CONF-9506162--56

DOE/MC/25006-96/C0531

Bench-Scale Testing of Fluidized-Bed Sorbents -- ZT-4

Authors:

Santosh K. Gangwal
Raghubir P. Gupta

Contractor:

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

Contract Number:

DE-AC21-88MC25006

Conference Title:

Advanced Coal-Fired Power Systems '95 Review Meeting

Conference Location:

Morgantown, West Virginia

Conference Dates:

June 27-29, 1995

Conference Sponsor:

U.S. Department of Energy, Morgantown Energy Technology Center (METC)

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, 175 Oak Ridge Turnpike, Oak Ridge, TN 37831; prices available at (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

4.5 Bench-Scale Testing of Fluidized-Bed Sorbents—ZT-4

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
Principal Investigator	Raghubir P. Gupta
METC Project Managers	Daniel C. Cicero
Period of Performance	September 21, 1988 to Setpember 30, 1995

Schedule and Milestones

FY95 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A	S
Life-Cycle Test with ZT-4	—	—	—	—									
CMP-5 Sorbent Testing					—	—	—	—					
CMP-5 Sorbent Production							—	—	—	—			
TRTU Testing at M.W. Kellogg										—	—	—	
Topical Report												—	—

OBJECTIVES

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

- Investigating various manufacturing methods to produce fluidizable zinc ferrite and zinc titanate sorbents in a particle size range of 50 to 400 μm;
- Characterizating and screening the formulations for chemical reactivity, attrition resistance, and structural properties;

- Testing selected formulations in an HTHP bench-scale fluidized-bed reactor to obtain an unbiased ranking of the promising sorbents;
- Investigating the effect of various process variables, such as temperature, nature of coal gas, gas velocity, and chemical composition of the sorbent, on the performance of the sorbent;
- Life-cycle testing of the superior zinc ferrite and zinc titanate formulations under HTHP conditions to determine their long-term chemical reactivity and mechanical strength;
- Addressing various reactor design issues;
- Generating a database on sorbent properties and performance (e.g., rates of reaction, attrition rate) to be used in the design and scaleup of future commercial hot-gas desulfurization systems;
- Transferring sorbent manufacturing technology to the private sector;
- Producing large batches (in tonnage quantities) of the sorbent to demonstrate commercial feasibility of the preparation method; and
- Coordinate testing of superior formulations in pilot plants with real and/or simulated coal gas.

BACKGROUND INFORMATION

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

PROJECT DESCRIPTION

In this program, regenerable ZnO-based mixed metal-oxide sorbents, including zinc ferrite and zinc titanate are being developed and tested. A brief description of pertinent project accomplishments is provided below.

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

During the first phase (1989) of this program, a 3-in. ID bench-scale HTHP semibatch fluidized-bed reactor system was designed and constructed. This reactor operates in a semibatch mode because the flow of gas phase is continuous while sorbent particles remain in the reactor. This system is capable of operation at up to 871 °C (1,600 °F) at 20 atm (294 psi). Any simulated coal gas can be generated in this system using a battery of eight mass flow controllers and three positive displacement pumps (for pumping liquid water to generate steam). This system is equipped with a state-of-the-art computer controlled data acquisition system. A series of gas chromatographs (GCs) and continuous on-line analyzers measure the concentrations of various species in the reactor exit gas such as H_2S, COS, SO_2, CO_2, H_2, CH_4, N_2, CO, O_2. A complete description of this test facility is given elsewhere (Gupta and Gangwal, 1992; 1993).

Development and Testing of Zinc Ferrite Sorbents

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

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

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

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

Development and Testing of Zinc Titanate Sorbents

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

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

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

100-Cycle Test with ZT-4

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

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

- The ZT-4 sorbent consistently reduced the H_2S content of coal gas from 11,400 ppmv to <20 ppmv in a semibatch bench-scale fluidized-bed at 750 °C (1,382 °F) and 15 atm.

- The sorbent was found to be fully regenerable, with negligible residual sulfate remaining. An oxygen concentration of 2 to 3 percent with N_2 diluent was found to result in adequate regeneration rates with no temperature control problems due to the exothermicity of the regeneration reaction.

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

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

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

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

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

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

Scaleup of the Granulation Technique

As discussed previously, the fluidizable zinc titanate sorbents (e.g., ZT-4) prepared by granulation technique exhibited superior performance during long-term testing. These sorbents were prepared in a laboratory-scale granulator of 2-L capacity. In order to prepare large sorbent batches for clean coal demonstration plants, the lab-scale granulator was replaced by a 35-L machine. A number of zinc titanate batches were prepared in this machine with the recipe used in preparation of ZT-4. The ZT-4 formulations prepared in the 35-L machine were designated as ZT-4L ('L' refers to the large machine). A comparison of physical and chemical properties indicated superior attrition resistance and chemical reactivity of ZT-4L sorbent compared to that of ZT-4, indicating successful scaleup as discussed in Gupta and Gangwal (1995).

After the successful scaleup of the granulation process from 2-L to 35-L batches, RTI entered into a subcontract agreement with Contract Materials Processing (CMP), Inc., Baltimore, MD, to produce about 5,000 lb of ZT-4L sorbent using this technique. CMP has extensive experience and facilities for manufacturing relatively large quantities of custom (toll) catalysts and adsorbents for variety of applications.

In the summer 1994, using the same 35-L granulator that was used in the demonstration runs for scaleup, CMP produced about 5,000 lb of ZT-4L at their Baltimore facility. The yield of the sorbent in 100- to 300-μm particle size range was not as good as was expected. Also the attrition resistance of the sorbent was somewhat poorer than the original material. The finer particle size and poor attrition resistance of the ZT-4L batch produced by CMP are attributed to high humidity levels in the summer months in the CMP plant in Baltimore. Humidity plays a vital role in formation of good sorbent particles in the granulator.

A qualitative comparison of physical and chemical properties of these two ZT-4L samples is provided in Table 1. As can be seen, the attrition resistance and yield in the 100- to 300-μm range of the production batch are significantly poor compared to the demonstration batch. However, no significant changes are evident in other physical or chemical properties. In fact, the TGA reactivity of the production batch is superior compared to the demo batch, perhaps due to its higher porosity.

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

	ZT-4L demonstration run	ZT-4L production run at CMP
Production time	Winter 1993	Summer 1994
Batch size	35 L	35 L
Chemical composition		
ZnO/TiO_2 (molar)	1.5	1.5
Bentonite (wt%)	5	5
Presence of additives	No	Yes
Free ZnO (wt%)	<2	<2
Particle density (g/cm^3)	2.06	2.30
Bulk density (g/cm^3)	1.37	1.36
BET surface area (m^2/g)	3.4	3.2
Pore size distribution		
Hg-pore volume (cm^3/g)	0.20	0.23
Median pore diameter (Å)	1,734	2,485
Porosity (%)	40.6	54.0
Chemical reactivity		
TGA[a] sulfur capacity (wt%)	22.5	23.2
Regenerability	Good	Fair
Attrition resistance (wt%)		
5-h loss	17.0	38.0
20-h loss	51.0	84.0
Particle size distribution		
Yield in 100 to 300 μm	60	40
APS[b] determined using a prescreened sample in 100- to 300-μm range	176	172
Fines problem	No	Yes

[a] TGA = thermogravimetric analysis.
[b] APS = average particle size.

A 2,000 kg (4,400 lb) batch of the production sample was shipped to Enviropower in Finland for testing in their 15-MW pilot plant with actual coal gas. Also, CMP shipped 200 lb of this sorbent to DOE/METC for testing in the modular gas cleaning rig (MGCR) connected to the METC fluidized-bed gasifier. A 60-lb batch of this sorbent was shipped to Particulate Solids Research (PSRI), Inc., for a loop attrition test.

Life Cycling Testing of ZT-4L Sorbent

The life cycle testing of the ZT-4L sorbent was carried out using the test conditions shown in Table 2 to demonstrate its long-term chemical reactivity and attrition resistance. The composition of simulated air-blown U-gasifier gas is included in Table 3. Testing was done in a 2-in. diameter reactor with 500 g sorbent. The detailed test procedure is described elsewhere (Gupta et al., 1994; Gupta and Gangwal, 1995). The sorbent was subjected to alternating periods of sulfidation and regeneration.

Table 2. Nominal Test Conditions

Sulfidation	
Sorbent	ZT-4L
Temperature	600 °C (1,112 °F)
Pressure	20 atm (294 psia)
Particle size	100 to 300 μm (APS = 172 μm)[a]
Sorbent inventory	500 g
Total gas flow rate	75 std L/min (159 std ft^3/h)
Superficial gas velocity	9.86 cm/s (0.32 ft/s)
Sulfidation gas	Simulated U-Gas gasifier gas[b]
H_2S content of coal gas	5,000 ppmv (0.5 mol%)
Reactor tube diameter	5.08 cm (2-in.) ID
Regeneration	
Initiation temperature	650 to 700 °C (1,202 to 1,292 °F)
Pressure	20 atm (294 psia)
Total gas flow rate	75 std L/min (159 std ft^3/h)
Regeneration gas	2 to 2.5 mol% O_2 in N_2

[a] Average particle size (APS) is calculated as harmonic mean.

[b] Gas composition is specified in Table 3.

Table 3. Nominal Gas Composition of the Simulated U-Gas

Component	Vol%
H_2	14.2
CO_2	5.8
H_2O	6.6
H_2S	0.5 (5,000 ppmv)
N_2	49.8
CO	23.1
Total	100.0

Initially 18 sulfidation-regeneration cycles were successfully completed. During startup for the 19th sulfidation, the pressure drop across the bed increased to 50-in. of H_2O with very poor fluidization. At this point, the reactor was cooled down and opened up. The reacted sorbent removed from the reactor had formed agglomerates and was yellowish in color. About 21 g of the sorbent was stuck to the alumina distributor and was removed by scrapping. The Inconnel thermocouple underwent delapidation as its size increased from 1/8-in. to about 1/4-in. It is suspected that some metal compounds (presumably Ni compounds) in the Inconnel thermocouple used in the reactor reacted with the sorbent forming inert compounds in the pore structure, thus reducing the surface area and pore volume. This theory was corroborated with chemical analysis results of the particles that were scrapped from the thermocouple surface. it is quite plausible that the actual temperature was 50 to 100 °C higher than that detected by the thermocouple, which would explain excessive sintering of the sorbent. Details of the test results for this 18-cycle test are described in Gupta and Gangwal (1995).

The 40-Cycle Test with ZT-4L

As noted above, the 18-cycle test that was carried out was repeated to obtain long-term chemical activity and mechanical strength data. The repeat test consisted of 40 sulfidation-regeneration cycles under the conditions listed in Tables 2 and 3. Additionally, to avoid temperature excursion problems, in addition to the two main thermocouples, additional thermocouples were inserted in the sorbent bed. The run was stopped after 25 cycles and the reactor was opened. A sample of 25-cycle reacted sorbent was removed for characterization. Cycles 26 to 40 were carried out with 400 g of sorbents in the cage. A detailed description of test results for this run is provided below.

Figure 1 shows the H_2S breakthrough curves for selected cycles. As can be seen from Figure 2, during the first 10 cycles no change in sorbent activity is evident. However, in the subsequent cycles, chemical reactivity of the sorbent gradually declined.

From the breakthrough data, the sulfur capture capacity of the sorbent was calculated for Cycles 1 to 40. Figure 2 shows the actual sulfur picked up by the sorbent as a function of cycle number at breakthrough—500 ppmv H_2S in the reactor outlet gas. During the first 10 cycles, the average sulfur capacity was 23.35 g S/100 g of the fresh sorbent, indicating nearly complete capacity utilization. As noted previously, a gradual decline in the capacity was observed thereafter. The sulfur capacities of the sorbent during the 25th and 40th cycles were 12.32 and 8.03 g S/100 g fresh sorbent, respectively. The average capacities over the first 25 cycles and the entire 40 cycles were 18.14 and 15.31 g S/100 g of fresh sorbent, respectively.

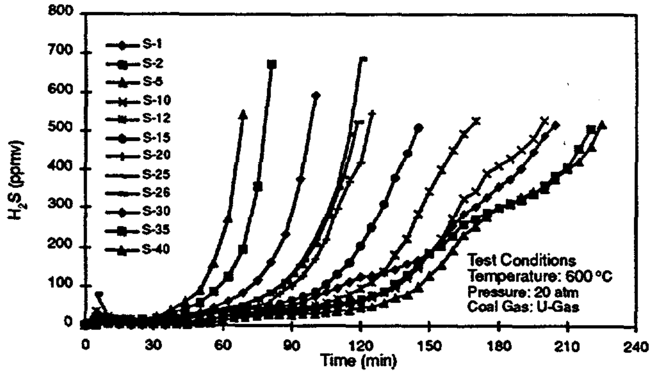

Figure 1. Breakthrough behavior of ZT-4L sorbent during selected cycles.

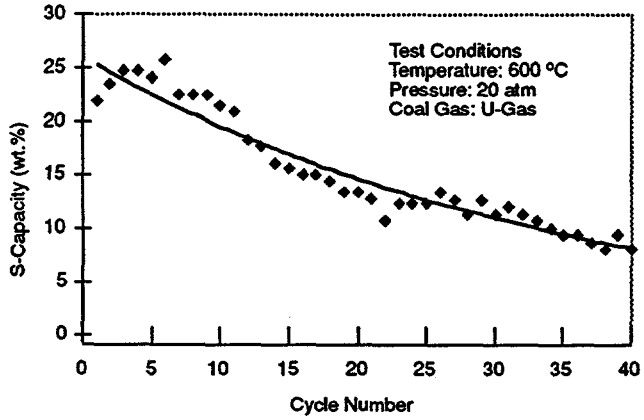

Figure 2. Sulfur capacity of the ZT-4L sorbent for Cycles 1 to 40.

Figure 3 shows the temperature profiles for selected regeneration cycles. As expected, similar to breakthrough curves, these temperature profiles shift to the left, indicating less time taken for regeneration resulting from gradual decline in sulfur pickup during sulfidation.

The SO_2 evolution profiles for selected cycles are shown in Figure 4. Similar to temperature profiles shown in Figure 3, SO_2 profiles also gradually shift toward the left, indicating gradual degradation in the sorbent performance. However, the shape of these curves remains unchanged, indicating good regenerability despite decline in the chemical reactivity.

Initially 500 g of the prescreened (in 100- to 300-µm particle size range) sorbent was loaded in the reactor. After the 25th regeneration, the

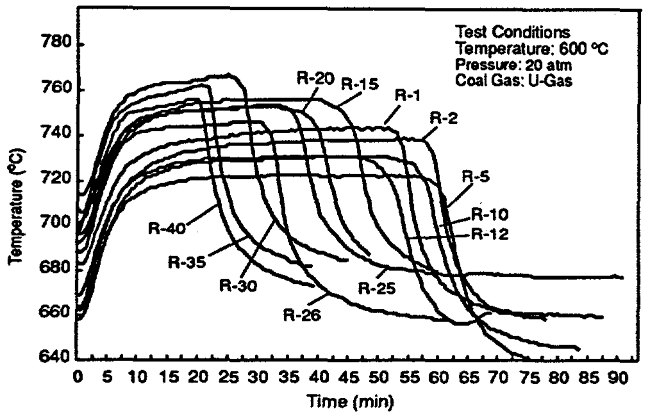

Figure 3. Temperature profiles during selected regeneration cycles.

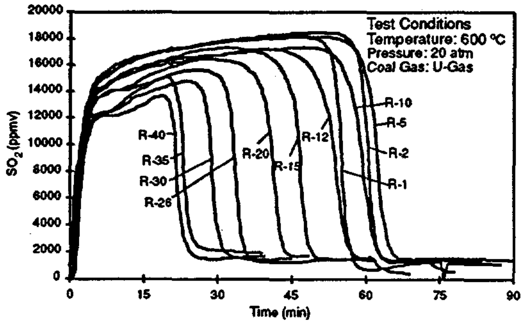

Figure 4. SO_2 evolution profiles during selected regeneration cycles.

reactor was cooled and dismantled to remove the sorbent. After removal of the sorbent, inside reactor walls, regeneration and sulfidation lines and filters, thermocouples, and distributor were examined for particle buildup. The primary thermocouple that was immersed in the sorbent bed had a considerable amount of deposit on the first 5-in. of the length from the tip. Visually these deposits appeared to be fine dust particles stuck together like a ceramic coating, presumably due to metal corrosion and interaction of thermocouple metals with the sorbent.

The weight of the sorbent removed from the reactor was 496.2 g. Some sorbent agglomeration did occur, but unlike the 18-cycle run, these agglomerates were fairly soft and broke during gentle screening through a 50-mesh screen. Out of 496.2 g of the sorbent, 481.5 g was below 50 mesh. Out of these, 400 g of the sorbent was loaded in the reactor and 81.5 g was kept for characterization. Sulfidation filter had a 2.2 g deposit, while the regeneration filter had 1.5 g of the particle deposits.

Cycles 26 to 40 were continued with 400 g of the sorbent. No change in coal gas flow rate was made; as a result, the breakthrough time reduced by 80 percent as noted previously. At the end of the 40th regeneration, the reactor was opened, and 395.1 g of the sorbent were recovered from the reactor. No agglomerates were found in the sorbent this time. The sulfidation filter had a 0.2 g deposit, while 5.0 g of sorbent deposited on the regeneration filter.

Table 4 shows the material balance of the sorbent over the 40 cycles. The net sorbent loss

Table 4. Sorbent Material Balance for Cycles 1 to 40

Initial	
Initial sorbent charge	500 g
After 25 Cycles	
Sorbent removed from the cage	496.2 g
Collected from sulfidation filter	2.2 g
Collected from regeneration filter	1.5 g
Total accounted	499.9 g
Net loss over 25 cycles	0.1 g
Sorbent loaded	400 g
After 40 Cycles	
Sorbent removed form the cage	395.1 g
Sorbent collected from sulfidation filter	0.2 g
Sorbent collected from regeneration filter	5.0 g
Total accounted	400.3 g
Net loss	(0.3) g

from the reactor was zero. Excluding the sorbent deposited on the filters, the gross sorbent loss was about 2 percent, indicating good attrition resistance of this material.

Table 5 shows a comparison of various physical and chemical properties of the fresh, 25-cycle reacted and 40-cycle reacted sorbent. Over 40 cycles of testing, sorbent underwent significant changes in the properties corroborating the capacity decline. The average particle size reduced by 12 percent over 25 cycles and by 19 percent over 40 cycles, indicative of gradual shrinkage of the particles with cycling possibly associated with internal structural changes.

Table 5. Physical and Chemical Characterization of Fresh, 25-Cycle Reacted and 40-Cycle Reacted ZT-4L Sorbent

	Fresh	25-Cycle Reacted	40-Cycle Reacted
Particle size distribution (wt%)			
MESH			
+ 50	0.0	0.0	0.0
- 50 + 60	20.0	2.7	0.0
-60 + 80	34.9	37.7	32.5
- 80 + 100	15.1	19.7	17.8
- 100 + 120	18.7	20.0	18.1
- 120 + 140	11.3	12.7	14.8
- 140	0.0	7.3	16.8
Total	100.0	100.0	100.0
Average particle size (µm)	178	157	144
BET surface area (m^2/g)	3.2	2.33	2.02
Pore size distribution			
Mercury pore volume (cm^3/g)	0.2341	0.0961	0.0653
Median pore diameter (Å)	2,495	1,126	848
Porosity (%)	55	48	31
Compacted bulk density (lb/ft^3)	91.6	112.0	129.3
Attrition resistance (%)			
5-h loss	38.0	0.6	0.4
20-h loss	84.0	7.2	5.8
XRD[a] phases	$Zn_2Ti_3O_8$, Zn_2TiO_4, and traces of TiO_2 and $ZnTiO_3$	$Zn_2Ti_3O_8$ and Zn_2TiO_4	$Zn_2Ti_3O_8$
ICP[b] analysis (wt%)			
Zn	42.7	41.6	41.6
Ti	23.0	22.6	20.6

[a] XRD = x-ray diffraction.

[b] ICP = inductively coupled plasma.

As expected, the BET surface area dropped by 37 percent over 40 cycles. However, this drop in surface area cannot explain the entire capacity decline. In RTI's previous study, it was found that BET surface area decline linearly correlates the capacity drop (Gupta and Gangwal, 1993). There had to be some other factors for such drastic decline in the capacity as will be discussed later. Comparison of the TGA reactivities of fresh and reacted sorbent samples confirmed the reactivity loss observed in the bench unit (Gupta and Gangwal, 1995).

The pore size distribution data indicated a rather unexpected drop in pore volume and median pore diameter. A good correlation was found between the drop in pore diameter and capacity decline. This indicates formation of inert unreactive species inside the pores of the sorbent.

Decline in the pore volume resulted in the decrease in sorbent's internal porosity and increase in compacted bulk density. As a result, the attrition resistance of the sorbent increased at least by an order of magnitude.

ICP analysis indicated very little, if any, changes in zinc and titanium content of the sorbent, showing no zinc loss due to ZnO reduction followed by vaporization despite the highly reducing nature of the coal gas.

The decrease in surface area did not completely explain the drop in sulfur capacity as discussed in the previous section. Furthermore, decline in median pore diameter and pore volume provided a good correlation with capacity decline. These two factors suggest formation of inert compounds inside the pores. XRD analysis of the 40-cycle reacted sorbent did not indicate any extraneous peaks, perhaps because of very small concentration of these inert compounds. To further investigate this, a complete inductively coupled plasma (ICP) scan was performed on the fresh, 25-cycle, and 50-cycle reacted zinc titanate sorbent samples. This completely automated ICP scan detects 16 elements in the sample as shown in Table 6.

A comparison of concentrations of various elements indicates a significant increase in the concentration of Ni and a modest increase in the Mo concentration. The Ni concentration increased from 10.3 to 523 ppmw after 25 cycles and 915 ppmw after 40 cycles. It is plausible that interaction of Ni with the zinc titanate sorbent is partially responsible for the capacity decline of the sorbent.

Independent Testing of ZT-4L

The Institute of Gas Technology (IGT) tested the ZT-4 sorbent for 10 sulfidation-regeneration cycles. These test results released by IGT on this sorbent have been reported in RTI's topical report (Gupta and Gangwal, 1993). In general, this sorbent exhibited excellent performance, both in terms of chemical reactivity as well as attrition resistance at IGT.

Table 6. ICP Scan of Fresh and Reacted Samples

Element	Fresh (ppmw)	25-Cycle Reacted (ppmw)	40-Cycle Reacted (ppmw)
Al	16,600	16,600	19,100
Ba	12.7	23.0	20.2
Be	1.37	1.47	2.26
Cd	10.6	<5.0	<5.0
Cr	<10.0	22.8	<10.0
Cu	<15	<15	<15
Fe	1,280	2,120	1,540
Pb	<30	32.6	<30
Mg	826	838	937
Mn	4.19	20.1	10.9
Mo	45.4	77.1	89.2
Ni	10.3	523	915
Sr	14.8	16.3	15.8
V	192	188	189

Testing of this sorbent in Enviropower's 15-MW pilot plant with actual coal gas indicated that the sorbent was able to remove the total sulfur content of coal gas from an inlet value of 500 to 550 ppmv to 5 to 40 ppmv over a 22-h stable operation at a temperature of 450 °C. Due to some problems in screening the sorbent at CMP, some fines were present in the sorbent which escaped during the operation at Enviropower. Besides this, the ZT-4 sorbent exhibited good performance with actual coal gas despite a low operating temperature.

This sorbent was also tested with actual coal gas from the METC fluidized-bed gasifier and Coal Technology Development Division (CTDD) in England. At METC, the ZT-4 consistently removed H_2S from coal gas down to <20 ppmv at 600 °C (1,112 °F) and 1.89 MPa (260 psig) over three cycles of operation. Tests at CTDD showed that at 525 °C and 10 atm, this sorbent was able to reduce the H_2S content of coal gas from 1,500 ppmv to <10 ppmv in an actual coal gas stream generated from a pilot-scale gasifier. The gas composition of the fuel gas in CTDD runs was similar to that of an air-blown fluidized-bed gasifier. Furthermore, CTDD could regenerate this sorbent at 600 °C using about 2 percent oxygen in nitrogen without any sulfate formation.

This sorbent was independently tested for its attrition properties at PSRI in a loop attrition test simulating an industrial fluidized-bed system. PSRI reported that the attrition resistance of this sorbent was better than a commercial fluid catalytic cracking (FCC) catalyst used in petroleum refineries (Gupta and Gangwal, 1995).

Developments of Sorbents by Spray Drying

RTI and CMP are jointly developing zinc titanate sorbents by spray drying. One of the superior spray-dried formulation CMP-5 was tested in RTI's HTHP bench unit. This sorbent exhibited excellent performance in the bench-scale tests. Currently, RTI and CMP have successfully produced larger size (100 to 300 µm) zinc titanate particles by spray drying. This sorbent formulation is currently being tested at the M.W. Kellogg Company in their transport reactor test unit. The details of the development and testing of spray-dried sorbents are described in a separate paper entitled "Spray Dried Sorbents—CMP-5," included in this proceedings volume.

FUTURE WORK

Future work in this contract is focussed on the testing of spray-dried sorbents at RTI and M.W. Kellogg.

REFERENCES

Gupta, R., and S.K. Gangwal. 1991. "Enhanced Durability of Desulfurization Sorbents for Fluidized Bed Applications." Topical Report to DOE/METC. Report No. DOE/MC/25006-3011. U.S. Department of Energy/Morgantown Energy Technology Center. Morgantown, WV. NTIS/DE91002090. June.

Gupta, R., S.K. Gangwal, and S.C. Jain. 1992. "Development of Zinc Ferrite Sorbents for Desulfurization of Hot Coal Gas in a Fluid-Bed Reactor." *Energy and Fuels* 6:21-27.

Gupta, R., and S.K. Gangwal. 1992. "Enhanced Durability of Desulfurization Sorbents for Fluidized-Bed Applications—Development and Testing of Zinc Titanate Sorbents." Topical Report to DOE/METC. Report No. DOE/MC/25006-3271. U.S. Department of Energy/Morgantown Energy Technology Center. Morgantown, WV. November.

Gupta, R., and S.K. Gangwal. 1993. "High-Temperature, High-Pressure Testing of Zinc Titanate in a Bench-Scale Fluidized-Bed Reactor for 100 Cycles." Topical Report to DOE/METC. Contract No. DE-AC21-88MC25006. June.

Gupta, R., and S.K. Gangwal. 1995. "Multicycle Testing of ZT-4L Sorbent." Topical Report to DOE/METC. Contract No. DE-AC21-88MC 25006. U.S. Department of Energy/Morgantown Energy Technology Center. Morgantown, WV. June.

Gupta, R. et al. 1993. "Fluidizable Zinc Titanate Materials With High Chemical Reactivity and Attrition Resistance." U.S. Patent No. 5,254,516. October 19.

Mei, J.S., L.D. Gasper-Galvin, C.E. Everitt, and S. Katta. 1993. Fixed Bed Testing of a Molybdenum-promoted Zinc Titanate Sorbent for Hot Gas Desulfurization. In *Proceedings of the Coal-fired Power Systems 93—Advances in IGCC and PFBC Review Meeting*. p. 315. DOE/METC–93/6131. NTIS/DE 93000289. Springfield, VA: National Technical Information Service.