	858.4	778.8	498.6	541.4

A-11

COS Breakthrough Data

Time(min)	Cycle									
	91	92	93	94	95	96	97	98	99	100
0	0	0	0	0	0	0	0	0	0	0
6	0	3.1	0	0	0	7	0	0	0	0
12	0	5.3	0	0	0	0	0	0	0	0
18	0	5.2	7.2	4.3	5.3	8.8	6.1	5.3	0	6.3
24	81.5	44.6	36	30.8	27	35.9	34.5	29.7	19.3	28.1

XRD Analysis Data

Appendix B

Fresh ZT-4

B-2

* Belongs to a compound with a structure similar to Zn_2SiO_4 Rhombohedral Unit Cell $a = 13.9$ $c = 9.3$ JCPDS Card #37-1485

$\text{ZnTiO}_3 = 2.6\%$
 TiO_2 (R) = 2.0%
 $\text{ZnO} = 1.2\%$
 $\text{Zn}_2\text{TiO}_4 = 94.2\%$
 Size + Strain = 2502.1 Å
 Size or Strain = 753.5 Å
 $\Delta = 1748.6$ Å

ZT-4 After 10 Cycles

B-3

* Belongs to a compound with a structure similar to Zn₂SiO₄ Rhombohedral Unit Cell
 $a = 13.9$ $c = 9.3$
 JCPDS Card #37-1485

Zn₂SiO₄ = 3.7%
 TiO₂ (R) = 1.1%
 ZnTiO₃ = 1.4%
 Zn₂TiO₄ = 93.8%
 Size $\div$ Strain = 1719.2 Å
 Size or Strain = 694.1 Å
 $\Delta = 1025.1$ Å

ZT-4 After 50 Cycles

* Belongs to a compound with a structure similar to Zn₂SiO₄
 Rhombohedral Unit Cell
 a = 13.9 c = 9.3
 JCPDS Card #37-1485

Zn₂SiO₄ = 3.5%
 ZnSO₄•H₂O = 0.1%
 TiO₂ (R) = 0.6%
 Zn₂TiO₄ = 95.8%
 Size + Strain = 1785.8 Å
 Size or Strain = 698.2 Å
 Δ = 1087.6 Å

ZT-4 After 85 Cycles

* Belongs to a compound with a structure similar to Zn_2SiO_4
 Rhombohedral Unit Cell
 $a = 13.9$ $c = 9.3$
 JCPDS Card #37-1485

$\text{Zn}_2\text{SiO}_4 = 4.1\%$
 $\text{ZnSO}_4 \cdot \text{H}_2\text{O} = 0.4\%$
 $\text{TiO}_2 (\text{R}) = 0.4\%$
 $\text{ZnTiO}_3 = 0.1\%$
 $\text{Zn}_2\text{TiO}_4 = 95.0\%$
 Size + Strain = 1594.1 Å
 Size or Strain = 817.3 Å
 $\Delta = 776.0 \text{ Å}$

ZT-4 After 100 Cycles

* Belongs to a compound with a structure similar to Zn₂SiO₄ Rhombohedral Unit Cell
a = 13.9 c = 9.3
JCPDS Card #37-1485

Zn₂SiO₄ = 4.1%
ZnSO₄ • H₂O = 0.4%
TiO₂ (R) = 0.3%
ZnTiO₃ = 0.2%
Zn₂TiO₄ = 95.0%
Size ÷ Strain = 1451.7 Å
Size or Strain = 750.4 Å
Δ = 701.3 Å

Sample	Zn ₂ SiO ₄	ZnSO ₄ ·H ₂ O	TiO ₂ (R)	ZnO	ZnTiO ₃	Zn ₂ TiO ₄	Size & strain	Size or Strain	Δ	2.5Å Pos
ZT40	-	-	2.0	1.2	2.6	94.2	2502.1	753.5	1742.6	2.546
ZT410	3.7	-	1.1	-	1.4	93.8	1719.2	694.1	1025.1	2.544
ZT450	3.5	0.1	0.6	-	-	95.8	1785.8	698.2	1087.6	2.546
ZT485	4.1	0.4	0.4	-	0.1	95.0	1594.1	217.3	776.8	2.544
ZT4100	4.1	0.4	0.3	-	0.2	95.0	1451.7	750.4	701.3	2.546

SEM Analysis Data

Appendix C

Scanning Electron Micrographs of Fresh ZT-4

(a) Surface Structure

(b) Zn Distribution

(c) Ti Distribution

ZT-4 Fresh

Label = ZT-4 Fresh

19-Nov-92 15:05:41

30.000 Live Seconds

ELEM	CPS	BKGD	P/B
TIK	177.633	12.000	14.803
ZNK	174.200	6.000	29.033

INTE-% :

Label = ZT-4 Fresh

19-Nov-92 15:05:55

30.000 Live Seconds

ELEM	CPS	AT % ELEM
TI K	177.633	28.535
ZN K	174.200	71.465
Total		100.000

Used PEIF: EDAX

19-Nov-92 15:02:58 EDAX Ready

Rate = 1383CPS Time = 30 Lsec

FS = 481CNT PRST = 30 Lsec

A = ZT-4 Fresh

Scanning Electron Micrographs of ZT-4 After 10 Cycles

(a) Surface Structure

(b) Zn Distribution

(c) Ti Distribution

ZT-4 After 10 Cycles

Label = ZT-4 Feed

19-Nov-92 15:43:51
30.000 Live Seconds

ELEM	CPS	BKGD	P/B
TIK	225.400	26.033	8.658
ZNK	215.100	6.667	32.265

INTE-% :

Label = ZT-4 Feed

19-Nov-92 15:44:05
30.000 Live Seconds

ELEM	CPS	AT % ELEM
TI K	225.400	29.094
ZN K	215.100	70.906
Total		100.000

Used PEIF: EDAX

19-Nov-92 15:42:14 EDAX Ready
Rate = 1452CPS Time = 30 Lsec
FS = 636CNT PRST = 30 Lsec
A = ZT-4 Feed

Scanning Electron Micrographs of ZT-4 After 50 Cycles

(a) Surface Structure

(b) Zn Distribution

(c) Ti Distribution

ZT-4 After 50 Cycles

Label = ZT-4 50

20-Nov-92 10:07:46

30.000 Live Seconds

ELEM	CPS	BKGD	P/B
TIK	313.500	11.000	28.500
ZNK	157.033	7.200	21.810

INTE-% :

Label = ZT-4 50

20-Nov-92 10:07:56

30.000 Live Seconds

ELEM	CPS	AT % ELEM
TI K	313.500	43.875
ZN K	157.033	56.125
Total		100.000

Used PEIF: EDAX

20-Nov-92 10:06:15 EDAX Ready

Rate = 1749CPS Time = 30 Lsec

FS = 837CNT PRST = 30 Lsec

A = ZT-4 50

Scanning Electron Micrographs of ZT-4 After 85 Cycles

(a) Surface Structure

(b) Zn Distribution

(c) Ti Distribution

ZT-4 After 85 Cycles

Label = ZT-4 85

19-Nov-92 16:22:59

30.000 Live Seconds

ELEM	CPS	BKGD	P/B
TIK	251.800	12.800	19.672
ZNK	177.167	6.000	29.528

INTE-% :

Label = ZT-4 85

19-Nov-92 16:23:09

30.000 Live Seconds

ELEM	CPS	AT % ELEM
TI K	251.800	35.754
ZN K	177.167	64.246
Total		100.000

Used PEIF: EDAX

19-Nov-92 16:30:39 EDAX Ready

Rate = 26CPS Time = 30 Lsec

FS = 665CNT PRST = 30 Lsec

A = ZT-4 85

Scanning Electron Micrographs of ZT-4 After 100 Cycles

(a) Surface Structure

(b) Zn Distribution

(c) Ti Distribution

ZT-4 After 100 Cycles

Label = ZT-4 100 cycles
06-Jan-93 15:02:04
35.088 Live Seconds

ELEM	CPS	BKGD	P/B
TiK	499.774	22.002	22.715
ZnK	389.423	12.426	31.339

INTE-% :
Label = ZT-4 100 cycles
06-Jan-93 15:02:13
35.088 Live Seconds

ELEM	CPS	AT % ELEM
Ti K	499.774	33.446
Zn K	389.423	66.554
Total		100.000

Used PEIF: EDAX

06-Jan-93 14:59:54 EDAX Ready
Rate = 3114CPS Time = 35 Lsec
FS = 1494CNT PRST = Off
A = ZT-4 100 cycles

***Determination of Heterogeneities and Phases
in Zinc Titanate Sorbents***

***Copy of the Correspondence with DOE/METC
on XPS Results***

Appendix D

Determination of Heterogeneities and Phases in RTI-Generated Zinc Titanate Sorbents

Cluster: Bench Scale Sorbent Development

Cluster Researchers: R. Siriwardane
J. Poston

OTM Requester: T. Dorchak

Overview:

The zinc titanate prepared by granulated technique is considered to be superior in performance. ZT-4 sorbent has been prepared by granulation technique and has been tested under fluidized-bed conditions. Fresh sorbent, sulfided sorbent (9-1/2 cycles), and regenerated sorbent (10 cycles) were provided by RTI. Various surface analytical techniques were employed to determine the changes in sorbent characteristics after reaction.

Results:

X-ray analysis (EDS) was conducted on each sorbent. Seven analysis points were selected at random locations on the sorbent(s). EDS analysis of the zinc titanate revealed that the Zn/Ti ratio of the unreacted sample was fairly uniform. This indicated that it is unlikely that unbound zinc oxide was present in any significant abundance in the fresh sample. However, after regeneration there were significantly strong heterogeneities detected in Zn/Ti. It was difficult to detect any zinc in some particles of the regenerated samples. This indicates that the sorbent has undergone drastic changes after the reaction. Thus, the incomplete reformation of the zinc titanate during regeneration will not be good for the durability of the sorbent.

X-ray photoelectron spectroscopy (XPS) analysis revealed that the Zn/Ti ratio on the surface (50 Å) of the unreacted sample was 1.3. This increased to 3.0 after sulfidation and it was 2.0 after regeneration. This indicates that there is migration of zinc to the surface during reaction. A very small amount of sulfate was also observed on the surface of the regenerated sample. These data also indicated that there was an elemental rearrangement of the sorbent material after reaction and the sorbent after regeneration did not have the characteristics of the fresh sorbent. Thus, the long-term durability of this sorbent under fluidized-bed condition is questionable. A complete study of the sorbent material after each sulfidation and regeneration cycle is necessary to determine the cause of these changes.