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**Slipstream Testing of Hot-Gas Desulfurization With Sulfur Recovery**

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### CONTRACT INFORMATION

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**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

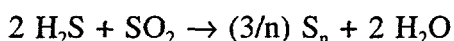
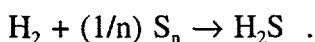
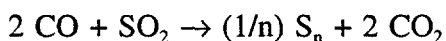
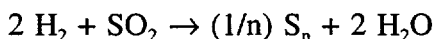
The objective of this work is to further the development of zinc titanate fluidized-bed desulfurization (ZTFBD), and the Direct Sulfur Recovery Process (DSRP) for hot-gas cleanup in integrated gasification combined cycle (IGCC) power generating systems. There are three main goals of this project:

- 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 (H<sub>2</sub>S) from raw coal gas. Regeneration of these sorbents produces a tailgas typically containing 1 to 3 percent sulfur dioxide (SO<sub>2</sub>). Reduction to elemental sulfur is a highly desirable option for the ultimate disposal of the SO<sub>2</sub> 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 SO<sub>2</sub> 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.

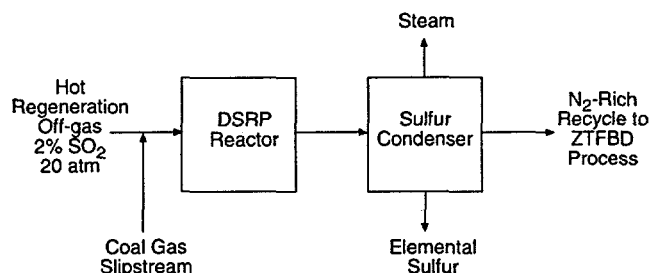


Figure 1. New Single-Stage DSRP

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.

## 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. The second phase involves design and commissioning of a six-fold larger-scale DSRP unit that is to be tested at the Enviropower pilot plant employing a U-gas gasifier coupled to a ZTFBD system. Enviropower, a subsidiary of Tampella Power Corporation, is attempting to commercialize clean coal technologies in the United States and abroad.

The slipstream equipment, consisting of RTI's ZTFBD/DSRP mobile laboratory (trailer), for the testing at METC was described in detail in last year's contractor's meeting paper (Portzer and Gangwal, 1994). The METC coal gasifier is a fluidized-bed gasifier providing approximately

4,750 std ft<sup>3</sup>/h of low Btu coal gas from a nominal charge rate of 80 lb/h of coal. A heated slipstream, approximately 170 std ft<sup>3</sup>/h (80 std L/min), is directed to the RTI trailer. The process flow diagram of the trailer equipment is shown in Figure 2.

The trailer is divided into two sections—a high-pressure process section and a control section with a partition in between. The process is operated remotely from the control side to protect the operators from high pressure operation and potential toxic gas leaks. The design of the system has undergone extensive METC safety review, and permits have been obtained for its operation.

As shown in Figure 2, the hot-gas slipstream is first directed 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. The ZTFBD reactor system is

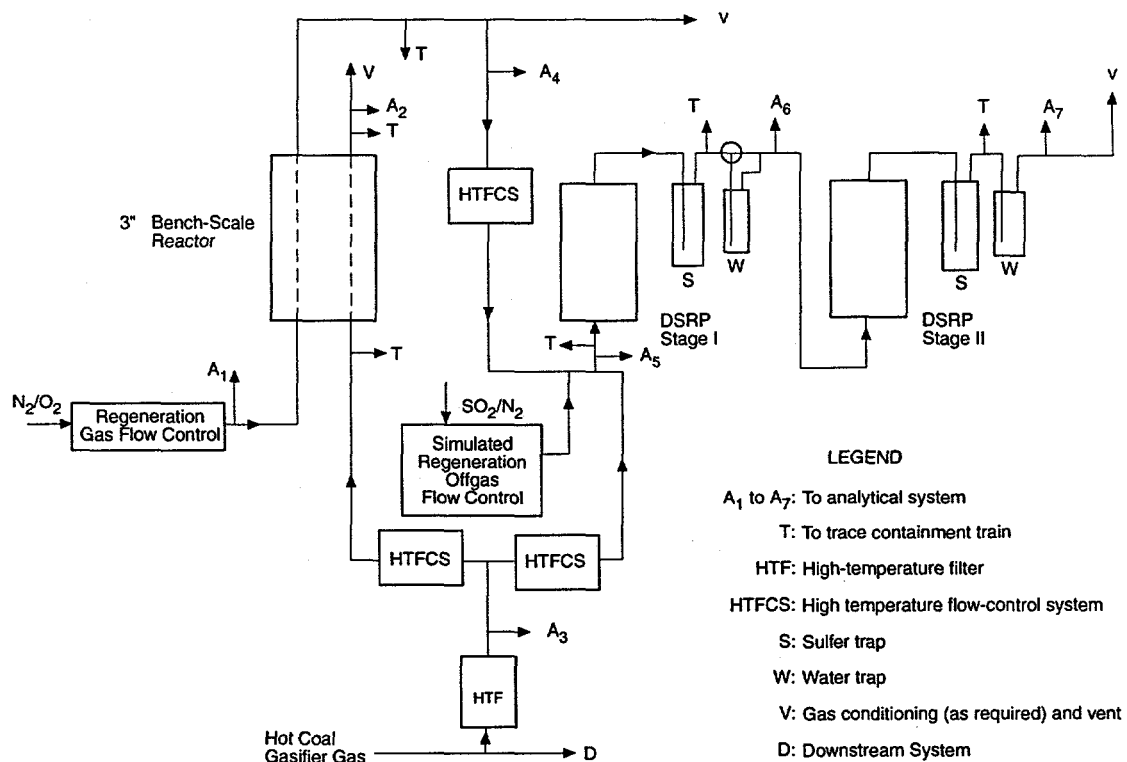


Figure 2. Integrated Zinc Titanate and DSRP Reactor System

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 SO<sub>2</sub>, is achieved after mixing. During the sulfidation portion of the cycle, the DSRP can also be run independently using simulated SO<sub>2</sub> (obtained using a liquid SO<sub>2</sub> 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 (H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>S, COS, SO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>). 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 NH<sub>3</sub> 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 cm<sup>3</sup> of catalyst and 1,500 cm<sup>3</sup> 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.

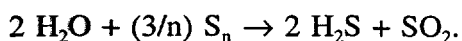
Two cycles, each consisting of a sulfidation and a regeneration/integrated DSRP operation, were conducted during the shakedown test. Problems were experienced in the testing due to plugging of the coal gas control valves for both sulfidation and DSRP reactors. Later it was discovered that entrained particles 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, NH<sub>3</sub> 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 H<sub>2</sub>S 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 H<sub>2</sub>S 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 <sub>4</sub>	1.97
H <sub>2</sub>	14.9
CO <sub>2</sub>	11.5
CO	9.87
H <sub>2</sub> O	11.0
H <sub>2</sub> S	0.1-0.75
N <sub>2</sub>	Balance
HCl	5-80 ppmv
As	<10 µg/m <sup>3</sup>
Se	16 µg/m <sup>3</sup>
Hg	<2 µg/m <sup>3</sup>
NH <sub>3</sub>	~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 H<sub>2</sub>S 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 <sub>s</sub> (cm/s)	4.3	4.9
Gas	Coal gas	2.25% O <sub>2</sub> in N <sub>2</sub>

The sorbent exhibited excellent removal efficiency and capacity even with the highly variable inlet H<sub>2</sub>S levels. Sorbent regeneration, which went very smoothly, is shown in Figure 4. Note that with 2.25 percent O<sub>2</sub> in the inlet, nearly two-thirds, i.e., ~1.5 percent, SO<sub>2</sub> 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 <sup>2</sup> /g)	3.2	7.56
Pore volume (cm <sup>3</sup> /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 <sup>3</sup> )	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



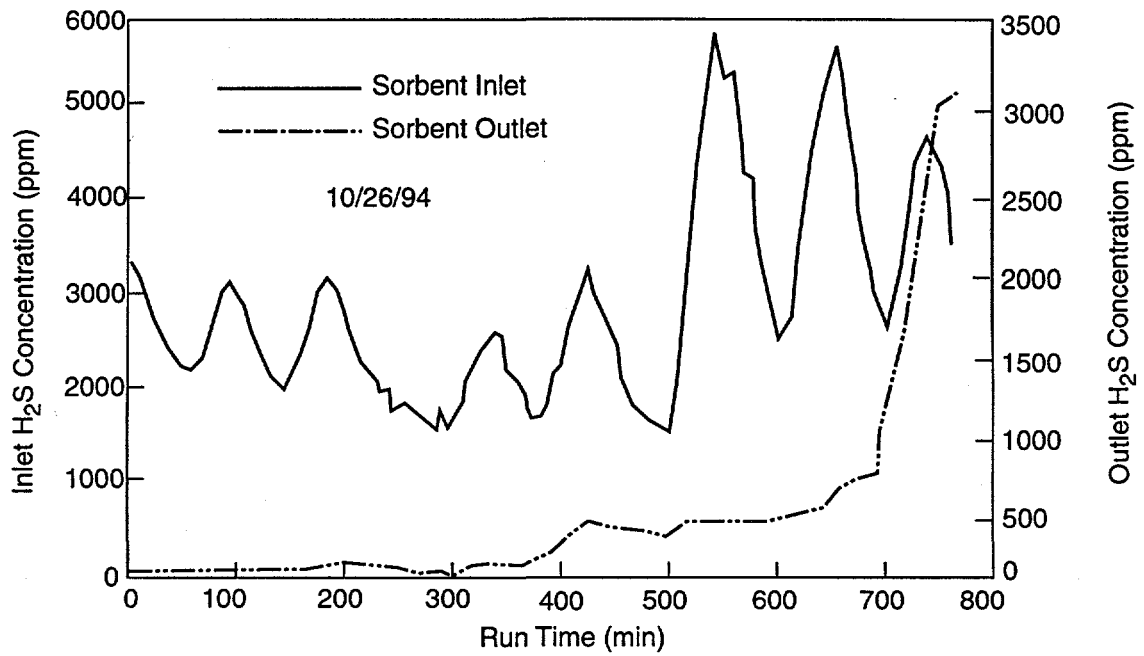


Figure 3. Sorbent Sulfidation Curves

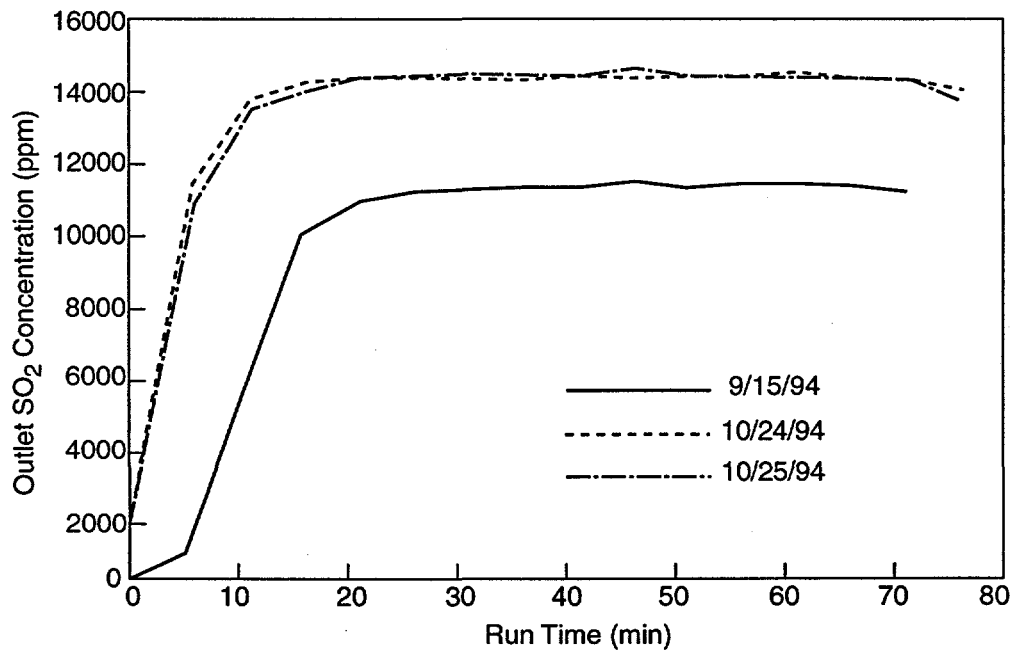


Figure 4. Sorbent Regeneration Curves

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  $\text{SO}_2$ -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  $\text{SO}_2$ -DSRP tests were highly successful. One of the simulated  $\text{SO}_2$ -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  $\text{H}_2\text{S}$  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 $\text{SO}_2$ (%)	1.8

**Table 5. Stage 1 DSRP Results During Lined-out Operation with Simulated  $\text{SO}_2$**

Run Time (min)	$\text{SO}_2$ Conversion (%)	$\text{SO}_2$ Conversion to $\text{H}_2\text{S}$ (%)	$\text{SO}_2$ 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 <sup>2</sup> /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 NH<sub>3</sub> decomposition at 850 °C and 150 psia.

The ZTFBD system will be modified for NH<sub>3</sub> decomposition testing. The two-stage DSRP system will be modified to a single stage with

improved control of stoichiometric ratio of reducing gas to SO<sub>2</sub> entering the reactor. Coordination meetings for the test and NH<sub>3</sub> 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 Tappella 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.

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