

DOE/MC/30010--5071
UC - 106

RTI Project No. 96U-5666

DOE Contract No. DE-AC21-93MC30010
April 1, 1995 to June 30, 1995

BENCH-SCALE DEMONSTRATION OF HOT-GAS DESULFURIZATION TECHNOLOGY

Quarterly Technical Progress Report

Submitted to

U.S. Department of Energy
Morgantown Energy Technology Center
3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880

Submitted by

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

DOE COR: Thomas P. Dorchak
RTI Project Manager: Santosh K. Gangwal
RTI Project Engineer: Jeffrey W. Portzer

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

ell

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.

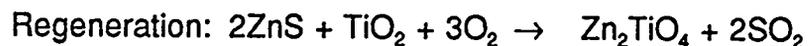
Available to DOE and DOE contractors from the Office of Scientific and Technical Information, 175 Oak Ridge Turnpike, Oak Ridge, TN 37831; prices available at (615) 576-8401.

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.

1.0 INTRODUCTION AND SUMMARY

The U.S. Department of Energy (DOE), Morgantown Energy Technology Center (METC), is sponsoring research in advanced methods for controlling contaminants in hot coal gasifier gas (coal gas) streams of integrated gasification combined-cycle (IGCC) power systems. The programs focus on hot-gas particulate removal and desulfurization technologies that match or nearly match the temperatures and pressures of the gasifier, cleanup system, and power generator. The work seeks to eliminate the need for expensive heat recovery equipment, reduce efficiency losses due to quenching, and minimize wastewater treatment costs.

Hot-gas desulfurization research has focused on regenerable mixed-metal oxide sorbents which can reduce the sulfur in coal gas to less than 20 ppmv and can be regenerated in a cyclic manner with air for multicycle operation. Zinc titanate (Zn_2TiO_4 or $ZnTiO_3$), formed by a solid-state reaction of zinc oxide (ZnO) and titanium dioxide (TiO_2), is currently one of the leading sorbents. Overall chemical reactions with Zn_2TiO_4 during the desulfurization (sulfidation)-regeneration cycle are shown below:



The sulfidation/regeneration cycle can be carried out in fixed-bed, moving-bed, or fluidized-bed reactor configuration, and all three types of reactors are slated for demonstration in the DOE Clean Coal Technology program. The fluidized-bed reactor configuration is most attractive because of several potential advantages including faster kinetics and the ability to handle the highly exothermic regeneration to produce a regeneration offgas containing a constant concentration of SO_2 . However, a durable

TABLE OF CONTENTS

Section	Page
1.0 Introduction and Summary	1-1
2.0 Technical Discussion	2-1
2.1 Field Testing of ZTFBD/DSRP at METC	2-1
3.0 Plans for Next Quarter	3-1
Appendix A Paper presented at the DOE Contractor's Meeting	
Appendix B paper to be presented at the Pittsburgh Coal Conference	

attrition-resistant sorbent in the 100- to 400- μm size range is needed for successful fluidized-bed operation.

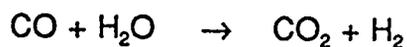
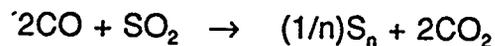
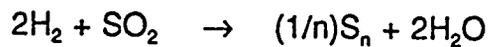
The SO_2 in the regeneration offgas needs to be disposed of in an environmentally acceptable manner. Options for disposal include recycle to the gasifier in which an in-bed desulfurization sorbent such as dolomite or limestone is being employed, conversion to sulfuric acid, and conversion to elemental sulfur. All three options are being pursued and/or proposed in the Clean Coal Technology program. Elemental sulfur recovery is the most attractive option because sulfur can be easily transported, stored, or disposed. However, elemental sulfur recovery using conventional methods from an offgas containing low levels of SO_2 (typically 3%) is an expensive proposition. An efficient, cost-effective method is needed to convert the SO_2 in the regenerator offgas directly to elemental sulfur.

Research Triangle Institute (RTI) with DOE/METC sponsorship has been developing zinc titanate sorbent technology since 1986. In addition, RTI has been developing the Direct Sulfur Recovery Process (DSRP) with DOE/METC sponsorship since 1988. Fluidized-bed zinc titanate desulfurization coupled to the DSRP is currently the most advanced and attractive technology for sulfur removal/recovery for IGCC systems, and it has recently been proposed in a Clean Coal Technology project.

RTI has developed a durable fluidized-bed zinc titanate sorbent, ZT-4, which has shown excellent durability and reactivity over 100 cycles of testing at 750 to 780°C. In bench-scale development tests, it consistently reduced the H_2S in simulated coal gas to <20 ppmv and demonstrated attrition resistance comparable to fluid cracking catalysts. The sorbent is manufactured by a commercially scalable granulation technique using commercial equipment available in sizes up to 1,000 L. The raw materials used are relatively

inexpensive, averaging about \$1.00/lb. It is anticipated that the impact on cost of electricity (COE) due to sorbent replacement for attrition will be less than 0.5 mil/kWh. ZT-4 has recently been tested independently by the Institute of Gas Technology (IGT) for Enviropower/Tampella Power, and showed no reduction in reactivity and capacity after 10 cycles of testing at 650°C.

In the DSRP SO₂ is catalytically reduced to elemental sulfur using a small slip stream of the coal gas at the pressure and temperature conditions of the regenerator offgas. A near-stoichiometric mixture of offgas and raw coal gas (2 to 1 mol ratio of reducing gas to SO₂) reacts in the presence of a selective catalyst to produce elemental sulfur directly:



The above reactions occur in Stage I of the process, and convert up to 96% of the inlet SO₂ to elemental sulfur, which is recovered by cooling the outlet gas to condense out the sulfur. Adjusting the stoichiometric ratio of coal gas to regenerator offgas to 2 at the inlet of the first reactor also controls the Stage I effluent stoichiometry since any H₂S and COS produced (by the reactions: 3H₂ + SO₂ → H₂S + 2H₂O, and 3CO + SO₂ → COS + 2CO₂) yields an (H₂S + COS) to SO₂ ratio of 2 to 1. The effluent stoichiometry plays an important role in the Stage II DSRP reactor (operated at 275 to 300°C), where 80% to 90% of the remaining sulfur species is converted to elemental sulfur most probably via COS + H₂O → H₂S + CO₂ and 2H₂S + SO₂ → (3/n)S_n + 2H₂O. The overall sulfur recovery is projected at 99.5%.

The DSRP technology is also currently at the bench-scale development stage with a skid-mounted system ready for field testing. Very recently, the process has been extended to fluidized-bed operation in the Stage I reactor. Fluidized-bed operation has proved to be very successful with conversions up to 94% at space velocities ranging from 8,000 to 15,000 scc/cc-h. Overall conversion in the two stages following interstage sulfur and water removal has ranged up to 99%.

A preliminary economic study for a 100 MW plant in which the two-stage DSRP was compared to conventional processes indicated the economic attractiveness of the DSRP. For 1% to 3% sulfur coals the installation costs ranged from 25 to 40 \$/kW and the operating costs ranged from 1.5 to 2.7 mil/kWh.

Through bench-scale development, both fluidized-bed zinc titanate and Direct Sulfur Recovery Process (DSRP) technologies have been shown to be technically and economically attractive. The demonstrations to date, however, have only been conducted using simulated (rather than real) coal gas and simulated regeneration off-gas. Thus, the effect of trace contaminants in real coal gases on the sorbent and DSRP catalyst is currently unknown. Furthermore, the zinc titanate work to date has emphasized sorbent durability development rather than database development to permit design of large-scale reactors. Discussions with fluidized-bed experts have indicated that data from a larger reactor than the present are required for scaleup, especially if the material does not have particle sizes similar to fluid catalytic cracking catalysts (typically ~80 μm). The fluidized-bed zinc titanate technology uses 100- to 400- μm particles. Finally, the zinc titanate desulfurization unit and DSRP have not been demonstrated in an integrated manner.

The goal of this project is to continue further development of the zinc titanate desulfurization and DSRP technologies by

- Scaling up the zinc titanate reactor system;
- Developing an integrated skid-mounted zinc titanate desulfurization-DSRP reactor system;
- Testing the integrated system over an extended period with real coal-gas from an operating gasifier to quantify the degradative effect, if any, of the trace contaminants present in coal gas;
- Developing an engineering database suitable for system scaleup; and
- Designing, fabricating and commissioning a larger DSRP reactor system capable of operating on a six-fold greater volume of gas than the DSRP reactor used in the bench-scale field test.

2.0 TECHNICAL DISCUSSION

2.1 FIELD TESTING OF ZTFBD/DSRP AT METC

Operating experience from the previous slip-stream test demonstrated the effectiveness of a single stage DSRP and several modifications to improve system performance. The DSRP system was converted to a single reactor and sulfur condenser. Modifications to the sulfur condenser consist of creating a separate pressure vessel for separating the liquid sulfur, installing immersion heaters to provide the required heat to drive the thermal siphon and using an annealed coil to reduce the stress corrosion. A flow orifice was installed in the coal gas feed to the DSRP system to provide an accurate measurement of the coal gas being introduced and for control purposes. Control options include remote manual valve operation, automatically maintaining a fixed flow rate and automatically maintaining a fixed ratio of coal gas to SO₂. Superior control of pressure in the DSRP system will be achieved with a Badger valve and PID controller. The system and pipes are maintained hot to prevent sulfur plugging until after the pressure is let down and the gases and entrained sulfur reach a large ambient pressure knock-out pot. The knock-out pot captures any remaining water and sulfur in the off-gas from the DSRP system. Currently, completion of these modifications is on schedule to be completed for the upcoming gasifier run to begin July 17, 1995.

Although the fluidized zinc-titanate reactor will be used as a fixed-bed reactor with an ammonia decomposition catalyst, no modifications of this system were necessary. The reactor has been charged with the catalyst and water traps and filters are being reconditioned or replaced. The sampling system has also been simplified to improve sampling efficiency for trace metals, chloride and ammonia to permit evaluation of the

ammonia decomposition catalyst.

A paper was presented at the METC Contractor's meeting (Appendix A). Also, a paper was prepared for the Pittsburgh Coal Conference (Appendix B).

2.1 SCALED-UP DSRP REACTOR SYSTEM

The following accomplishments were made in this quarter with respect to the large scale DSRP system.

- All long lead items were ordered.
- Vendors were selected for the special furnaces required by Enviropower and for the control panel.
- Construction of the skid frame began in earnest.
- The pressure vessel designs continued to slow down the delivery. The nozzle designs were evaluated for compatibility with stringent pressure vessel codes required by Enviropower.

3.0 PLANS FOR NEXT QUARTER

1. Field test at METC.
2. Complete design and secure Finnish authorities approval of pressure vessels.
3. Continue construction of the scaled-up DSRP system.
4. Pittsburgh conference meeting paper/presentation.

SKG/jks-12.25666A-J.QTR

APPENDIX A

PAPER PRESENTED AT THE
METC CONTRACTOR'S MEETING

*Per Judy Phillips, cannot
conference*

SLIPSTREAM TESTING OF HOT-GAS DESULFURIZATION WITH SULFUR RECOVERY

Jeffrey W. Portzer and Santosh K. Gangwal
Research Triangle Institute
P.O. Box 12194, Research Triangle Park, NC 27709

Thomas P. Dorchak
U.S. Department of Energy
Morgantown Energy Technology Center
Morgantown, WV 26505

ABSTRACT

The U.S. Department of Energy's Morgantown Energy Technology Center (METC) is developing and supporting the commercialization of integrated gasification combined cycle (IGCC) power generating systems. Certain designs for these advanced systems rely on hot-gas desulfurization using regenerable metal oxide sorbents for improved efficiency, economics and environmental control. To further development of required technologies, personnel from the Research Triangle Institute (RTI), assisted by METC personnel, are conducting a series of slipstream tests at METC's fluidized bed gasifier. The objective is to demonstrate the operation of fluidized-bed desulfurization sorbents and the Direct Sulfur Recovery Process (DSRP) using actual, high-pressure, high-temperature coal gas. During a run of four-days duration in October, 1994, the zinc titanate sorbent, ZT-4 consistently removed H₂S from the coal gas down to less than 20 ppmv. The DSRP was very effective in converting SO₂ to elemental sulfur, achieving 96 to 99% conversion after the first stage of the two-stage bench-scale test rig. A longer term test of DSRP is scheduled for July, 1995, to assess new control logic and the longer term effects of trace contaminants in the coal gas. A single stage reactor system will be used. Also, RTI is designing and constructing a six-fold larger pilot scale DSRP unit that will be tested at Enviropower's 15 MW (thermal) gasifier, beginning in early 1996.

INTRODUCTION

Hot-gas desulfurization processes for IGCC and other advanced power applications utilize regenerable mixed metal-oxide sorbents to remove hydrogen sulfide (H₂S) from raw coal gas. Regeneration of these sorbents produces a tailgas typically containing 1 to 3 percent sulfur dioxide (SO₂). Reduction to elemental sulfur is a highly desirable option for the ultimate disposal of SO₂ in the tailgas. In the DSRP, the SO₂ is reacted with a slipstream of coal gas over a fixed bed of a selective catalyst to directly produce elemental sulfur at the high-temperature, high-pressure (HTHP) conditions of the tailgas and coal gas.

The goal of the work is to further the development of zinc titanate fluidized-bed desulfurization (ZTFBD), and the DSRP for hot-gas cleanup in IGCC power generating systems.

Specifically, testing the DSRP would be conducted over an extended period with a slipstream of actual coal gas to quantify the degradation in performance, if any, caused by the trace contaminants present in coal gas, including heavy metals, chlorides, fluorides, and ammonia. Prior demonstrations at the laboratory and bench scale, were conducted using simulated coal gas and simulated regeneration gas.

PROJECT DESCRIPTION

The slipstream testing activities are being conducted in two distinct phases. The first testing phase is being conducted at METC using a slipstream from a 10-in. experimental fluidized-bed gasifier, firing 80 pounds of coal per hour. The second phase involves design and commissioning of a six-fold larger-scale DSRP unit which will be tested at the Enviropower pilot plant employing a U-gas gasifier coupled to a ZTFBD system. Enviropower, Inc., a subsidiary of Tampella Power Corporation, is commercializing clean coal technologies in the United States and abroad.

RTI designed and assembled a mobile reactor laboratory in a modified trailer to conduct slipstream testing. The process flow diagram of the trailer equipment is shown in Figure 1. A heated slipstream, approximately 170 std ft³/h (80 std L/min), flows from the gasifier to the RTI trailer. Inside the trailer, the hot-gas slipstream then flows through a high-temperature filter. It then divides into two flows, one going to the 3-in. ZTFBD bench-scale reactor and the other to the DSRP system, a two-stage system with 3-in. fixed-bed 1-L catalytic reactors and a sulfur trap after each reactor. The ZTFBD reactor system is operated batch-wise using cyclic sulfidation and regeneration. The regeneration tailgas is directed to the DSRP system. It mixes with the coal gas so that a molar ratio of 2 to 1, reducing gases to SO₂, is achieved after mixing. During the sulfidation portion of the cycle, the DSRP can

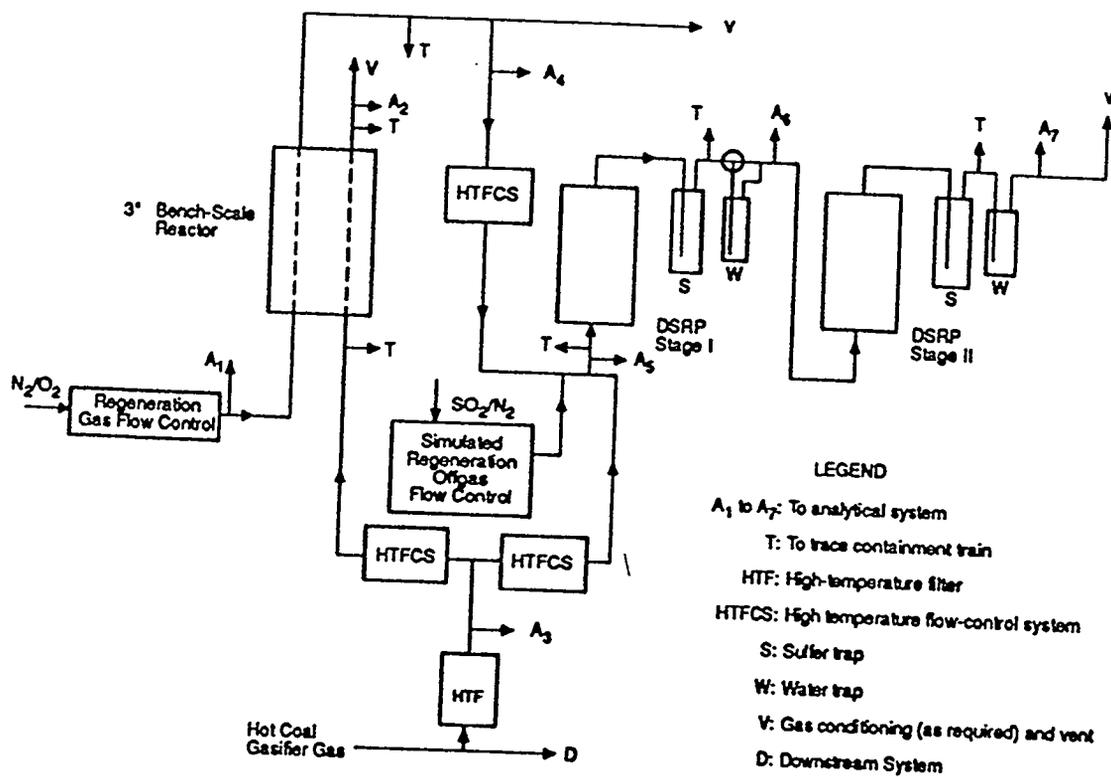


Figure 1. Integrated Zinc Titanate and DSRP Reactor System

also be run independently using simulated SO₂ (obtained using a liquid SO₂ pumping system) and actual coal gas.

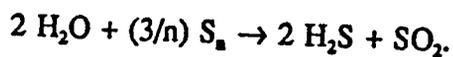
A number of analytical and trace contaminant sampling points are installed throughout the system. The gases are analyzed using a number of gas chromatographs and continuous analyzers for all of the necessary key components (H₂, CO, CO₂, H₂S, COS, SO₂, N₂, O₂). Samples to enable trace contaminant measurements are collected using impinger trains. An EPA Method 29 multimetals train is used to test for volatile heavy metals including As, Se, and Hg. An acidic impinger train is used to test for NH₃, whereas a basic impinger train is used to test for chlorides and fluorides.

TEST RESULTS

After obtaining the necessary permits, shakedown testing began during the week of September 12, 1994. Two cycles, each consisting of a sulfidation and a regeneration with integrated DSRP operation, were conducted during the shakedown period. The testing was successful in that promising results were demonstrated with the sorbent and DSRP even though the integrated regeneration-DSRP operation was carried out with erratic system pressure and coal gas flow. The objective of the testing was met since problems were identified that could be corrected prior to the formal testing.

The formal slipstream test began on October 24, 1994. There was coal gas available at the RTI trailer for a total of 70 hours during the run. RTI was taking coal gas for 45.5 of those hours, for a utilization factor of 65 percent. Three sulfidation cycles (~25 h), two integrated DSRP tests (2.5 h) and four simulated DSRP tests (18 h) were conducted. Although the run was curtailed due to mechanical problems with METC's gasifier, there was sufficient on-stream time to demonstrate highly successful operation of both the ZTFBD and the DSRP with actual coal gas. Also, the multimetals, NH₃ and HCl/HF impinger trains were successfully used during the run to determine the level of trace contaminants. No significant effect of the contaminants was detected on either the ZTFBD or DSRP.

The process equipment in the ZTFBD unit worked well in both the sulfidation and regeneration modes. The fluidizable zinc titanate formulation ZT-4L demonstrated 99+ percent removal of H₂S from actual coal gas over three cycles and up to 20 lb sulfur per 100 lb sorbent loading capacity. It also demonstrated consistent, smooth regeneration behavior. For the most part, the DSRP unit also ran smoothly with actual coal gas. As planned, to obtain extended operation of the DSRP, provisions were made to produce simulated regeneration offgas using liquid sulfur dioxide which was successful. During periods of lined-out operation, the DSRP had concentrations of sulfur compounds in the exit gas corresponding to up to 99+ percent conversion in Stage 1 and 95 to 96 percent overall conversion for the two-stage system. This suggested problems of reverse Claus reactions in Stage 2:



For a commercial system one stage may be sufficient, thus further improving the economics of the DSRP.

Test conditions for sulfidation and regeneration of ZT-4L over the 2.5 cycles are shown in Table 1. Under these conditions, an H₂S breakthrough curve during cycle 3 is shown in Figure 2. The sorbent exhibited excellent removal efficiency and capacity even with the

Table 1. ZT-4 Reactor Conditions
(3.0-in. reactor; 600 g sorbent loaded)

	Sulfidation	Regeneration
Temperature (°C)	600	730
Pressure (psig)	260	260
U_s (cm/s)	4.3	4.9
Gas	Coal gas	2.25% O ₂ in N ₂

highly variable inlet H₂S levels. Sorbent regeneration, which went smoothly, is shown in Figure 3. Note that with 2.25 percent O₂ in the inlet, nearly two-thirds, i.e., ~1.5 percent, SO₂ is obtained in the offgas, indicating that sulfation did not occur. The properties of the fresh and three-cycle

(sulfided) materials are compared in Table 2. Note that the surface area of the sulfided material is higher and the pore volume is lower. The material significantly improved in attrition resistance over the three cycles. The thermogravimetric analysis measured capacity did not change from fresh to used material, both standing at 20 lb-S/100 lb sorbent.

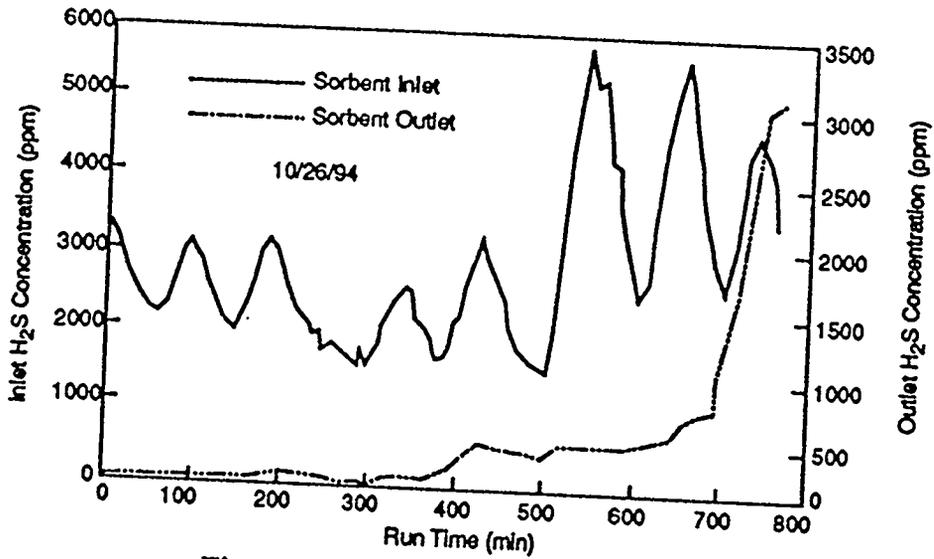


Figure 2. Sorbent Sulfidation Curves

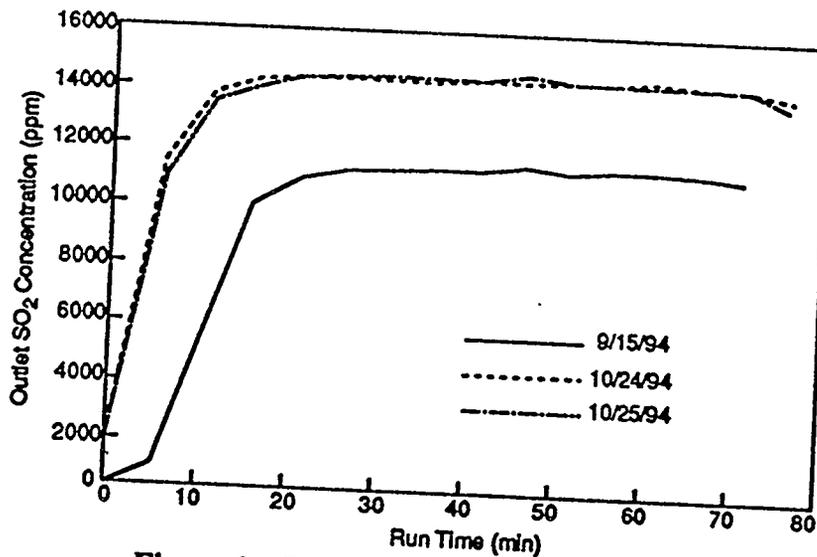


Figure 3. Sorbent Regeneration Curves

The DSRP unit was also successfully run in a fully integrated mode using actual regeneration tail gas. However, the ZTFBD run times in this mode were fairly short (due to a limited capacity to produce actual tail gas) and because of the longer response time of the DSRP unit, lined-out operation could not be achieved.

The test conditions for the DSRP Stage I reactor are shown in Table 3. During the integrated tests, it was not possible to obtain lined-out operation in the short duration of regeneration due to a larger time constant (~2 h) of the DSRP. However, three of the simulated SO₂-DSRP tests were highly successful. One of the simulated SO₂-DSRP tests was not successful due to plugging of the coal gas line from METC's gasifier. The results of the successful DSRP tests are shown in Table 4. Note that in Run 1 (with fresh catalyst) high sulfur conversion (up to 99.7 percent) is achieved. Some selectivity toward H₂S is seen in later runs, probably due to a less than optimum stoichiometric ratio, although even in these tests a 96 percent sulfur conversion level is achieved.

Table 3. DSRP Stage I Reactor Conditions

Temperature (°C)	550-610
Pressure (psig)	260
Space velocity (std cm ³ /cm ³ ·h)	4,560
Reactor diameter (in.)	3.0
Inlet SO ₂ (%)	1.8

To conclude, both ZT-4L and DSRP showed very promising results in short-term testing with actual coal gas. Based on the results of the slipstream testing, the new DSRP is envisioned as a single-stage process rather than a two-stage process. This will further improve the economics of the DSRP.

Table 2. Properties of Fresh and Reacted ZT-4L

	Fresh	3-Cycle Sulfidated
Exposure time (h)	0	Coal gas (25); temperature (>100)
Surface area (m ² /g)	3.2	7.56
Pore volume (cm ³ /g)	0.234	0.11
Pore diameter (Å)	2,500	1,800
Particle size (µm)	112	95
Air-jet attrition (%)		
5-h loss	16	1.4
20-h loss	36	6.2
Compacted density (lb/ft ³)	91.6	107
Zn/Ti	1.35 ± 0.05	1.42 ± 0.05
TGA capacity (g/100 g)	21.0	20.5
As (µg/g)	0.7	8.4
Se (µg/g)	<0.57	0.72
Pb (µg/g)	<30	50
Cl (µg/g)	NM	38

NM = Not measured.

The fresh and used catalyst properties are shown in Table 5. The used catalyst showed better crush strength but a lower surface area. Also, chloride is picked up by the catalyst but does not appear to affect its activity significantly even at 300 ppmv level. No other trace contaminants are detected in the catalyst. DSRP sulfur purity was checked using a differential scanning calorimeter. It was found that the sulfur exhibited the same peaks as pharmaceutical grade sulfur.

Table 4. Stage 1 DSRP Results During Lined-out Operation with Simulated SO₂

Run Time (min)	SO ₂ Conversion (%)	SO ₂ Conversion to H ₂ S (%)	SO ₂ Conversion to Sulfur (%)
Run No. 1			
32	99.4	0.0	99.4
36	99.4	0.0	99.4
40	99.5	0.0	99.5
44	99.7	0.0	99.7
48	99.5	0.0	99.5
52	98.5	0.0	98.5
56	98.0	0.0	98.0
Run No. 3			
117	99.6	1.2	98.4
121	100.0	4.1	95.9
125	100.0	4.9	95.1
129	100.0	2.4	97.6
Run No. 4			
175	100.0	4.9	95.1
179	100.0	4.1	95.9
183	100.0	4.9	95.1
199	100.0	4.7	95.3

Table 5. DSRP Stage I Catalyst

	Fresh	Used
Size (in.)	1/8	1/8
Crush strength (lbf/mm)	2.0	2.5
Surface area (m ² /g)	208	158
Exposure (h)	0	Coal gas (20); Temperature (>100)
Cl (ppmw)	21	300
As (ppmw)	<11	<10
Se (ppmw)	<10	<10

FUTURE PLANS

Since the October test was curtailed, a decision was made to conduct an additional slipstream test of 160 h to achieve a total 200 h of operation of the DSRP. This test is currently scheduled to begin on July 17, 1995, and will include:

- A 160-h test of single-stage DSRP with actual coal gas and simulated regeneration offgas, and due to a change in priority,
- A 100-h test of NH₃ decomposition catalyst at 850 °C and 150 psia.

The ZTFBD system will be modified for NH₃ decomposition testing. The two-stage DSRP system will be modified to a single stage with improved control of stoichiometric ratio of reducing gas to SO₂ entering the reactor. For the larger-scale DSRP system, two detailed meetings have been held, one on site in Finland and one at Tampella Power offices in Atlanta with METC and Enviropower. Significant progress is being made toward the goal of supplying the reactor system to Enviropower which is currently on schedule for delivery later this year.

APPENDIX B

PAPER TO BE PRESENTED AT THE
PITTSBURGH COAL CONFERENCE

*Per Judy Phillips cannot
conference*

Slipstream Testing of Hot-Gas Desulfurization with Sulfur Recovery

CONTRACT INFORMATION

Contract Number DE-AC21-93MC30010

Contractor Research Triangle Institute
P.O. Box 12194
Research Triangle Park, NC 27709-2194
Telephone: (919) 541-8033
Facsimile: (919) 541-8000

Other Funding Sources None

Contractor Project Manager Santosh K. Gangwal

Principal Investigators Jeffrey W. Portzer

METC Project Manager Thomas P. Dorchak

Period of Performance July 1, 1993 to December 31, 1995

Schedule and Milestones

FY95-96 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D
MET Field Test																
Large-Scale System																

OBJECTIVES

The objective of this work is to further the development of zinc titanate fluidized-bed desulfurization (ZTFBD), and the Direct Sulfur Recovery Process (DSRP) for hot-gas cleanup in integrated gasification combined cycle (IGCC) power generating systems. There are three main goals of this project:

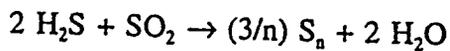
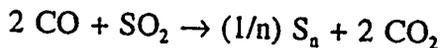
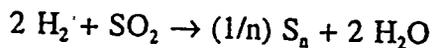
- Development and testing of an integrated, skid-mounted, bench-scale ZTFBD/DSRP reactor system with a slipstream of actual coal gas;

- Testing the DSRP over an extended period with a slipstream of actual coal gas to quantify the degradation in performance, if any, caused by the trace contaminants present in coal gas (including heavy metals, chlorides, fluorides, and ammonia) and
- Design, fabrication, and shipment of a six-fold larger-scale DSRP reactor system for the Enviropower U-Gas 15-MW (thermal) pilot plant.

BACKGROUND INFORMATION

Hot-gas desulfurization processes for IGCC and other advanced power applications utilize regenerable mixed metal-oxide sorbents to remove hydrogen sulfide (H₂S) from raw coal gas. Regeneration of these sorbents produces a tailgas typically containing 1 to 3 percent sulfur dioxide (SO₂). Reduction to elemental sulfur is a highly desirable option for the ultimate disposal of the SO₂ content of this offgas. Elemental sulfur, an essential industrial commodity, is easily stored and transported. The DSRP is a simple and attractive process for production of elemental sulfur from the regeneration offgases.

In the DSRP (Dorchak et al., 1991; Gangwal et al., 1993), the SO₂ tailgas is reacted with a slipstream of coal gas over a fixed bed of a selective catalyst to directly produce elemental sulfur at the high-temperature, high-pressure (HTHP) conditions of the tailgas and coal gas. Overall reactions involved are shown below:



The DSRP was initially developed as a two-stage process using simulated coal gas in the laboratory. The original process concept employed two catalytic reactors in series, each followed by a sulfur condenser. Hot regeneration tailgas was mixed with a hot coal gas slipstream (to act as the reducing gas) and fed to the first DSRP reactor. Approximately 95 percent of the combined sulfur in the inlet stream to the first reactor was converted to elemental sulfur. The outlet gas of the first reactor was then cooled, condensing out the sulfur. The cooled gas stream was reheated and sent to the second DSRP reactor where 80 to 90 percent of the remaining sulfur compounds

were converted to elemental sulfur via the modified Claus reaction at high pressure. The total efficiency of the two reactors for the conversion of sulfur compounds to elemental sulfur was projected to be 99 percent.

However, based on the initial results, reported here, from the slipstream tests with actual coal gas, the second stage does not appear necessary. Greater than 99 percent sulfur recovery could be achieved in the first stage with careful control of the stoichiometric ratio of the gas input. The new simple single-stage process is shown in Figure 1 with a potential for "zero" sulfur emissions if the gas is recycled.

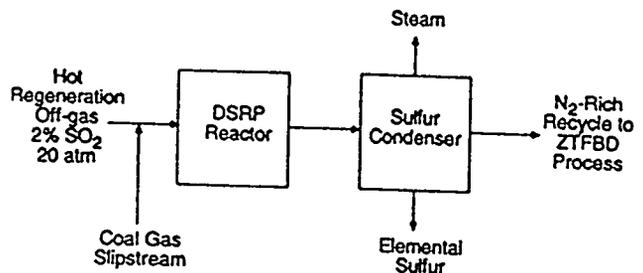


Figure 1. New Single-Stage DSRP

In addition to the patented DSRP, the Research Triangle Institute (RTI) under contract with the Morgantown Energy Technology Center (METC) has been developing zinc titanate sorbent technology since 1986 and has recently patented a fluidizable zinc titanate sorbent called ZT-4. The ZT-4 sorbent manufacture has been scaled up to pilot-scale quantities and the sorbent has been independently tested at a number of organizations including the Institute of Gas Technology, the Particulate Solids Research Institute; Enviropower, Inc. in Finland and the Coal Technology Development Division in England. Indeed, Enviropower (Konttinen et al., 1995) has now successfully tested ZT-4 in a 33-inch fluidized bed at their 15-MW (thermal) pilot gasifier. However, the slipstream testing, reported here, supported the pilot testing of ZT-4.

operated batch-wise using cyclic sulfidation and regeneration. The regeneration tail gas is directed to the DSRP system. It mixes with the coal gas so that a molar ratio of 2 to 1, reducing gases to SO₂, is achieved after mixing. During the sulfidation portion of the cycle, the DSRP can also be run independently using simulated SO₂ (obtained using a liquid SO₂ pumping system) and actual coal gas. This provides the flexibility for extended operation of the DSRP with actual coal gas. As mentioned earlier, the DSRP, as originally installed, was a two-stage system with 3-in. fixed-bed 1-L catalytic reactors and a sulfur trap after each reactor.

A number of analytical and trace contaminant sampling points are installed throughout the system. The gases are analyzed using a number of gas chromatographs and continuous analyzers for all of the necessary key components (H₂, CO, CO₂, H₂S, COS, SO₂, N₂, O₂). Samples to enable trace contaminant measurements are collected using impinger trains. An EPA Method 29 multi-metals train is used to test for volatile heavy metals including As, Se, and Hg. An acidic impinger train is used to test for NH₃, whereas a basic impinger train is used to test for halides (chloride and fluoride).

RESULTS - SHAKEDOWN TESTING

After completing construction and preliminary checkout of the mobile laboratory unit (trailer) consisting of the ZTFBD and DSRP reactor systems, the trailer was transported to METC and parked during August 15-17, 1994. The trailer weighed about 16 tons with the equipment in place. A commercial crane company, assisted by METC personnel, lifted the trailer into place near the METC fluidized-bed gasifier (B-12) location. After the trailer was in position, intense activity followed to hook up the utilities (cooling water, city water, sewer, electricity, incinerator vent line, stack vent line) and the heated coal gas delivery line to the trailer. Preparations were made for shakedown testing of the RTI trailer in mid-

September. Parallel to these preparations, the final application for the operating plan along with final design drawings was submitted. Pressure testing of the reactors at the operating temperature and 1.5 times the operating pressures was conducted on site.

The operating plan application was successfully defended on August 25, 1994. Comments provided by the safety committee were incorporated into the final operating plan. All indicated corrective actions to comply with the Occupational Safety and Health Administration (OSHA) and Environmental Safety and Health (ES&H) were successfully implemented in time for shakedown testing. METC personnel provided support to RTI throughout this critical period.

After obtaining an operating permit, the shakedown testing was ready to begin during the week of September 12, 1994. The ZTFBD reactor was loaded with 500 g of sorbent. The Stage I DSRP reactor was loaded with 1,000 cm³ of catalyst and 1,500 cm³ of catalyst was loaded in the Stage II DSRP reactor. Nitrogen flow was established through the coal gas line and the reactors at the desired set point. Heaters and furnaces were turned on and adjusted to obtain the desired temperature in each reactor, and backpressure regulators were used to control the reactor pressures.

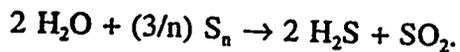
Two cycles, each consisting of a sulfidation and a regeneration/integrated DSRP operation, were conducted during the shakedown test. Problems were experienced in the testing due to plugging of the coal gas control valves for both sulfidation and DSRP reactors. Later it was discovered that entrained particles from the gasifier cleanup system made their way to the RTI system through the 3/8-in. coal gas line. Also, the ceramic filter in the RTI trailer did not perform as well as expected and allowed some of these particles to get into the valves. Most likely the filter problem was due to differential thermal expansion of the alumina ceramic filter and the stainless steel housing.

The shakedown testing was successful in that promising results were demonstrated with the sorbent and DSRP even though the integrated regeneration-DSRP operation was carried out with erratic system pressure and coal gas flow. The objective of the testing was met since problems were identified that could be corrected prior to the formal test to be conducted.

RESULTS - FORMAL TESTING

The formal 160-h slipstream test began on October 24, 1994, after correcting the problems found in the shakedown test. Although the run was curtailed due to mechanical problems with METC's gasifier, there was sufficient on-stream time to demonstrate highly successful operation of both the ZTFBD and the DSRP with actual coal gas. Also, the multimetals, NH₃ and HCl/HF impinger trains were successfully used during the run to determine the level of trace contaminants. No significant effect of the contaminants was detected on either the ZTFBD or DSRP over the 70 h of operation.

The process equipment in the ZTFBD unit worked extremely well in both the sulfidation and regeneration modes. The fluidizable zinc titanate formulation ZT-4L demonstrated 99+ percent removal of H₂S from actual coal gas over three cycles and up to 20 lb sulfur per 100 lb sorbent loading capacity. It also demonstrated consistent, smooth regeneration behavior. For the most part, the DSRP unit also ran smoothly with actual coal gas. As planned, to obtain extended operation of the DSRP, provisions were made to produce simulated regeneration offgas using liquid sulfur dioxide which was successful. During periods of lined-out operation, the DSRP had concentrations of sulfur compounds in the exit gas corresponding to up to 99+ percent conversion in Stage 1 and 95 to 96 percent overall conversion for the two-stage system. This suggested problems of reverse Claus reactions in Stage 2:



For a commercial system one stage may be sufficient, thus further improving the economics of the DSRP.

The DSRP unit was also successfully run in a fully integrated mode using actual regeneration tail gas. However, the ZTFBD run times in this mode were fairly short (due to a limited capacity to produce actual tail gas) and because of the longer response time of the DSRP unit, lined-out operation could not be achieved.

The DSRP unit experienced some plugging problems that resulted in unscheduled outages. At the high temperature, high pressure (HTHP) conditions, the flow of coal gas required by the DSRP was very small, requiring a fine orifice in the control valve. It tended to plug if there were any particulate matter in the coal gas. The high-temperature ceramic filter on the RTI equipment was apparently not completely effective and suggests that a stainless steel filter may be better for small equipment. There were also some problems with sulfur plugging in the cold end of the unit that required depressurization and disassembly to unblock. This suggests that the exit gases must be kept hot to prevent pluggage for continuous operation.

There was coal gas available at the RTI trailer for a total of 70 hours during the shortened October run. RTI was taking coal gas for 45.5 of those hours, for a utilization factor of 65 percent. Three sulfidation cycles (~25 h), two integrated DSRP tests (2.5 h) and four simulated DSRP tests (18 h) were conducted. Test conditions and main results of the testing are presented. A typical METC coal gas composition is shown in Table 1.

Points to note are that H₂S and HCl vary due to coal's variability and at times doping of the coal with salt to increase the HCl level for a slipstream test on chloride removal. The ammonia analysis is an estimated value due to coal gas line plugging during the sampling. The trace

contaminant values were below or near the detection limit of our sampling system.

Table 1. METC Gasifier Coal Gas Composition (vol%)

CH ₄	1.97
H ₂	14.9
CO ₂	11.5
CO	9.87
H ₂ O	11.0
H ₂ S	0.1-0.75
N ₂	Balance
HCl	5-80 ppmv
As	<10 µg/m ³
Se	16 µg/m ³
Hg	<2 µg/m ³
NH ₃	~800 ppmv

Test conditions for sulfidation and regeneration of ZT-4L over the 2.5 cycles are shown in Table 2. Under these conditions, an H₂S breakthrough curve during cycle 3 is shown in Figure 3.

Table 2. ZT-4 Reactor Conditions (3.0-in. reactor; 600 g sorbent loaded)

	Sulfidation	Regeneration
Temperature (°C)	600	730
Pressure (psig)	260	260
U _s (cm/s)	4.3	4.9
Gas	Coal gas	2.25% O ₂ in N ₂

The sorbent exhibited excellent removal efficiency and capacity even with the highly variable inlet H₂S levels. Sorbent regeneration, which went very smoothly, is shown in Figure 4. Note that with 2.25 percent O₂ in the inlet, nearly two-thirds, i.e., ~1.5 percent, SO₂ is obtained in the

offgas, indicating that sulfation did not occur. The properties of the fresh and three-cycle (sulfided) materials are compared in Table 3.

Table 3. Properties of Fresh and Reacted ZT-4L

	Fresh	3-Cycle Sulfidated
Exposure time (h)	0	Coal gas (25); temperature (>100)
Surface area (m ² /g)	3.2	7.56
Pore volume (cm ³ /g)	0.234	0.11
Pore diameter (Å)	2,500	1,800
Particle size (µm)	112	95
Air-jet attrition (%)		
5-h loss	16	1.4
20-h loss	36	6.2
Compacted density (lb/ft ³)	91.6	107
Zn/Ti	1.35 ± 0.05	1.42 ± 0.05
TGA capacity (g/100 g)	21.0	20.5
As (µg/g)	0.7	8.4
Se (µg/g)	<0.57	0.72
Pb (µg/g)	<30	50
Cl (µg/g)	NM	38

NM = Not measured.

Note that the surface area of the sulfided material is higher and the pore volume is lower. The material significantly improved in attrition resistance over the three cycles. The thermogravimetric analysis (TGA) measured capacity did not

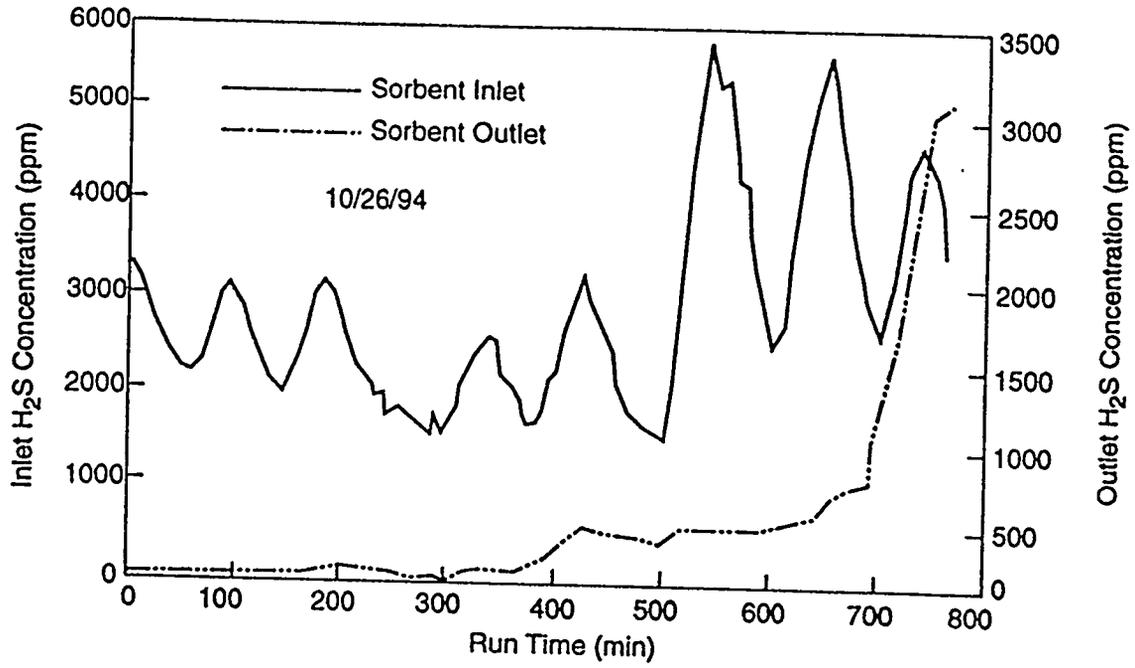


Figure 3. Sorbent Sulfidation Curves

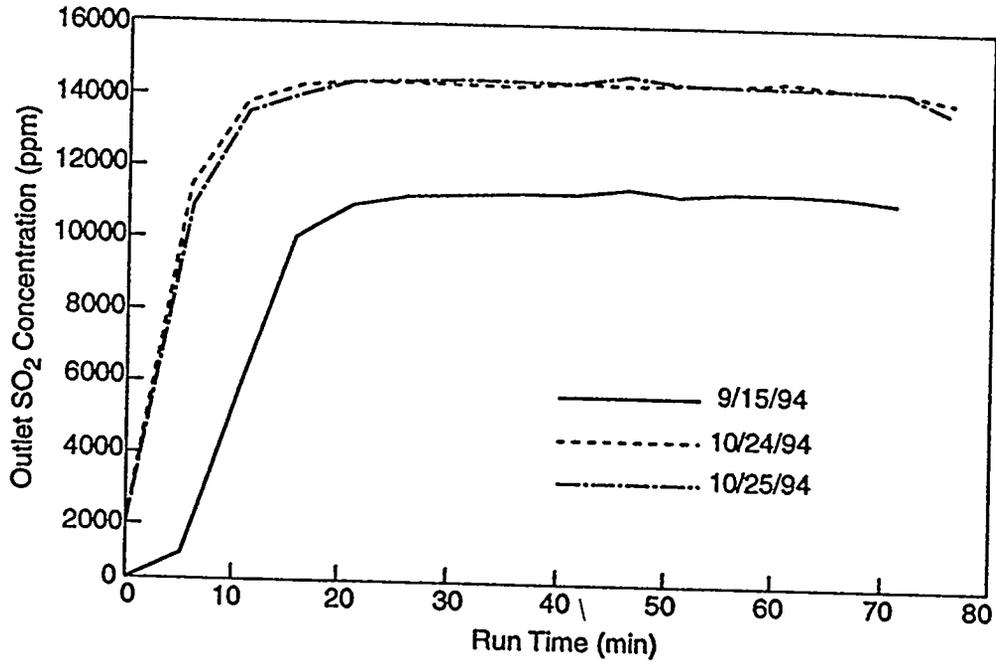


Figure 4. Sorbent Regeneration Curves

change from fresh to used material and was at 20 lb/100 lb sorbent.

Preliminary indications are that the actual coal gas-sulfided sorbent required somewhat higher temperature for regeneration than a sorbent sulfided with simulated coal gas. This may be due to reactions of one or more of the contaminants in coal gas with the sorbent. Analysis of trace contaminants in the sorbent indicated a buildup of As (from 0.7 to 8.4 ppm), Se (from <0.57 ppm to 0.72 ppm), Pb (from <30 ppm to 50 ppm), and Cl (up to 38 ppm). No Hg was detected in the gas or sorbent. The estimated gaseous concentrations of As and Se in the gas are ~100 and ~10 $\mu\text{g}/\text{m}^3$, respectively. The requirement for higher regeneration temperatures for the coal-gas exposed sorbent needs further validation.

The test conditions for the DSRP Stage I reactor are shown in Table 4. As indicated earlier, two integrated ZTFBD-DSRP and four simulated SO_2 -DSRP tests were conducted using the METC gasifier coal gas. During the integrated tests, it was not possible to obtain lined-out operation in the short duration of regeneration due to a larger time constant (~2 h) of the DSRP. However, three of the simulated SO_2 -DSRP tests were highly successful. One of the simulated SO_2 -DSRP tests was not successful due to plugging of the coal gas line from METC's gasifier. The results of the successful DSRP tests are shown in Table 5. Note that in Run 1 (with fresh catalyst) extremely high sulfur conversion (up to 99.7 percent) is achieved. Some selectivity toward H_2S is seen in later runs, probably due to a less than optimum stoichiometric ratio, although even in these tests a 96 percent sulfur conversion level is achieved. This is an excellent performance by the DSRP.

The fresh and used catalyst properties are shown in Table 6. The used catalyst showed better crush strength but a lower surface area. Also, chloride is picked up by the catalyst but does not appear to affect its activity significantly even at 300 ppmv level. No other trace

contaminants are detected in the catalyst. DSRP sulfur purity was checked using a differential scanning calorimeter. It was found that the DSRP sulfur exhibited the same endotherms as pure sulfur.

Table 4. DSRP Stage I Reactor Conditions

Temperature ($^{\circ}\text{C}$)	550-610
Pressure (psig)	260
Space velocity (std $\text{cm}^3/\text{cm}^3\cdot\text{h}$)	4,560
Reactor diameter (in.)	3.0
Inlet SO_2 (%)	1.8

Table 5. Stage 1 DSRP Results During Lined-out Operation with Simulated SO_2

Run Time (min)	SO_2 Conversion (%)	SO_2 Conversion to H_2S (%)	SO_2 Conversion to Sulfur (%)
Run No. 1			
32	99.4	0.0	99.4
36	99.4	0.0	99.4
40	99.5	0.0	99.5
44	99.7	0.0	99.7
48	99.5	0.0	99.5
52	98.5	0.0	98.5
56	98.0	0.0	98.0
Run No. 3			
117	99.6	1.2	98.4
121	100.0	4.1	95.9
125	100.0	4.9	95.1
129	100.0	2.4	97.6
Run No. 4			
175	100.0	4.9	95.1
179	100.0	4.1	95.9
183	100.0	4.9	95.1
199	100.0	4.7	95.3

Table 6. DSRP Stage I Catalyst

	Fresh	Used
Size (in.)	1/8	1/8
Crush strength (lbf/mm)	2.0	2.5
Surface area (m ² /g)	208	158
Exposure (h)	0	Coal gas (20); Temperature (>100)
Cl (ppmw)	21	300
As (ppmw)	<11	<10
Se (ppmw)	<10	<10

To conclude, both ZT-4L and DSRP showed very promising results in short-term testing with actual coal gas. Based on the results of the slipstream testing, the new DSRP is envisioned as a single-stage process rather than a two-stage process. This further improves on the already attractive economics of the DSRP. The long-term test of 160 h needs to be completed to fully evaluate longer-term degradation effects.

FUTURE PLANS

Since the October test was curtailed, a decision was made to conduct an additional slipstream test of 160 h to achieve a total 200 h of operation of the DSRP. This test is currently scheduled to begin on July 17, 1995, and will include:

- A 160-h test of single-stage DSRP with actual coal gas and simulated regeneration offgas, and due to a change in priority,
- A 100-h test of NH₃ decomposition at 850 °C and 150 psia.

The ZTFBD system will be modified for NH₃ decomposition testing. The two-stage DSRP system will be modified to a single stage with

improved control of stoichiometric ratio of reducing gas to SO₂ entering the reactor. Coordination meetings for the test and NH₃ analysis have already been held at METC and the test is on schedule.

For the larger-scale DSRP system, two detailed meetings have been held, one on site in Finland and one at Tampella Power offices in Atlanta with METC and Enviropower. Significant progress has been made toward the goal of supplying the reactor system to Enviropower which is currently on schedule for delivery later this year.

REFERENCES

- Dorchak, T.P., S.K. Gangwal, and W.J. McMichael. 1991. "The Direct Sulfur Recovery Process." *Environmental Progress* 10(2):68.
- Gangwal, S.K., W.J. McMichael, and T.P. Dorchak. 1992. "The Direct Sulfur Recovery Process for Refinery Gas Processing." AIChE Meeting, New Orleans, March.
- Kontinen J., A. R. Ghazanfari 1995 "Pilot Scale Experience on IGCC Hot Gas Cleanup" *Proceedings of the Coal-Fired Power System 95 Review Meeting*, U.S. Department of Energy, Office of Fossil Energy, Morgantown Energy Technology Center, Morgantown, WV.
- Portzer, J., and S.K. Gangwal. 1994. "Slipstream Testing of the Direct Sulfur Recovery Process," in *Proceedings of the Coal-Fired Power System 94—Advances in IGCC and PFBC Review Meeting*, Vol. I. U.S. Department of Energy, Office of Fossil Energy, Morgantown Energy Technology Center, Morgantown, WV.