

**Figure 10. Sorbent sulfidation curves (9/15/94).**

to 99+ percent conversion in Stage I and 95 to 96 percent overall conversion for the two-stage system. The decrease in conversion following the second stage suggested problems of “reverse Claus” reactions in Stage II. For a commercial system one stage may be sufficient, thus further improving the already attractive economics of DSRP.

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

The DSRP unit did experience some plugging problems that resulted in unscheduled outages. The very small flow of coal gas used by the DSRP means that the HTHP control valve that is required is very small. 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 for small equipment a SS filter may be better. There were also some problems with sulfur plugging in the cold end of the unit that required depressurization and disassembly to unblock, suggesting that keeping the exit gases hot will be necessary for continuous operation, free of plugs.

There was one time period when it appeared that the “RTI Interface Line” that FETC-Morgantown had installed between the MGCR and the RTI trailer had become plugged. Efforts to clear the line while maintaining system pressures were not effective. Subsequently, the line was taken out of service and some particulates were removed from the line when it was depressurized and

disassembled. Because this cleanup did not reveal any large amount of solids, it remains unclear as to why there was apparently no flow for awhile.

By RTI's calculations, summarized below, there was coal gas available at the RTI trailer for a total of 70 h during the shortened October run. RTI was taking coal gas for 39.5 of those hours, for a utilization factor of 56 percent.

### 2.3.3 Chronology of Run

Highlights of the day-to-day operation of the bench-scale process equipment are shown below.

#### Monday, October 24, 1994

- 00:01 Startup sequence initiated by FETC-Morgantown.
- 08:45 RTI personnel started heating up furnaces, etc., in RTI trailer.
- 16:00 The operators for the MGCR started hot nitrogen flowing through their unit, and also into the RTI Interface line connected to the RTI trailer. Hot nitrogen began flowing into RTI's ZTFBD unit.
- 16:40 Coal gas started flowing into the MGCR and simultaneously into the interface line. Started **Sulfidation Run #1**.
- 22:30 H<sub>2</sub>S breakthrough at 1,100 ppm (according to the Carle GC on sample point A-2). Stopped Sulfidation Run #1 (total time was 5:50).
- 23:14 Started **Regeneration Run #1** with *integrated operation of the DSRP*.

#### Tuesday, October 25, 1994

- 00:32 End of Regeneration Run #1 (total time 1:18).
- 02:05 Began **Sulfidation Run #2**.
- 09:08 H<sub>2</sub>S breakthrough at approximately 1,000 ppm. End Sulfidation Run #2 (total time was 7:03). Set up trace contaminant sampling trains.
- 12:20 Started coal gas flowing for **Regeneration Run #2**.
- 12:30 Started air flowing for Regeneration Run #2. The acid gas trace contaminant sampling train was used on Stage I offgas (TCT-5) and the multimetals sampling train was used on the regeneration offgas (TCT-3).
- 13:46 End of Regeneration Run #2 (total time 1:16). At this point, the DSRP was depressurized and hardware modifications were made to move the sample point for the Western SO<sub>2</sub> analyzer from A-4 to A-5A (which is more suitable when DSRP is run using LSO<sub>2</sub>). In order that both sample points would be available in the future without depressurization again, sample conditioning equipment was cannibalized from sample point A-5 for use with A-5A. During this time period it was also determined that the Omega MFC (being used as a flow meter) installed on the DSRP (designated FT-240 on the P&ID) was no longer functioning properly and it was removed from the system.
- 18:13 Started LSO<sub>2</sub> flowing and adjusted controller by comparing with Western SO<sub>2</sub> analyzer.
- 18:43 Started coal gas flowing into DSRP for start of **DSRP/LSO<sub>2</sub> Run #1**.
- 23:30 Problems with maintaining coal gas flow were noted; assumed problem was plugging of Badger control valve FCV-2.

### Wednesday, October 26, 1994

- 00:12 Stopped coal gas flow; took nitrogen through interface line. End of DSRP/LSO<sub>2</sub> Run #1 (total time 6 h).
- 01:15 Started **Sulfidation Run #3**.
- 10:10 Continuing Sulfidation Run #3; some irregularity noted in automatic control of Badger valve FCV-1. Coincident with plugging problems noted by MGCR operators. Nitrogen was substituted for coal gas in MGCR (and, hence, in interface line) for approximately 1 h. During this time the multimetals trace contaminant sampling train was running on raw coal gas (TCT-1), and the acid gas train was running on the Stage I offgas (TCT-5).
- 11:10 MGCR advised RTI that coal gas was flowing in MGCR again, and that the gasifier had started taking chloride-doped coal.
- 11:30 Coal gas flow through the interface line was interrupted at RTI's request so that maintenance could be performed on FCV-2 (DSRP).
- 12:11 Coal gas flow to sulfidation run restarted.
- 14:10 End of Sulfidation Run #3 with H<sub>2</sub>S breakthrough of >3,000 ppm H<sub>2</sub>S (total time: 13 h). Set up trace contaminant sampling trains.
- 16:10 Coal gas flow to DSRP started for **DSRP/LSO<sub>2</sub> Run #2**. The ammonia trace contaminant sampling train was run on Stage I offgas (TCT-5), and the acid gas train was run on Stage II offgas (TCT-6).
- 17:49 Run was stopped when it was determined that little or no coal gas was actually flowing. Various means were attempted to clear the line; evidence suggested that the FETC-Morgantown interface line (or orifice) was plugged. DSRP was left hot with 67 std L/min of nitrogen flowing through it.

### Thursday, October 27, 1994

- AM FETC at the Morgantown site and EG&G staff worked to clear the Interface Line. RTI worked to re-install sample conditioning equipment at Sample Point A-5 (cannibalized from Point A-3) in order to run Carle GC on mixture of regeneration gas and coal gas as an additional aid to determination of coal gas flow rate.
- 12:00 Coal gas was available again, through the interface line. RTI could not operate DSRP, however, due to sulfur plugging in cold end. Attempted to clear the plug; eventually switched to alternative flow path in cold end train #2. Drained sulfur condenser #1. No sulfur was collected in condensers #2 and #3.
- 16:26 Started LSO<sub>2</sub> flowing for **DSRP/LSO<sub>2</sub> Run 3**.
- 16:27 Started coal gas flowing. The multimetals trace contaminant sampling train was run on the first stage offgas (TCT-5).
- 20:10 Plugging in DSRP noted; stopped DSRP/LSO<sub>2</sub> Run 3. Determined that cold end train #2 had plugged. Worked to clear plugging from cold end.
- 23:19 Started LSO<sub>2</sub> and coal gas flowing for **DSRP/LSO<sub>2</sub> Run 4**.

### Friday, October 28, 1994

- 05:12 Safety relief valve on Sulfur Condenser #1 popped. Coal gas released to equipment room; detected by toxic gas monitoring system. Coal gas flow stopped; end of DSRP/LSO<sub>2</sub> Run 4.
- 10:00 MGCR advised that they were going off coal gas for approximately 24 h. Also, gasifier operators decided to stop feeding coal and go into a "hot hold" with no coal gas production for approximately 24 h. RTI determined that the #1 sulfur condenser was leaking process gas into the water jacket. The condenser was drained of sulfur,

removed from service, and disassembled. The leak was determined to be in the coil; a new coil was fabricated and the condenser was reassembled and reinstalled by 18:00. Sulfur was also drained from condenser #3; none was collected in condenser #2.

21:00 FETC-Morgantown advised RTI that the gasifier team had decided to stop the run due to the discovery of a heat-deformed pipe in the ash-removal system. RTI turned off heat to furnaces and heat tracing. Left a small nitrogen purge through the equipment. Bled off the unused LSO<sub>2</sub> to the incinerator stack.

**Saturday, October 29, 1994**

All Day FETC operating crews at Morgantown had finished up during the night. RTI staff cleaned up and put away equipment. Finished purging SO<sub>2</sub>. Diluted reagents from the trace sampling project were disposed of. Sorbent, catalyst, and recovered sulfur samples were removed and packed for transport back to RTI. Some instruments and tools were removed and packed for transport. Cooling water was removed from the system. All equipment was depressurized; cylinders were capped, power to the control panel and the equipment skids was shut off. The HVAC units were left on with set points of 55 and 80 °F for heating and cooling, respectively.

Table 8 shows the summary of total hours.

Highlights of results of the tests are described in Section 2.3.4.

**2.3.4 Results**

During the October test, three sulfidation cycles (~25 h), two integrated DSRP tests (2.5 h), and four simulated DSRP tests (18 h) were conducted. The test conditions and the main results of the testing are presented. A typical FETC coal gas composition is shown in Table 9.

Points to note in Table 9 are that H<sub>2</sub>S and HCl are quite variable because of the coal's variability and because at times the FETC staff at Morgantown doped coal with salt to increase the HCl level (needed for a concurrent Shell slipstream test on chloride removal). The ammonia analysis is an estimated value because of coal gas line plugging during the sampling. The trace contaminant values were below or near the detection limit of our sampling system.

**Table 8. Summary of Total Hours**

| Coal gas availability |              | RTI onstream operation (taking coal gas) |       |                              |             |
|-----------------------|--------------|--|-------|------------------------------|-------------|
|                       | Hours        |  | Hours |                              | Hours       |
| Monday                | 7:20         | Sulfidation Run #1                       | 5:50  | Sulfidation Run #3           | 7:00        |
| Tuesday               | 24:00        | Regeneration Run #1                      | 1:15  | DSRP/LSO <sub>2</sub> Run #2 | 1:30        |
| Wednesday             | 17:00        | Sulfidation Run #2                       | 7:00  | DSRP/LSO <sub>2</sub> Run #3 | 3:40        |
| Thursday              | 12:00        | Regeneration Run #2                      | 1:15  | DSRP/LSO <sub>2</sub> Run #4 | 6:00        |
| Friday                | 10:00        | DSRP/LSO <sub>2</sub> Run #1             | 6:00  | <b>Total</b>                 | <b>39.5</b> |
| <b>Total</b>          | <b>70:20</b> |  |       |                              |             |

Test conditions for sulfidation and regeneration of ZT-4L over the 2.5 cycles are shown in Table 10.

Under these conditions, an H<sub>2</sub>S breakthrough curve during Cycle 3 is shown in Figure 11. The sorbent exhibited excellent removal efficiency and capacity even with highly variable inlet H<sub>2</sub>S values.

Sorbent regeneration, which went very smoothly, is shown in Figure 12. 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 during the October run indicating essentially no sulfidation. The properties of the fresh and three-cycle (sulfided) materials are compared in Table 11.

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) capacity showed only a small change from fresh to used material and was at 20 g S/100 g sorbent (20 lb S/100 lb sorbent).

The trace contaminants were below the detection limit, although chloride up to 38 ppmv and possibly some selenium up to 15

ppmv do appear to accumulate on the sorbent. Preliminary indications are that the sorbent sulfided with actual coal gas required a 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. This problem needs further investigation.

The test conditions for the DSRP Stage I reactor are shown in Table 12. As indicated earlier, two integrated ZTFBD-DSRP and four simulated regeneration offgas (ROG) (N<sub>2</sub> + SO<sub>2</sub>)-DSRP tests were conducted using the FETC gasifier coal gas. During the integrated tests, it was not possible to obtain steady-state operation in the short duration of the regeneration half-cycle due to the larger time constant (~2 h) of the DSRP. However, three of the simulated SO<sub>2</sub>-DSRP tests were highly successful. One of the simulated SO<sub>2</sub>-DSRP tests was not successful due to plugging of the coal gas line from FETC's gasifier. The results of the successful DSRP tests are shown in Table 13. Note that in Run 1, with fresh catalyst, an extremely high sulfur conversion (up to 99.7 percent) is achieved. Some selectivity toward H<sub>2</sub>S is seen in later runs, although even in these tests a 96 percent sulfur conversion level is achieved.

**Table 9. FETC 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             |

**Table 10. ZT-4 Reactor Conditions<sup>a</sup>**

|                       | 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> |

<sup>a</sup>3.0-in. Reactor; 600 g sorbent loaded.

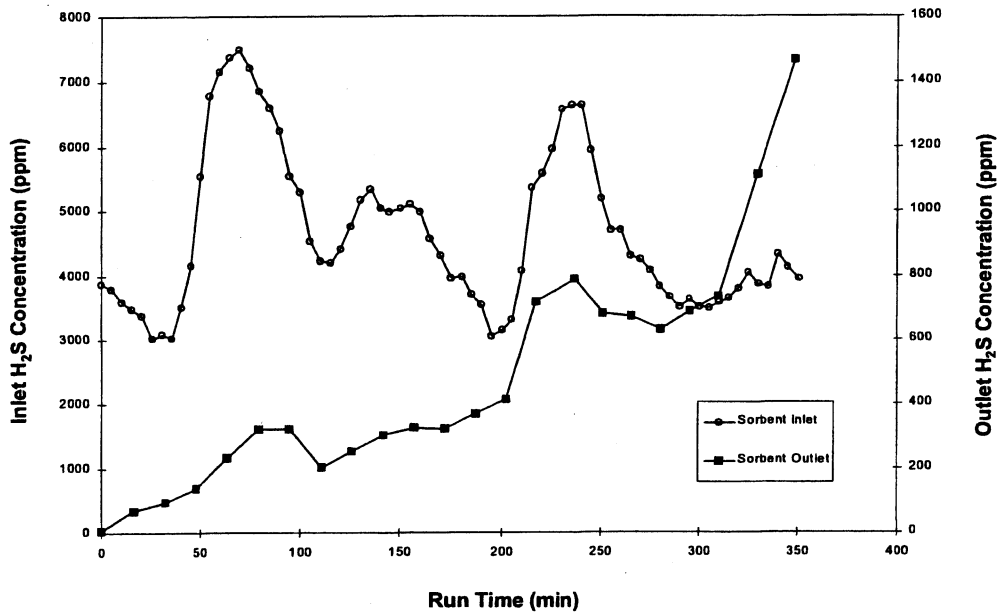


Figure 11. Sorbent sulfidation curves (10/24/94).

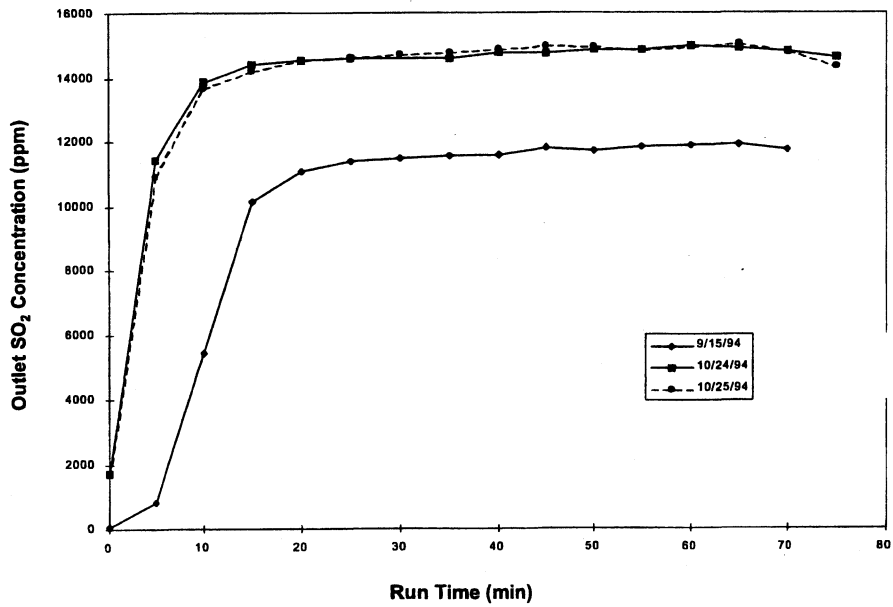


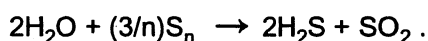
Figure 12. Sorbent regeneration curves.

**Table 11. Properties of Fresh and Reacted ZT-4L**

|   | Fresh           | Three-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)                               | NM <sup>a</sup> | <10                               |
| Se (µg/g)                               | NM              | 15                                |
| Cl (µg/g)                               | NM              | 38                                |

<sup>a</sup>NM = Not measured.

The overall conversion to elemental sulfur, Stage I plus Stage II, was 95 to 96 percent when the Stage I conversion was 99+ percent. This observation suggested that the "reverse Claus" reaction may have been occurring in Stage II:



For a commercial system, one stage may be sufficient, and a single-stage process would have improved economies.

The fresh and used catalyst properties are shown in Table 14. The used catalyst showed better crush strength but a lower surface area. Chloride is picked up by the catalyst but does not appear to affect its activity significantly even at a 300-ppmv level. No other trace contaminants were detected in the catalyst.

To conclude, both ZT-4L and DSRP showed very promising results in short-term testing with actual coal gas. The test of 160 h needs to be completed to evaluate longer-term effects.

The TGA of reacted ZT-4L from the ZTFBD/DSRP Mobile Laboratory showed some reduction in sulfur capacity, up to 10 percent. To further evaluate the influence of trace contaminants, several metals were analyzed in the ZT-4L sorbent used in the mobile lab, tested in the MGR at FETC-Morgantown, and tested at the Enviropower (Finland) pilot plant. The purity of the DSRP sulfur was also examined using a differential scanning calorimeter (DSC).

**Table 12. DSRP Stage I Reactor Conditions**

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

### 2.3.4.1 Trace Contaminants in ZT-4L

The sulfided ZT-4 sorbent from the RTI trailer was subjected to regeneration using RTI's standard regeneration procedure of 2 percent O<sub>2</sub> at 650 °C in an atmospheric pressure TGA. Compared to a typical ZT-4L, sulfided using simulated coal gas, it appeared that the mobile lab ZT-4L, sulfided using actual coal gas, regenerated slower. Some poisoning of the regeneration active sites due to trace contaminants was suspected. Several trace contaminants were measured on the sulfided ZT-4L and the results are compared in Table 15.

The increase in concentration of As, Pb, or other metals in the sulfided materials is noteworthy and could have contributed to the slower regenerability. However, controlled tests on ZT-4L with H<sub>2</sub>S and metal vapor addition are needed to ascertain this. The estimated gaseous concentrations based on the measurements are about 100 µg/m<sup>3</sup> for As and 10 to 40 µg/m<sup>3</sup> for Se. No Hg was detected in the gas or sorbents.

### 2.3.4.2 Sulfur Purity

The sulfur purity of the DSRP sulfur was examined using a DSC. Figure 13 compares the DSC profile of pure sulfur obtained from the drugstore with that of sulfur obtained from the DSRP condensers. There are three phase

transitions that are typical of sulfur. The middle transition, due to melting, occurs at the same temperature for all samples. There is a slight shift in the other two transitions for the "DSRP" sulfur versus the "drugstore" sulfur. This could be due to small amounts of undissolved metal impurities in the DSRP sulfur caused by corrosion of the SS vessel or due to metal vapor in the coal gas (such as AsH<sub>3</sub> or H<sub>2</sub>Se) dissolving in the sulfur. A more likely possibility can be ascertained by melting a relatively large sample of the sulfur and examining the melted sulfur for undissolved impurities.

**Table 13. Stage I DSRP Results During Steady-State Operation with Simulated Regeneration Offgas**

| Run time (min)   | SO <sub>2</sub> conversion (%) | SO <sub>2</sub> conversion to H <sub>2</sub> S (%) | SO <sub>2</sub> conversion to sulfur (%) |
|------------------|--------------------------------|--|--|
| <b>Run No. 1</b> |                                |  |  |
| 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                                     |
| <b>Run No. 3</b> |                                |  |  |
| 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                                     |
| <b>Run No. 4</b> |                                |  |  |
| 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 14. DSRP Stage I Catalyst**

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



Table 15. Trace Contaminants in ZT-4L Sulfided with Actual Gas ( $\mu\text{g/g}$ )

| Trace contaminants | ZT-4L fresh | ZT-4L sulfided Enviropower | ZT-4L sulfided (600 °C) RTI trailer (10/26/94) | MGC-10, ZT4-94 (sulfided FETC-MGCR) |
|--------------------|-------------|----------------------------|--|-------------------------------------|
| As                 | 0.7         | 5.1                        | 8.4  | NA <sup>a</sup>                     |
| Ba                 | 12.7        | NA                         | 19.8   | 35.4                                |
| Be                 | 1.4         | NA                         | 2.0  | 2.7                                 |
| Cd                 | 10.6        | NA                         | 11.6   | 10.2                                |
| Cr                 | <10         | NA                         | <10.0  | <10.0                               |
| Pb                 | <30         | NA                         | 49.6   | 45.2                                |
| Mn                 | 4.2         | NA                         | 11.2   | 9.4                                 |
| V                  | 192         | NA                         | 192  | 171                                 |
| Se                 | <0.57       | 2.9                        | 0.72   | NA                                  |
| Cl                 | NA          | NA                         | 38   | NA                                  |

<sup>a</sup>NA = Not available.

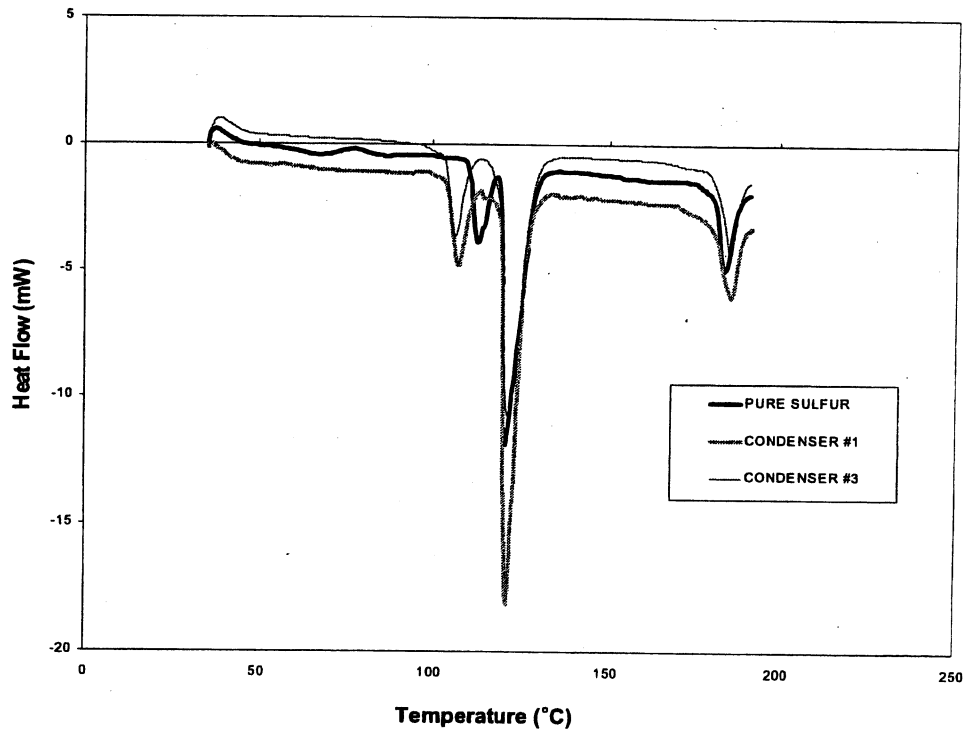


Figure 13. DSC test of pure sulfur and sulfur from DSRP.

## 2.4 DESIGN/CONSTRUCTION FOR 1995 FIELD TEST

Based on the interrupted October 1994 field test, a decision was made to conduct a 160-h slipstream test in 1995. This test was scheduled to begin on July 17, 1995, to coincide with a planned gasifier campaign with the experiment design to include

- A 160-h test of single-stage DSRP with actual coal gas and simulated regeneration
- A 100-h test of  $\text{NH}_3$  decomposition at 850 °C and 1.1 MPa (150 psia).

The ZTFBD system was modified for the  $\text{NH}_3$  decomposition testing. The two-stage DSRP system was modified to a single stage with improved control of the stoichiometric ratio of reducing gas to  $\text{SO}_2$  entering the reactor. Figure 14 is a block diagram of the simplified, single-stage DSRP.

### 2.4.1 Equipment Modifications

Based on the experience gained in the interrupted October 1994 field test, the following modifications were undertaken in order to increase the possibility of a successful 160-h test:

- Convert DSRP system to single stage and run continuously on simulated  $\text{SO}_2$  with actual coal gas.
- Temperature/pressure corrected orifice flow meter for coal gas
- Process control computer to input  $\text{SO}_2$  mass flow and hydrogen and CO concentrations and output required coal gas flow set point to the coal gas flow control valve
- Modify sulfur condenser to have a separate external separator pot with a heating jacket and nonfreezing drain valve
- Install Pall metal HTHP filter on coal gas line to trailer
- Install HTHP back-pressure control valve system
- Install heating system for DSRP offgas vent
- Install dedicated DDAS terminal to obtain  $\text{H}_2$ ,  $\text{CO}$  signals from FETC
- Install large knockout pot for DSRP offgas vent.

### 2.4.2 Construction Chronology

The mobile lab was de-winterized in early April 1995 and active modification of the process equipment was started. RTI

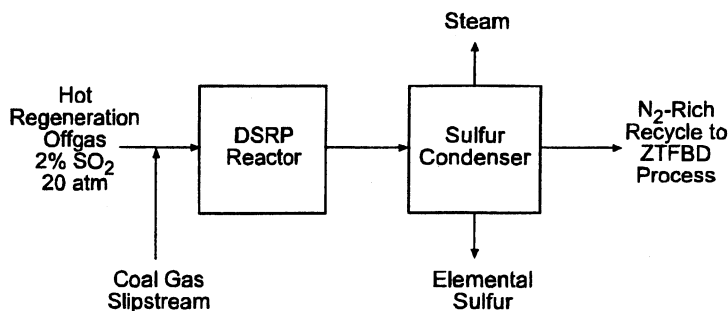


Figure 14. New single-stage DSRP.

technical and supervisory personnel traveled to Morgantown, West Virginia, usually biweekly, in order to accomplish the required modifications.

- The DSRP bench-scale unit was modified to have
  - Single reaction stage (the second stage reactor and furnace, plus two sulfur condensers were removed).
  - Improved sulfur condenser (an external, electric heat-jacketed separator pot with drain valve was fabricated and installed on the No. 1 condenser. The coil inside the steam-jacketed condenser shell was replaced with a longer, annealed/stress-relieved coil. Immersion heaters were installed in the shell to replace external heat tapes.)
  - Better coal gas filter (the ceramic thimble-type filter in a large metal housing was replaced with an off-the-shelf porous metal disposable filter: Mott "Gas Shield" rated for 99.9999999 percent removal of particles down to 0.1  $\mu\text{m}$ ).
  - Improved offgas piping design (the gas exiting from the external separator pot was reheated with a small furnace, and exited from the system through heated lines to the back pressure control valve. Downstream of the control valve, an unheated 36-gal knock-out pot was installed to collect sulfur particles prior to venting to the FETC incinerator stack.)
  - Automatic back pressure control replaced the mechanical BPR (the hot exit gas was routed to a "Badger-Research" HTHP control valve controlled by a pressure transducer and solid-state "P-I-D" controller.)
- Orifice flow meter and automatic control of the "Badger-Research" coal gas control valve were added.
- Process control computer and software were added for stoichiometric control of coal gas (with temperature and pressure compensation to give true mass flow basis) to DSRP.
- The ZTFBD unit was modified slightly to permit fixed-bed testing of ammonia decomposition catalyst.

To meet the test program objectives, provision had to be made for trace contaminant sampling and analysis. Several sampling trains were prepared and shipped to the RTI trailer at the Morgantown site. The trains consisted of "mini" impingers immersed in ice-water baths. Separate trains were designed to measure the trace metals (following a modification of EPA Reference Method 29), volatile chlorides, and ammonia. Sample points on the ZT unit were set up before and after the catalyst bed, and after the DSRP reactor on the DSRP unit.

A staffing plan was developed to provide at least three-person coverage on a 24-h basis. This would allow for one individual to be dedicated to operating the trace contaminant sampling trains, while another individual operated the process equipment. A third individual was designated as the shift supervisor. A fairly nontraditional schedule rotation was devised in order to optimize coverage by experienced personnel, provide adequate supervision of student assistants (summer interns), and allow for transportation needs to and from the hotel.

To meet the FETC site requirements of their Safety Analysis and Review System (SARS) an application for a modification to an operating permit was prepared. This information was

presented in writing to the site process safety committee on July 6, 1995, and was defended orally on July 13, 1995. Permission to operate was granted, in preparation for the scheduled start of the gasifier run.

## **2.5 FIELD TESTING IN 1995**

### **2.5.1 Actual Operating Parameters**

- DSRP unit operated at
  - 1.3 to 1.9 MPa (180 to 260 psig)
  - 580 to 630 °C
  - 4.2 Nm<sup>3</sup>/h (70 std L/min) of synthetic regeneration offgas with 1.4 to 4.9 percent SO<sub>2</sub>
  - 0.45 Nm<sup>3</sup>/h to 0.96 Nm<sup>3</sup>/h (7.5 to 16 std L/min) of actual coal gas
  - Space velocity of 5,100 std cm<sup>3</sup>/cm<sup>3</sup>·h.
- ZTFBD unit operated at
  - 1.1 MPa (150 psig)
  - 780 °C
  - 4.1 Nm<sup>3</sup>/h (68 std L/min) of actual coal gas
  - Space velocity of 5,000 std cm<sup>3</sup>/cm<sup>3</sup>·h.
- DSRP catalyst exposed to coal gas for 160 h.
- DSRP took coal gas 91 percent of the time it was available from FETC-Morgantown.
- DSRP operated with simulated regeneration offgas (LSO<sub>2</sub> flowing; producing molten sulfur) for nine periods during run, totaling 44 h.
- NH<sub>3</sub> decomposition catalyst exposed to coal gas for 102 h.

### **2.5.2 Summary of Results**

- Single-stage DSRP design resulted in high conversion of sulfur compounds to elemental sulfur—98+ percent during steady-state operation.
- No effect on DSRP of the trace contaminants in actual coal gas over duration of run; conversion at end was as high as at beginning.
- Measured NH<sub>3</sub> decomposition ranged from 85 to 95 percent (depending on analytical technique).
- No effect of exposure time on NH<sub>3</sub> decomposition.

### **2.5.3 Chronology of July 1995 Run**

On Monday, July 17, 1995, the FETC gasifier at Morgantown started up on schedule, and in parallel RTI personnel heated up reactors and heat tracing in the RTI trailer in preparation for receiving coal gas.

The initial operating strategy was to operate the DSRP for 160 h continuously with coal gas feed and simulated regeneration offgas (using vaporized LSO<sub>2</sub>). In parallel, the ZTFBD unit was to

operate for 100 h. Startup of both units was smooth, and after about 3 h of operation, steady-state performance of the DSRP was achieved. Unfortunately, after the DSRP had been operating with coal gas for only 4 h, the FETC gasifier shut down. This initial period of operation was designated as **Run #1**.

Coal gas was available again on the morning of Tuesday, July 18, 1995. This next period of operation was designated as **Run #2**; the same operating parameters were chosen as were used for Run #1. During this period, the filter on the RTI end of the coal gas slipstream line started to plug up. The differential pressure transmitter across the filter went overrange. Also, sulfur plugging in the sample line at the outlet of the DSRP was noted, so that some of the analysis data are unreliable. A period of steady-state operation was achieved, however.

For **Run #3**, which was contiguous with Run #2 and started about noon on July 18, the DSRP reactor furnace setpoint was raised 20 °C. This caused the reaction temperature (the bottom catalyst bed temperature) to increase from 612 to 622 °C. The sulfur plugging in the low-temperature DSRP outlet piping was first noticed during this run. The flow of LSO<sub>2</sub> was stopped briefly several times during this run in order to allow time for clearing plugs.

In the late afternoon of July 18, the DSRP reactor furnace temperature setpoint was lowered (by 40 °C) to 580 °C and was designated the start of **Run #4**. This caused the reaction temperature (the bottom catalyst bed temperature) to decrease from 622 to 588 °C. During this run the plugging of the coal gas filter became more severe. The DSRP system pressure had to be reduced from 1.91 to 1.77 MPa (262 to 242 psig) in order to maintain flow of coal gas into the unit. At midnight on July 18 the reactor furnace temperature was raised 20 °C back to the original setpoint, and the temperature experiment series ended.

The pressure drop across the coal gas filter continued to increase, so that **Run #5** (early morning of July 19) became a de facto reduced pressure run. The DSRP system pressure was reduced to 1.5 MPa (202 psig). Also, severe plugging of the outlet of DSRP was noticed. The coal gas flow to both the ZT unit and the DSRP was stopped so the equipment could be worked on to remove plugs in the DSRP outlet piping.

The morning of July 19 was spent clearing sulfur plugs from the outlet piping and devising a temporary piping arrangement that would permit back-pulsing of the coal gas (Mott) filter. At this point in the test program it became apparent that with continuous operation of the DSRP with LSO<sub>2</sub> feed, the production rate of sulfur by the reactor system was overwhelming the capacity of the offgas system (including the knock-out pot) to handle it. It was surmised that not all of the condensed sulfur was being removed from the gas stream by the separator pot. The presumed "mist" was then being vaporized in the reheater, passing through the back-pressure control valve as a vapor, and finally condensing elsewhere in the cool offgas system either as a crystalline form or as a sublimed "flowers of sulfur" form. A decision was made to modify the operating strategy for the remainder of the test program.

The new operating plan was to run coal gas through the DSRP at all times in order to expose the catalyst for 160 h. The nitrogen portion of the simulated regeneration offgas would also be flowing through the DSRP reactor. The LSO<sub>2</sub> would only be run at selected times to observe how the catalyst was continuing to perform. The coal gas flow was restarted the afternoon of July 19 with the revised operating plan.

The coal gas filter back-pulsing procedure was followed for the first time, and it successfully reduced the pressure drop across the Mott filter from 517 to 69 KPa (75 to <10 psi). At this time

the small Balston filters were removed from trace contaminant sampling points TCT-1 and TCT-2 (on the ZT unit). It was decided that gas from those sample points would not have large amounts of particulate that would clog the sampling apparatus and so would need to be filtered out in order to get reliability. Furthermore, any small amount of particulate should preferably be collected as part of the sample in order to get a valid reading of the trace contaminants present.

Unfortunately, after several hours of coal gas and nitrogen flow, the DSRP outlet piping plugged up again. It appeared that residual sulfur in the offgas lines was "migrating" along and forming new plugs. Plugging of the lines outside the RTI trailer was also noted, and the critical flow orifice in the bypass line was cleared by FETC personnel. Coal gas flow was interrupted for several hours to permit line-clearing efforts. A copper coil for cooling water was fabricated for installation in the knock-out pot.

Coal gas flow was restarted the evening of July 19 and continued to flow through the night. The flow was interrupted in the late morning in order to install the cooling coil inside the knock-out pot. LSO<sub>2</sub> was not used again until the afternoon of July 20, the start of Run #6. There were a number of control problems encountered during this run. The pressure had to be continually decreased due to rising pressure drop across the coal gas filter. The output of the Western SO<sub>2</sub> analyzer appeared to be at odds with the reading on the LSO<sub>2</sub> rotameter. A brief experiment in which the automatic valve on the LSO<sub>2</sub> supply was closed showed an immediate effect on the rotameter but no effect on the Western reading. Only a very brief period of steady-state operation was achieved during this run. The LSO<sub>2</sub> flow was stopped in the late afternoon of July 20, and coal gas continued to flow.

A modification was made to the DSRP equipment to add heat tracing to the LSO<sub>2</sub> feed line where it intersected the nitrogen line upstream of the preheater. This modification was expected to prevaporize the liquid and ensure more complete mixing of the stream before the sample point for the Western SO<sub>2</sub> analyzer. The results were apparent during Run #7 on the afternoon of July 21. The analyzer output was steady and consistent with the rotameter reading. Steady-state operation was achieved easily.

On July 22, the FETC gasifier was shut down in order to make a repair of the incinerator stack. Coal gas would not be available to the MGCR (and hence to the RTI trailer) from that afternoon until the evening of July 25. At this time the test run of the ammonia decomposition catalyst in the ZT unit was ended. Also, it was decided to end the trace contaminant sampling program. The total staffing of the RTI trailer was reduced. The ZT and DSRP reactors were maintained hot with a small nitrogen purge.

During the outage, some minor maintenance activities of the process equipment were accomplished. A stainless steel coil was installed in the knock-out pot, replacing the copper coil (which had corroded substantially). The Mott filter was replaced with a fresh spare. The used filter was dumped out and found to be plugged with a large quantity of what looked like pure carbon (soot).

In the early evening of Tuesday, July 25, coal gas flow was restored to the DSRP unit. Coal gas also flowed to the ZT unit (in order to maintain a sufficiently large coal gas flow through the slipstream line), although that reactor was not maintained at the high test temperature.

Early Wednesday morning, July 26, the coal gas flow from the gasifier was interrupted once again and was not available until that evening. During this outage the mechanical BPRs on the ZT unit were removed and replaced to correct a problem noted the previous day.

During this second half of the test program, the pressure drop across the replaced Mott filter was greater than the range of the differential pressure (DP) transmitter, but unlike the first day of the test, no continued large increase was observed. The back-pulsing procedure was not used.

With the coal gas flow restored on the evening of July 26, **Run #8** was started. A higher SO<sub>2</sub> concentration (3.6 percent compared to 2.5 percent typically for the previous runs) was used, with the same DSRP furnace set points, so that the reaction temperature was slightly higher. Some experimentation with controllability of the process was attempted, as described below.

Following several hours of operation of Run #8 with LSO<sub>2</sub> flowing, the flow of coal gas into the DSRP unit was stopped briefly, in order to clear sulfur plugs. Even with the additional cooling inside the knock-out pot, sulfur (vapor or aerosol) apparently passed through and into the outlet piping. Plugging continued to be observed at tees and elbows in the 19-mm (3/4-in.) outlet piping. Plugging in the 1-in. line outside the trailer was also suspected. Coal gas flow through the DSRP unit was restored to continue exposing DSRP catalyst to coal gas.

Later in the morning of July 27 a problem was noted with coal gas flow through the ZT unit. A plug in the condensate receiver was cleared. But then later that afternoon a plug developed in the ZT outlet piping so that coal gas would no longer flow. The hypothesis was that with a reduced temperature in the ZT reactor (but not a cold reactor) the nickel-based ammonia decomposition catalyst was causing a dissociation of the CO in the coal gas to carbon and CO<sub>2</sub>. The soot particles could then plug up the outlet piping. The outlet lines were not disassembled, though, to test this hypothesis.

With the ammonia decomposition experiment no longer being conducted, the only effect of the plugging problem was that total coal gas flow through the slipstream line was now reduced to just that small quantity needed by the DSRP unit. The ZT reactor furnace temperature setpoints were reduced to allow the reactor to cool down.

Early in the morning of July 28, the toxic gas alarm went off; a high CO concentration in the equipment room was noted. This was identified to be a flange leak on the ZT reactor. Even though coal gas was not supposed to be flowing through this unit, the isolation valve was evidently allowing some flow, and the cooling reactor flange sprang a leak. The coal gas line was capped off to stop this problem.

The final DSRP runs were started during the late evening of July 28. For **Run #9A** the goal was to achieve the best operation possible, with operating conditions the same as earlier in the run. This was achieved with an operating temperature of 620 °C, 1.8 MPa (250 psig), and 3.5 percent SO<sub>2</sub> in the simulated regeneration offgas. For **Run #9B** the system pressure was raised to 1.9 MPa (265 psig)—the maximum that could be achieved given the pressure of the coal gas, and the observed pressure drop through the Mott coal gas filter. Steady-state operation was easily achieved.

For the final experiment of the 160-h DSRP test run, **Run #9C**, the nitrogen flow making up the simulated regeneration offgas, was reduced, thereby increasing the SO<sub>2</sub> concentration. A distinct increase in reactor temperature was noted. There was some difficulty getting the proper coal gas flow to line out the unit. During this time the LSO<sub>2</sub> in the supply tank was exhausted, so the DSRP runs were ended.

The FETC gasifier continued to operate to conduct other tests, but early in the morning of July 29 the RTI process equipment stopped taking coal gas. Hot purging was followed by cooldown and shutdown procedures.

### **DSRP Engineering/Design Success Stories**

- Automatic/stoichiometric computer control of coal gas resulted in smooth operation of DSRP for extended periods.
- Automatic control of DSRP system pressure using HTHP control valve improved the stability of the system pressure.
- LSO<sub>2</sub> delivery system worked smoothly, as previously; consistency of measured gas composition was improved with addition of preheating of liquid line.
- Sintered metal filter on coal gas slipstream line completely eliminated particles from entering the RTI process equipment.
- Coal gas flow control valves and orifice flow meter worked perfectly throughout the duration of the run.
- The addition of more temperature controllers on heat tracing simplified long-duration operation of the units.
- Improved design of sulfur condenser (immersion heaters, separate collection pot, annealed coil, new drain valve) worked smoothly and leak free.
- Draining of molten sulfur occurred routinely with no plugging.
- Heated DSRP offgas outlet line did not plug up with carryover sulfur.
- Continuous online analyzers and GC worked smoothly and reliably.

### **Areas Requiring Further Development**

- Process control software running under Windows<sup>®</sup> 3.1 was not rugged enough for continuous operation; "General Protection Faults" and other Windows<sup>®</sup>-based errors resulted in temporary loss of process control.
- Laboratory-type heat tapes are not rugged enough for continuous operation of bench- and pilot-scale equipment. In order to achieve sufficient heating, an overwrap of insulation was used. In those cases where the heat tapes could receive full line voltage from the temperature controllers, there were problems with burned-out tapes. Variacs had to be inserted into the circuit.
- A second problem also occurred with the laboratory-type heat tapes. Due to concern that the tapes could short out to the metal tubing, an insulation underwrap was also typically used. This was done even though it would result in reduced efficiency of heat transfer and even though the manufacturer claims that direct contact with metal would be acceptable. Nevertheless, one incident of a short to ground through the insulation (and resultant overheating) did occur. The problems with heat tapes threatened to impact the onstream time of the unit. No



such problems occurred with the lines traced with Temptrace<sup>®</sup> metal-sheathed mineral-insulated heat tracing.

- The operating conditions of the DSRP unit condensation loop (low sulfur concentration; large temperature drop) seem to favor production of a sulfur aerosol or "smoke." Not all the molten sulfur was captured in the separator pot, as designed. Additional improvement in solid/liquid sulfur recovery is required.
- Unheated vent line to FETC incinerator was troublesome; untrapped sulfur particles tended to collect and plug all unheated lines.
- Improved tuning of the control loop (i.e., selection of appropriate P-I-D constants) would be needed in order to make DSRP responsive to rapid changes in SO<sub>2</sub> inlet concentration.
- The SO<sub>2</sub> response time from sample point A6 probably needs to be improved. An apparent lag time was suspected, perhaps caused by the Drierite trap. An alternative sample preparation approach could probably be devised.
- More alarms are needed to alert operators who are monitoring a continuous process for long hours. A relay board with annunciator could be interfaced with existing process monitoring and control software.
- The MFC used as a meter for the ZTFBD unit was ruined when water inadvertently was drawn backwards through it from the vent header. A similar problem occurred in the 1994 test program. A more rugged flow metering scheme (e.g., orifice flow meter) would be required to make the process immune from this type of problem.
- The mechanical BPRs used on the ZTFBD unit experienced a small amount of plugging (for no apparent reasons). This may be corrosion-induced; the concept of using BPRs in a flow stream that is potentially moist needs to be reevaluated.
- The "Mott" porous metal filter was very effective at eliminating plugging in the coal gas control valve. However, since the filter itself plugged up, a proper back-pulsing system needs to be designed into the piping layout.

## **2.5.4 Details of Results/Parametric Studies**

### **2.5.4.1 Data Reduction**

The critical parameter used to judge the performance of the DSRP is the conversion of the incoming gaseous sulfur compounds to elemental sulfur. The conversions shown in this report are rigorous calculations based on gas concentrations, as obtained from the continuous analyzers and GCs. The calculations take into account the incoming sulfur species in both the regeneration offgas (sulfur dioxide) and the coal gas used as the reducing gas (hydrogen sulfide). Volume changes in the flow rates due to the formation of, and eventual condensation of, water are included. Specifically, the calculations are discussed below.

The flow rate of nitrogen making up the synthetic regeneration offgas was known from the electronic MFC. The concentration of SO<sub>2</sub> in the mixture of nitrogen and vaporized LSO<sub>2</sub> was measured by a continuous SO<sub>2</sub> analyzer, so that the molar flow rate of SO<sub>2</sub> into the reactor could be calculated. The coal gas flow into the reactor was measured on a wet basis by the orifice flow

meter used as part of the flow control instrumentation. The composition of the coal gas ( $H_2S$ ,  $H_2$ , and  $CO$ ) on a dry sample basis was measured by an online GC/MS operated by FETC and located near the gasifier. The water content of the coal gas was determined gravimetrically from timed condensate samples, by FETC (with confirming information from RTI condensate sampling). The wet basis coal gas composition was then calculated, and the molar flow rates of  $H_2S$ ,  $H_2$ ,  $CO$  and  $H_2O$  were determined.

An RTI GC was used to measure the sulfur species in the DSRP outlet gas stream ( $H_2S$ ,  $COS$ , and  $SO_2$ ) on a water-free basis. The flow rate of this stream was not measured directly, however. Rather, it was derived from the stoichiometry of the reactions that occurred. For purposes of the flow rate calculations, complete reaction of the sulfur dioxide and the active components of coal gas was assumed. Thus, all the inlet sulfur dioxide disappears and all the moles of hydrogen in the coal gas are converted to the same number of moles of water. That water, plus the water coming in with the coal gas, was condensed before the sample was analyzed for sulfur compounds. The  $CO$  in the coal gas is converted to  $CO_2$  with no change in the number of moles. Thus, the dry basis outlet flow rate was calculated as the sum of the nitrogen flow in and the coal gas flow in, less the water in the coal gas and the water produced.

Knowing the dry basis total outlet flow rate, the individual sulfur species flow rates could be calculated from the GC concentrations. All inlet sulfur molecules (from the regeneration offgas and from the coal gas) that were not still present in the outlet gas as one of the three measured species— $H_2S$ ,  $COS$ , and  $SO_2$ —were assumed to be converted to elemental sulfur. The percent conversion was thus calculated as inlet molar flows minus outlet molar flows divided by inlet molar flows.

The instrumentation in the RTI Mobile Laboratory also included an Ametek analyzer (operating on an ultraviolet photometric principle) for continuous, online measurement of  $H_2S$  and  $SO_2$  concentrations in the DSRP offgas. This instrument provided continuous feedback to the operator to optimize the coal gas flow rate, but it did not accurately measure the absolute concentrations of the gaseous sulfur species in the outlet gas. Carbonyl sulfide ( $COS$ ) is not detected by the Ametek unit; however, its presence interferes with an accurate measure of the  $H_2S$  concentration. According to information from Ametek, the  $COS$  parts-per-million value adds to the  $H_2S$  parts-per-million value according to:

$$(H_2S)_{Ametek} = [H_2S] + [COS]/2 .$$

This relationship did not seem to be completely accurate, though, as it was not substantiated by the GC analyses of the same stream. The elemental sulfur yield can be calculated from the Ametek values; but because the total concentration of gaseous sulfur compounds in the offgas is underreported (there is not a one-to-one correspondence between  $COS$  and  $H_2S$  concentrations), calculations based on Ametek data overstate the conversion to elemental sulfur.

#### 2.5.4.2 Summary of Results

Table 16 summarizes the conditions in each of the designated run periods and reports the calculations of the conversion to elemental sulfur made according to the description above.

#### 2.5.4.3 Parametric Studies

Although the basic concept of the July 1995 run was to operate continuously at steady state, there were some opportunities to make small changes in some operating parameters to observe

Table 16. Summary of July 1995 DSRP Test Runs

|   | Run #1    | Run #2    | Run #3    | Run #4    | Run #5                            | Run #6                        | Run #7           | Run #8    | Run #9    |            |              |
|---|-----------|-----------|-----------|-----------|-----------------------------------|-------------------------------|------------------|-----------|-----------|------------|--------------|
|   |           |           |           |           |                                   |                               |                  |           | A         | B          | C            |
| Date  | 7/17/95   | 7/18/95   | 7/18/95   | 7/18/95   | 7/18-19/95                        | 7/20/95                       | 7/21/95          | 7/26/95   | 7/28/95   | 7/28-29/95 | 7/29/95      |
| Start time  | 18:25     | 5:40      | 12:17     | 17:11     | 23:45                             | 13:13                         | 14:15            | 23:35     | 21:00     | 23:37      | 00:19        |
| End time  | 22:25     | 12:17     | 17:11     | 23:45     | 06:25                             | 17:55                         | 17:09            | 04:30     | 23:37     | 00:19      | 01:43        |
| Duration, h, w/LSO <sub>2</sub> on                                      | 4.0       | 6.40      | 3.82      | 6.57      | 5.30                              | 4.70                          | 2.90             | 5.0       | 153.5     | 4.75       | 155.6        |
| Cum. time @ end of run  | 4.0       | 10.57     | 15.68     | 22.35     | 28.92                             | 52.64                         | 76.40            | 112.1     | 605       | 154.1      | 605          |
| RXTR  | 602       | 601-603   | 613       | 576       | 609                               | 596                           | 601              | 607       | 605       | 606        | 605          |
| Temp. Middle TE-203   | 610       | 611-613   | 621       | 584       | 616                               | 605                           | 611              | 616       | 614       | 615        | 616          |
| Temp. Bottom TE-202   | 610       | 612-614   | 622       | 588       | 620                               | 600                           | 612              | 620-623   | 617       | 620        | 630          |
| System pressure (psig)  | 262       | 262       | 262       | 262-242   | 242-202<br>(212-202) <sup>a</sup> | 260-250<br>(252) <sup>a</sup> | 258              | 250       | 250       | 265        | 265          |
| SO <sub>2</sub> concentration in simulated regenerated offgas (ROG) (%) | 3.1-3.2   | 2.8       | 2.5-2.7   | 2.5-2.7   | 2.8                               | 4.0 <sup>b</sup>              | 2.4 <sup>c</sup> | 3.6       | 3.4-3.5   | 3.56       | 4.9          |
| LSO <sub>2</sub> rotameter reading (cm <sup>3</sup> /min)               | 0.9       | 0.9-1.0   | 1.0       | 1.0       | 1.0                               | 0.52                          | 0.9              | 1.4       | 1.4       | 1.4        | 1.4          |
| Coal gas flow (std L/min)   | 11.9-12.1 | 11.8-13.6 | 11.3-11.7 | 10.4-16.6 | 9.7-12.7                          | 7.5-8.4                       | 11.2-12.0        | 15.8-16.1 | 15.4-16.1 | 15.6-16.2  | 14-16        |
| COS concentration (ppm)   | 294-322   | 388-444   | 395-412   | 477-537   | 510-542                           | 180-243                       | 360-380          | 680-715   | 570-610   | 616-650    | 670-815      |
| Percent conversion to elemental sulfur (per GC)                         | 98.0-98.6 | 97.6-98.0 | 97.7      | 94-95     | 95.0-95.5                         | 97.9-98.5 <sup>d</sup>        | 94.8             | 97.8      | 97.7-98.1 | 97.5       | 96.6 (avg'd) |

<sup>a</sup>System pressure when steady-state.

<sup>b</sup>Probably false high value from SO<sub>2</sub> analyzer. Based on LSO<sub>2</sub> rotameter, the concentration was probably actually about 1.4%.

<sup>c</sup>Additional heat tape added to LSO<sub>2</sub> line for this and subsequent runs. SO<sub>2</sub> analyzer values should be more reliable.

<sup>d</sup>Calculated percent reduction of sulfur compounds in 96% based on inlet SO<sub>2</sub> concentration of 1.4%.

their effect on the DSRP reactions. Table 16 summarizes the operating conditions during all of the times that  $\text{LSO}_2$  was being fed to the reaction system. The parameters that were changed to form a series of independent variables were

- Reactor catalyst bed temperature
- System pressure
- $\text{SO}_2$  concentration in the simulated regeneration offgas.

Examining the results, the apparent dependent variables that were measured were

- Percent conversion to elemental sulfur (when the coal gas flow was optimized to minimize the  $\text{H}_2\text{S}$  and  $\text{SO}_2$  content of the offgas)
- COS concentration in the offgas.

During the operation of the various runs, it was noted that the COS concentration could not be affected by changing the coal gas flow rate. Therefore, some other variable of operation was influencing that value.

With three independent variables and two dependent variables, six combinations are possible. Figures 15 through 20 are plots of the results. In previous work, higher conversions were achieved with higher bed temperatures. In these runs, however, Figure 15 shows that the higher temperatures appeared to result in slightly lower conversions. There is a great deal of scatter in the data, though, and the range of temperatures covered is narrow. Probably no conclusion should be drawn about the effect of temperature.

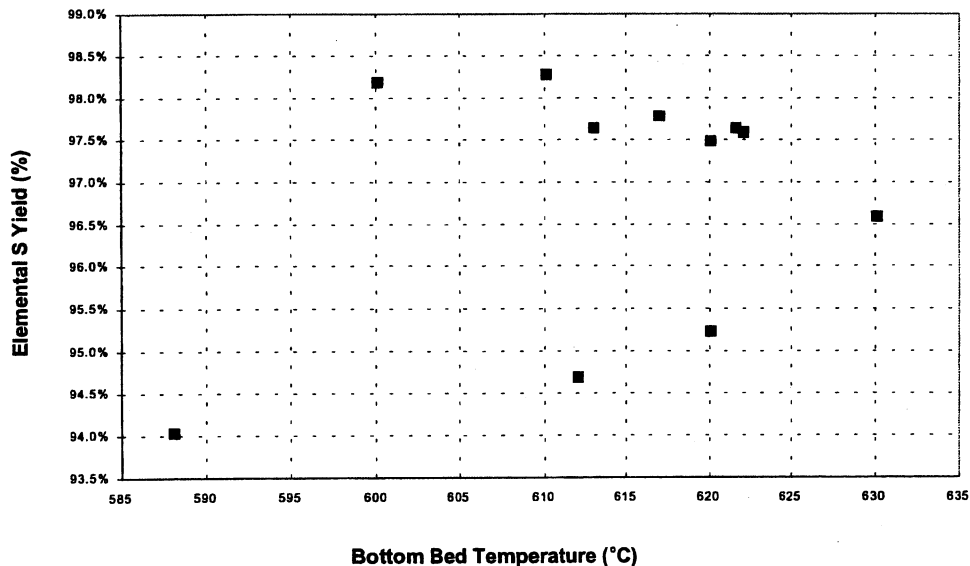


Figure 15. Effect of catalyst bed temperature on yield of elemental sulfur.

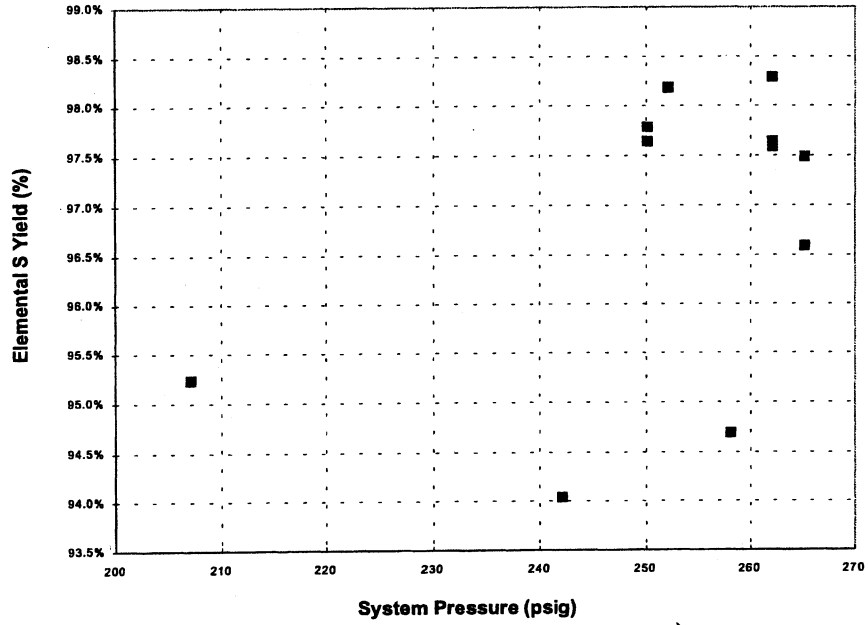


Figure 16. Effect of system pressure on yield of elemental sulfur.

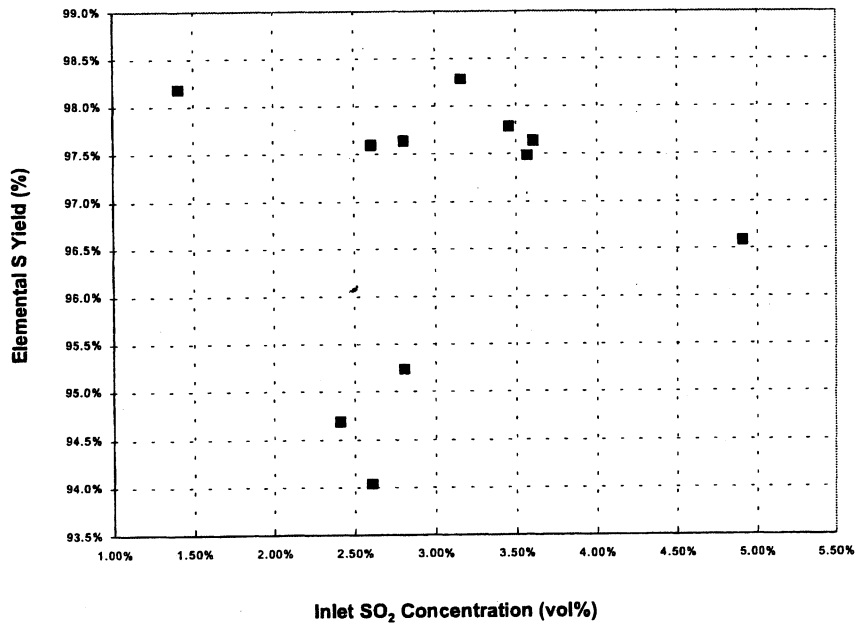


Figure 17. Effect of inlet SO<sub>2</sub> concentration on yield of elemental sulfur.

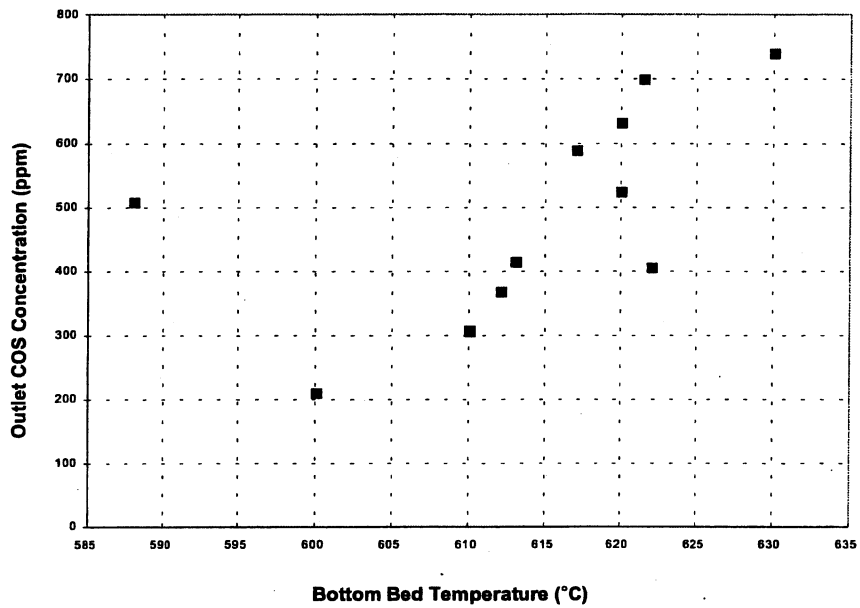


Figure 18. Effect of catalyst bed temperature on outlet COS concentration.

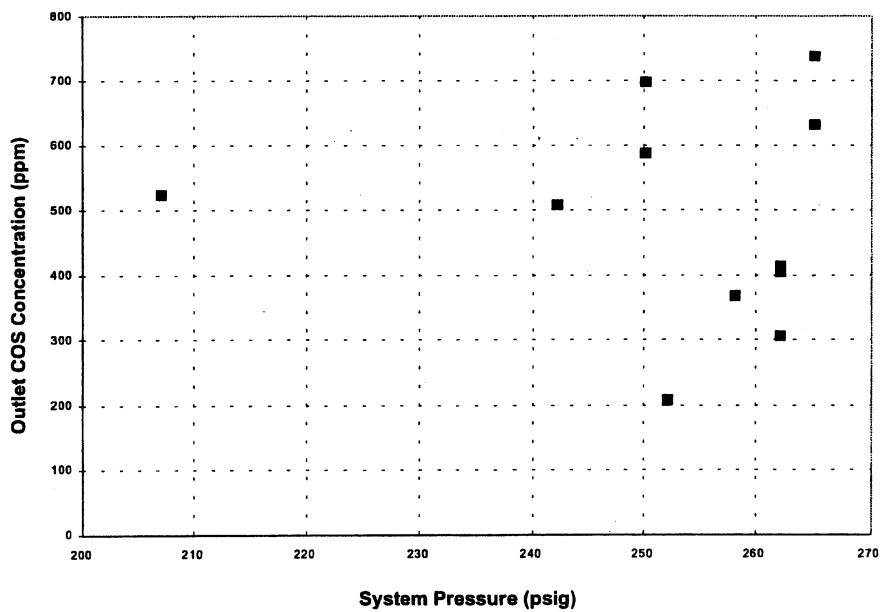
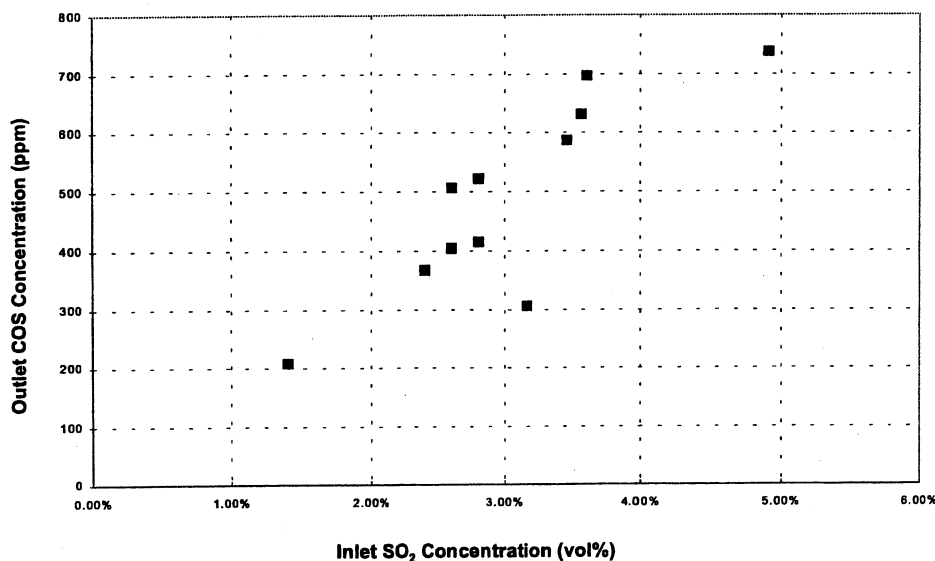


Figure 19. Effect of system pressure on outlet COS concentration.



**Figure 20. Effect of inlet SO<sub>2</sub> concentration on COS concentration.**

In previous work, higher conversions were also achieved with higher system pressure (Gangwal and Chen, 1994). Figure 16, reporting the data from the July 1995 runs, suggests that this conclusion held true. However, all but two data points were in a very narrow pressure range.

Figure 17 reports the effect of inlet SO<sub>2</sub> concentration on conversion. The data cover a good range of concentrations: from 1 to 5 percent. Most of the conversions to sulfur range from 97.5 to 98.3 percent. The three data points around 2.5 percent SO<sub>2</sub> that lie below this value were taken at lower pressures. Conversion at 5 percent inlet SO<sub>2</sub> concentration was also slightly lower, at 96.6 percent. This was the last run and during this run it was not clear if the conditions had been fully optimized.

Figure 18 reports the effect of catalyst bed temperature on COS concentration in the offgas. An apparent increase in COS formation with higher temperature is observed. However, it should be noted that reactor temperature is not entirely an isolated, independent variable. Figure 21 shows the relationship of reactor temperature to inlet SO<sub>2</sub> concentration, a variable suspected of influencing COS formation. It can be seen that the higher reactor temperatures are associated with higher SO<sub>2</sub> concentrations.

Figure 19 reports the effect of system pressure on COS concentration in the offgas. The data seem widely scattered. Thus, there does not appear to be an effect of pressure on COS concentration, at least over the narrow range of pressures studied.

Finally, Figure 20 reports the effect of inlet SO<sub>2</sub> concentration on COS concentration in the offgas. This is the clearest trend observed in this series of parametric studies, with COS increasing with increasing SO<sub>2</sub>. This trend is consistent with the understanding of the chemistry

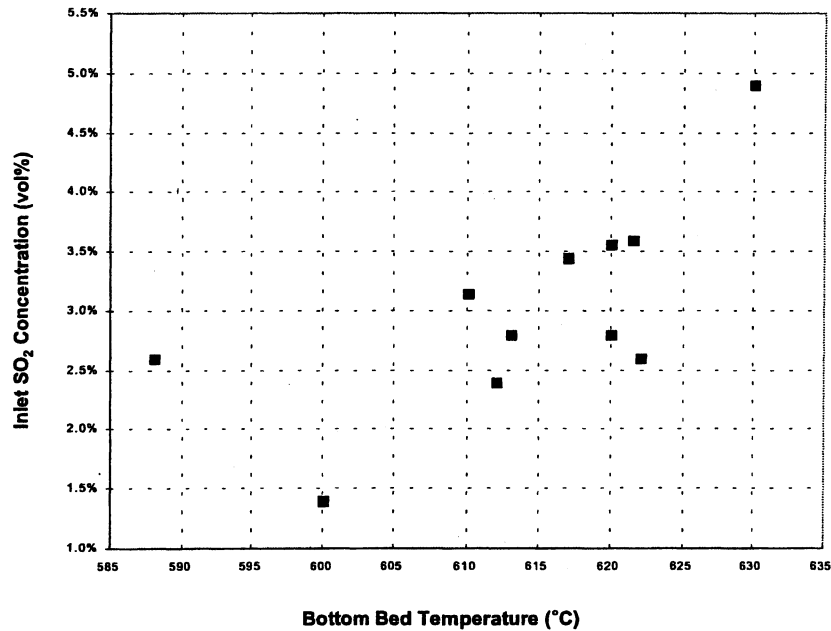


Figure 21. Relationship of inlet SO<sub>2</sub> concentration to catalyst bed temperature.

of the DSRP where COS is produced from the reaction of SO<sub>2</sub> with CO. Very little steam was present in the gas mixture inlet to the DSRP. As has been predicted previously by experimental and modeling methods, it is believed that the presence of more steam will increase the degree of the shift reaction, thereby increasing hydrogen, increasing sulfur conversion, and reducing COS formation.

A major goal of the long duration testing of the DSRP was to determine if the presence of trace contaminants (principally volatile heavy metals) affects performance over time. Table 17 reports the results of sampling of the FETC coal gas for trace metals. It is apparent that the heavy metals of concern—As, Hg, Pb and Se—are present, although at low levels, in the coal gas being fed to the DSRP. The fact that performance of the process did not seem to deteriorate with 160 h of exposure at FETC suggests that trace metals are not a factor. However, some additional analysis was undertaken to determine if the DSRP catalysts act to sequester trace contaminants.

Table 17. Trace Metal Content of FETC Coal Gas (1995 Test)

| Trace metal | Concentration (µg/L) |
|-------------|----------------------|
| As          | 0.0015               |
| Hg          | 0.0075               |
| Pb          | 0.0075               |
| Se          | 0.0015               |

Table 18 reports the results of the analysis of the DSRP catalyst. No sequestering of mercury was detected. The arsenic and selenium analyses were confounded by the background signals from the matrix of the catalyst components and only rough values were obtained. Lead was not



**Table 18. Results of Trace Metal Testing**

| Trace metal     | Concentration on catalyst (µg/g) |                      |                               |                          |
|-----------------|----------------------------------|----------------------|-------------------------------|--------------------------|
|                 | Fresh                            | After 160 h<br>@FETC | After 200 h<br>additional @GE | After testing in<br>DSRP |
| As <sup>a</sup> | <1                               | ~5                   | 10 to 100                     | 10 to 100                |
| Hg              | <0.005                           | <0.005               | <0.005                        | <0.005                   |
| Pb              | 2.5                              | 3.0                  | 167                           | 144                      |
| Se <sup>a</sup> | <0.5                             | <0.5                 | <0.5                          | <0.5                     |

<sup>a</sup>As and Se analyses are unreliable. See text.

found after exposure at FETC, but an appreciable amount was found after the General Electric (GE) exposure test described in Section 2.6.

## 2.6 CANISTER EXPOSURE TESTING IN 1996

### 2.6.1 Concept and Experimental Plan

The 160-h test of the DSRP at FETC-Morgantown was a significant undertaking, but compared to the expected duration of continuous operation in a commercial system it was a relatively short time. One technique suggested by representatives of M.W. Kellogg to obtain additional information on the effect on the catalyst of long-term operation in an actual coal gas environment would be merely to expose a canister of catalyst to actual coal gas. The exact same catalyst that was used for the FETC slipstream test could be used for a canister test and gain additional exposure time. This concept was implemented in 1996.

In early March 1996, several months following completion of the 160-h slipstream run, the DSRP catalyst was removed from the reactor, placed in a canister, and installed in a coal gas line at the GE pilot gasifier in Schenectady, New York. The canister was a simple fabrication of perforated SS with a capacity of approximately 850 mL. Thus, the entire charge of 1 L of catalyst could not be subjected to this additional exposure. The canister was placed in the piping prior to the start of a 200-h gasifier campaign and was removed following completion of the campaign. No trace contaminant sampling of the GE gasifier gas was performed. Table 19 summarizes the exposure conditions. The canister and catalyst were shipped in tightly closed bottles that had been purged with dry nitrogen prior to filling; however, the bottles were not hermetically sealed.

The idea of the canister exposure test was that the DSRP catalyst would have 200 h of additional exposure to actual coal gas (beyond what was achieved during the FETC 160-h campaign) so that the effect, if any, of the trace contaminants could be determined. In normal DSRP operation, the catalyst is exposed to a mixture of gases containing about 15 percent coal gas. Assuming that concentration and exposure time are directly related, 200 h of pure coal gas would be equivalent to 1,330 h of diluted (15 percent) coal gas.

**Table 19. GE Exposure Test Conditions**

|                                 |
|---------------------------------|
| 20 atm (294 psia)               |
| 482 to 538 °C (900 to 1,000 °F) |
| Illinois #6 coal gas            |
| 200 h                           |
| Downstream of absorber          |

The most effective way to demonstrate the continued activity of the DSRP catalyst is to install it in an HTHP reactor and actually conduct the SO<sub>2</sub> reduction reaction using a reducing gas mixture. Thus, to determine if additional coal gas exposure of the catalyst had any deleterious effects, the doubly exposed catalyst was tested in a bench-scale DSRP unit set up in a laboratory in RTI's main campus in Research Triangle Park, North Carolina. The reactor design was essentially identical to that of the trailer-mounted unit; the sulfur condenser design was identical. The coal gas was simulated by using a purchased custom gas mixture, and the simulated regeneration offgas was generated similar to the method used in the slipstream testing at FETC: vaporization of LSO<sub>2</sub> under pressure. The continuous H<sub>2</sub>S/SO<sub>2</sub> tail gas analyzer used in the mobile laboratory was moved to RTI for the duration of the bench-scale testing.

## 2.6.2 Results of Bench Unit Testing

Following 200 h of additional coal gas exposure in early 1996, the catalyst charge was tested in the RTI laboratory DSRP bench unit using simulated ROG and simulated coal gas. Table 20 summarizes the operating conditions of the DSRP reactor in the mobile laboratory (1995 slipstream test) and compares them to the conditions used for the followup testing of the exposed catalyst (1996 testing) in the RTI laboratory. The conditions are very similar, with the exception that less catalyst was available for the laboratory tests (due to a limitation of canister volume, as described). However, the gas flow rate was reduced to maintain the same space velocity

Table 21 summarizes the results from operating the DSRP bench unit with the "canister" catalyst. Several test runs were made, with a total operating time (with SO<sub>2</sub> feed) of 22 h. Known optimum conditions, as well as less-than-optimum conditions were used. The single number in the table that is most interesting is the conversion to elemental sulfur, expressed as percent of inlet sulfur dioxide. While only 86 percent conversion was obtained initially, by the end of the series the conversion was up to 96 percent. This value compares to 98 percent that was achieved using the same catalyst during the July 1995 FETC campaign.

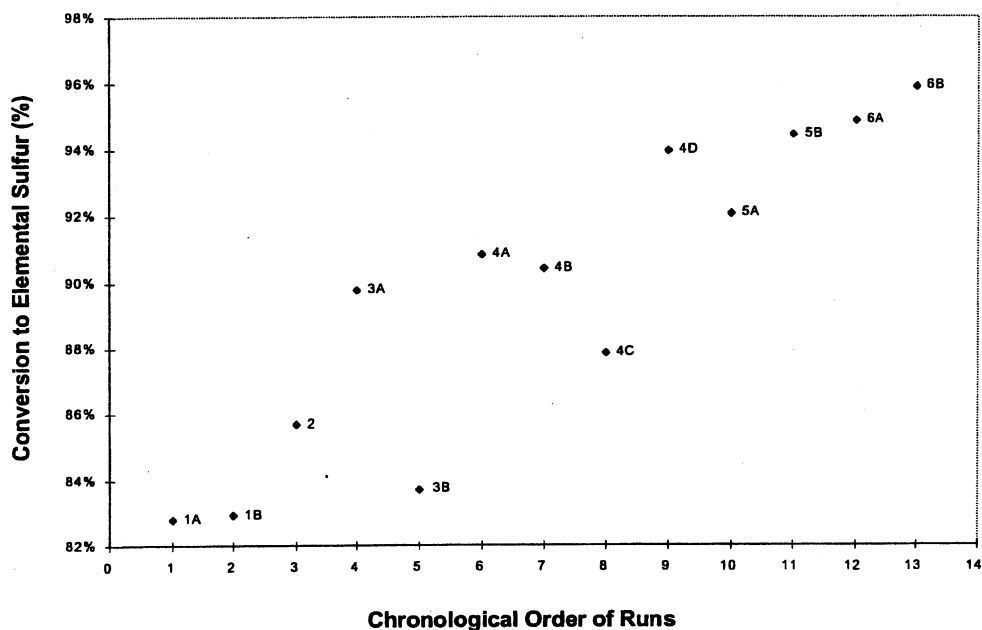
Examining the data, it is difficult to determine the effect of any of the operating variables, because of the overwhelming effect of an uncontrolled variable—operating time. Figure 22 plots the conversion to elemental sulfur from each run, in chronological order.

**Table 20. Reactor Test Conditions**

|  | 1995 Field test | 1996 Lab test |
|--|-----------------|---------------|
| Temperature (°C)   | 590–630         | 575–640       |
| Pressure (psig)  | 210–265         | 275           |
| Space velocity (std cm <sup>3</sup> /cm <sup>3</sup> ·h) | 5,100           | 2,700–8,200   |
| Reactor diameter (in.)                                   | 3.0             | 3.0           |
| Catalyst volume (cm <sup>3</sup> )                       | 1,000           | 600           |
| Inlet SO <sub>2</sub> (%)                                | 2.4–4.9         | 2.1–5.4       |

**Table 21. Results of Carbon Testing**

|                                 | Percent |
|---------------------------------|---------|
| Fresh DSRP catalyst             | 0.036   |
| After 160+ h at FETC            | 0.037   |
| After 200 additional h at GE    | 31.32   |
| After testing in RTI bench unit | 5.70    |



**Figure 22. Conversion improvement with operating time.**

Run #1 was a shakedown run conducted with an unoptimized fresh catalyst, whereas Runs #2 through #6 were carried out with the “canister” catalyst. One can see that, independent of the changes of the controlled variables, the conversion to elemental sulfur improves steadily with increasing operating time. This effect was especially noted on day 4 where the conditions were quite similar between Runs #4B and #4D, yet Run #4D had more than 3 percent greater conversion to sulfur. This improved operation was noted with no change in operating parameters.

The improvement in conversion with increased operating time suggests that some sort of “induction period,” not previously observed with the DSRP, was involved with the doubly exposed DSRP catalyst. It was planned that the coal gas would be relatively particulate-free, and to that end the canister was installed downstream of the desulfurizer at the GE pilot plant. Nevertheless, when the catalyst was received back from GE, it was covered with soot and tar (a possible experimental artifact that is also related to the specifics of the fixed-bed gasifier used at GE). It is possible that the tar has had an effect on conversion, as noted below.

The hypothesis is that the soot and tar buildup on the catalyst pellets initially inhibited the sulfur reduction reactions. With additional exposure time to the SO<sub>2</sub> reaction mixture, however, there was a gradual removal, and the catalyst regained some lost activity. The highest activity (96 percent conversion) was somewhat lower than the previous level achieved in the trailer runs (98 percent). It is possible that with more run time the activity would improve further and reach its original value.

Table 22 reports the results of carbon analysis of the DSRP catalyst. Normally, carbon is not a factor with the DSRP process, as the fresh catalyst and that used at FETC-Morgantown are both essentially carbon free. However, the catalyst exposed at GE had over 30 wt% carbon clinging to

**Table 22. Summary of "Canister Test" Results**

| Run no. | Bed temp. (°C) | Press. (atm. abs.) | Inlet space velocity (h <sup>-1</sup> ) | Inlet SO <sub>2</sub> Conc'n (vol%) | Outlet gas composition (dry) |                        |                        | Conv. to sulfur (%) |
|---------|----------------|--------------------|---|-------------------------------------|------------------------------|------------------------|------------------------|---------------------|
|         |                |                    |   |                                     | H <sub>2</sub> S (ppmv)      | SO <sub>2</sub> (ppmv) | SO <sub>2</sub> (ppmv) |                     |
| 2       | 575            | 19.7               | 4,858                                   | 2.15                                | 1,995                        | 361                    | 717                    | 85.69               |
| 3A      | 618            | 19.7               | 4,907                                   | 2.46                                | 1,528                        | 276                    | 731                    | 89.76               |
| 3B      | 610            | 19.7               | 8,187                                   | 2.24                                | 1,130                        | 1,008                  | 1,484                  | 83.72               |
| 4A      | 630            | 19.7               | 5,114                                   | 3.84                                | 1,377                        | 491                    | 1,627                  | 90.84               |
| 4B      | 632            | 19.7               | 3,963                                   | 3.71                                | 1,987                        | 457                    | 1,101                  | 90.40               |
| 4C      | 628            | 19.7               | 3,905                                   | 3.09                                | 2,272                        | 390                    | 1,033                  | 87.86               |
| 4D      | 628            | 19.7               | 3,914                                   | 3.17                                | 798                          | 385                    | 698                    | 93.95               |
| 5A      | 638            | 19.7               | 5,137                                   | 3.57                                | 538                          | 1,111                  | 1,104                  | 92.09               |
| 5B      | 633            | 19.7               | 3,983                                   | 3.49                                | 810                          | 587                    | 504                    | 94.45               |
| 6A      | 642            | 19.7               | 2,789                                   | 5.42                                | 896                          | 680                    | 1,054                  | 94.88               |
| 6B      | 630            | 19.7               | 2,692                                   | 5.39                                | 656                          | 632                    | 864                    | 95.90               |

the pellets, and even after testing in the reactor in the RTI lab it still had nearly 6 percent carbon. The carbon presence is believed to be the reason for the conversion shortfall experienced by the doubly exposed catalyst. It is interesting to note that even with 5.7 percent carbon contamination, the DSRP performance is nearly as good as that obtained with fresh catalyst.

### 2.6.3 Conclusions and Future Work

There was an apparent loss of catalyst activity after 200 h of exposure to coal gas in the GE pilot plant. The pure coal gas exposure of 200 h is equivalent to exposure at DSRP conditions of around 1,330 h. Thus, total exposure of the catalyst including the 160-h test at FETC-Morgantown is approximately 1,500 h.

The loss of activity is believed to be due to the tar and soot covering the catalyst as received from GE. However, following an induction period, a significant portion of the activity was restored. The data taken after five DSRP runs of approximately 4 h each with the canister catalyst indicate that the induction period was not complete even after nearly 22 h of tests in the bench-scale unit. The activity is likely to improve to its original value of 98 percent sulfur recovery with further run time. A surface cleaning phenomenon is apparently occurring, leading to removal of impurities and improved activity. This run demonstrates that the DSRP catalyst is quite rugged in the presence of tar laden coal gas even after 1,330 equivalent hours of exposure.

Additional canister exposure testing is warranted, to gain even more hours and increase the confidence in the ruggedness of the process for future commercialization. Ideally, this exposure testing should be with a coal gas that is lower in tar content, and more typical of what would be encountered with IGCC coal gas.

## 2.7 DESIGN AND CONSTRUCTION OF SIX-FOLD LARGER DSRP UNIT

The second phase of this slipstream test project called for the design and construction of a DSRP test unit that would have substantially higher capacity than the bench-scale unit. Early in

the design period the pilot plant operated by Enviropower, Inc. (subsidiary of Tampella Power), a DOE Cooperative Research and Development Agreement (CRADA) partner, was identified as a potential site for testing. Enviropower operates a 10-MW (thermal) U-Gas gasifier coupled to a fluidized-bed hot-gas desulfurization system at the pilot plant near Tampere, Finland. This site offered the advantage of a steady supply of actual regeneration offgas, as well as actual coal gas. Balancing the desire for a larger unit, and practical limitations on the size of a coal gas slipstream from this unit, the six-fold larger size was arrived at. Therefore, the design of the six-fold larger (6X) DSRP was initially influenced by the requirements of that particular site. Subsequently, the CRADA agreement between DOE and Enviropower was dissolved, and a non-site-specific unit was constructed, as described in more detail below.

### **2.7.1 Design Concept**

At the March 1994 Enviropower CRADA review meeting held at FETC-Morgantown, RTI presented a block flow diagram and preliminary material balance for the initial design concept for a six-fold larger DSRP. A two-stage design was proposed, consistent with the bench-scale unit that was at that point being remodeled for use in the mobile laboratory. The concept of the CRADA test program was that DOE, with RTI as the contractor, would supply the items of process equipment necessary for a 6X DSRP, and that Enviropower would assemble them in an appropriate place and test them. Enviropower personnel described the conditions at which the coal gas slipstream and actual regeneration offgas would be available to the DSRP, and also what utilities (steam, hot water, cooling water, etc.) would be available at the pilot plant.

With the specific process gas conditions in mind, RTI calculated the preliminary equipment sizes and a revised block flow diagram. Then, in June 1994, RTI met again with Enviropower personnel in conjunction with the annual contractors conference at FETC. RTI presented the preliminary equipment designs and discussed possible arrangements of the individual items in the Enviropower pilot plant. The concept remained for "loose pieces" to be supplied, although those and subsequent discussions suggested that a skid-mounted unit might be more practical. With that thought in mind, RTI also prepared a preliminary design for the skid.

In the September to October 1994 time frame RTI conducted the bench-scale slipstream tests at FETC-Morgantown described elsewhere in this report. Excellent performance of the first stage of the DSRP was observed. At a meeting with Enviropower in November of that year, it was decided, based on the FETC field test results, to develop a single-stage fixed-bed 6X DSRP reactor system rather than a two-stage system. Also, the unit would be skid-mounted. At this point the design concept was essentially finalized. Table 23 compares the key parameters of the bench-scale and the "6X" DSRP units.

### **2.7.2 Construction Chronology**

By December 1994, significant accomplishments had been made toward the goal of supplying the reactor system for slipstream testing at Enviropower. These are highlighted below:

- Preliminary schedule for system delivery was prepared.
- A meeting was planned and scheduled at the Enviropower pilot plant on January 9 and 10, 1995.
- Prior to the end of the calendar year, the following documents were delivered to Enviropower in preparation of a detailed face-to-face meeting:

**Table 23. 6X "Pilot" DSRP Unit**

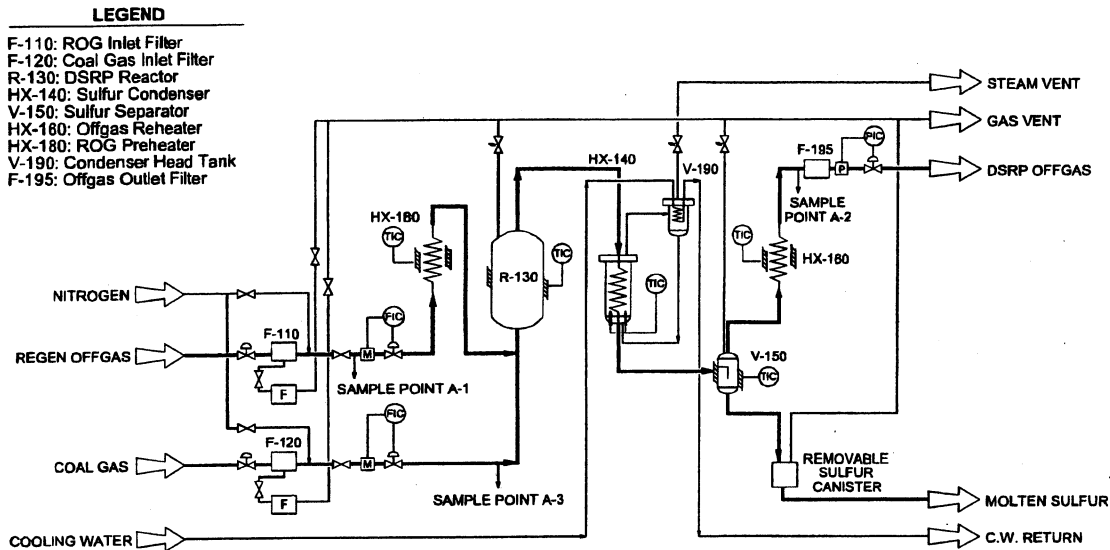
|  | <b>1X "Bench-scale"</b> | <b>6X "Pilot" unit</b> |
|--|-------------------------|------------------------|
| Flow rate (ROG + CG), stdL/min (std ft <sup>3</sup> /h)                    | 75 (170)                | 460 (1,050)            |
| Catalyst volume  | 1L                      | 6L                     |
| Space velocity (std cm <sup>3</sup> /cm <sup>3</sup> ·h)                   | 5,000                   | 5,000                  |
| Reactor I.D. (in.)   | 3.0                     | 5.76                   |
| Tubing O.D. (in.)  | 3/8                     | 3/4                    |
| Elemental sulfur production rate, based on 2% SO <sub>2</sub> in ROG (g/h) | 115                     | 690                    |

- Draft process flow diagram (PFD)
  - Process material balance
  - Draft P&IDs.
- Preliminary mechanical designs for reactors and other vessels and preliminary electrical diagrams were prepared.
  - Vendors for long lead items were contacted and preliminary quotes were obtained.

In January 1995, RTI staff visited the Enviropower pilot plant in Finland to discuss the proposed design. The team viewed the proposed location of the skid and discussed in detail interfacing the DSRP with the pilot plant process lines, utilities, and process control system. A joint decision was made during that meeting to use the site's distributed control system (DCS) as the process control computer. This represented a change from the original concept, in which the DSRP was an independent unit (analogous to the approach taken with the mobile laboratory). The special requirements for electrically heated furnaces and the special design requirements for pressure vessels were clarified. The DOE/RTI scope would include a stand-alone furnace and heat tracing control panel and a separate stand-alone analyzer panel. These would be located remotely from the DSRP process equipment skid.

A second detailed meeting with FETC and Enviropower personnel was held in March 1995 at the Tampella Power offices in Atlanta, Georgia. As a result of the two meetings, the following milestones were accomplished:

- The PFD (Figure 23) and P&ID were completed and frozen. Material balances were completed.
- Preliminary pressure vessel drawings were completed.
- Heater and analyzer control panels underwent preliminary design and a potential vendor was identified to supply the panels.
- Operating procedures were developed to enable Enviropower to successfully conduct a hazard and operability (HAZOP) analysis of the process.
- The responsibilities of DOE/RTI and Enviropower were clearly defined.



**Figure 23. Process flow diagram for 6X DSRP unit.**

- A preliminary schedule was developed for supply of the DSRP system. Delays had been experienced up to this point due to the highly stringent and detailed pressure vessel and safety requirements at Enviropower.

In late spring and summer of 1995 the detailed process design was completed, equipment specifications were finalized, and all equipment was ordered. The vessel design calculations were prepared to be consistent with the requirements of the Finnish authorities, who would review them. Throughout this period an active communication with the key Enviropower personnel in Finland took place using e-mail and fax machines.

By September 1995, the following milestones had been reached:

- The special furnace designs (to satisfy the Enviropower site safety requirements) had been approved and fabrication was under way.
- The steel skid support frame had been fabricated and painted in preparation for having the equipment mounted.
- The electrical control panel was essentially complete and was being stored temporarily at the subcontractor's facility.
- The design check and minor redesign of the pressure vessels had been completed and all parts are on hand for the final welding.
- Except for the furnaces and the pressure vessels, all other long equipment items, such as valves, filters, and orifice flow meters, had been received.

In October 1995, RTI relocated the fabrication shop facilities from an annex location to facilities on the main campus. During this time it became known that the CRADA between DOE and Enviropower had been discontinued, so the construction of the 6X facility was temporarily put on hold. In January 1996, RTI received direction from DOE that construction of the 6X should proceed, and to make that unit as "flexible" as possible to be used at any future test site. Thus, site-specific equipment that had been envisioned for the Enviropower site (e.g., special heat tracing; interfaces to the distributed control system [DCS]) was not installed.

After an unexpected delay at the vendor, the furnaces arrived at RTI in March 1996. Although these items had special construction provisions that had originally been dictated by the Enviropower site requirements, they could be used at other locations without modification. Thus, construction of the six-fold larger DSRP equipment skid began in earnest. The final versions of the first two sheets of the P&ID were issued for fabrication. The sampling and analysis PID was not issued for construction, and the analyzer control panel order was canceled due to the requirement of making the 6X unit non-site-specific.

A gantry crane and hoist assembly were installed in the RTI shop so that furnaces and heavy reactors could be lifted and positioned by one person. The final assembly and welding of the pressure vessels was started in April 1996. Throughout the remainder of FY 1996 (through August 1996) construction proceeded with these major activities:

- The furnaces were mounted on custom-fabricated brackets and frames.
- The pressure vessels were welded up and mounted in the furnaces, again with custom-fabricated brackets, as required.
- The pneumatically operated shutoff and control valves were mounted, as were the flowmeter orifice runs.
- The field instrumentation (pressure transducers, pressure gauges) along with the impulse lines was installed.
- Major runs of process tubing runs were put in place.
- All items of process equipment, automatic valves, instruments, and major hand valves that had been ordered during 1995 were installed on the equipment skid.

### **2.7.3 Status of 6X DSRP Unit**

Figures 24 through 28 are photographs of the 6X unit as it now exists. The process vessels and process tubing are essentially complete. The separate heater control panel, shown in Figure 29 at the vendor's shop, is also complete and in storage at RTI. The major remaining items to be acquired and installed for the 6X unit to be a fully functioning test unit would be the heat tracing, insulation, thermocouples, instrument air lines, and cooling water lines. Also, because the unit had been designed for interfacing with a DCS, there is no separate, stand-alone process control system.



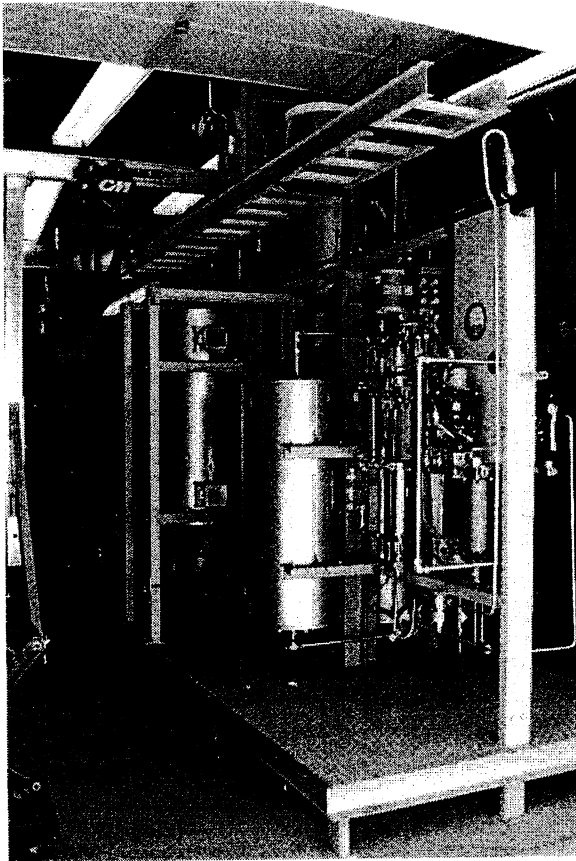


Figure 24. Skid-mounted 6X DSRP unit in fabrication shop at RTI (gas inlet end).

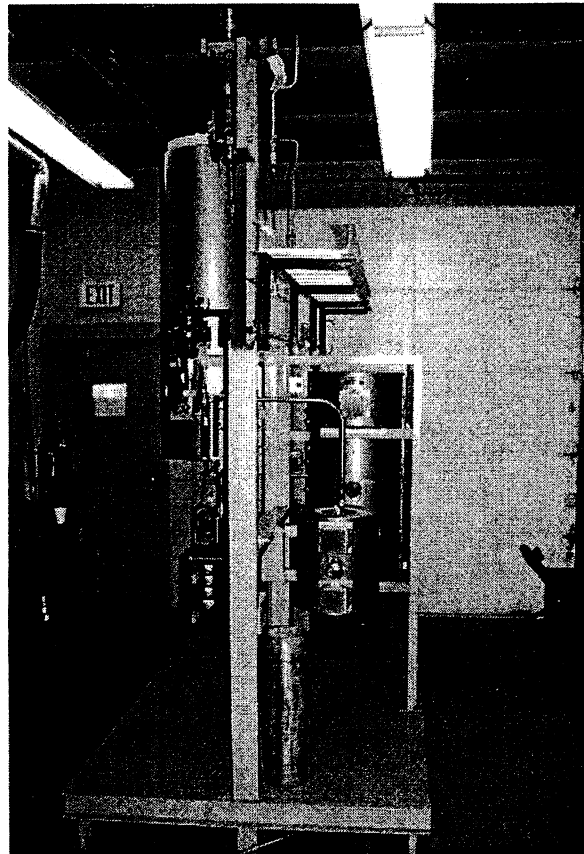
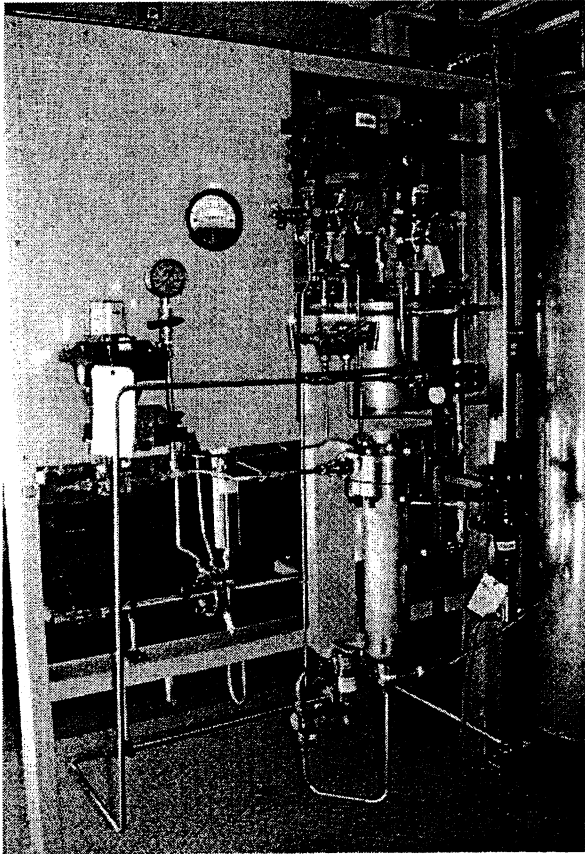


Figure 25. Gas outlet end of 6X unit.

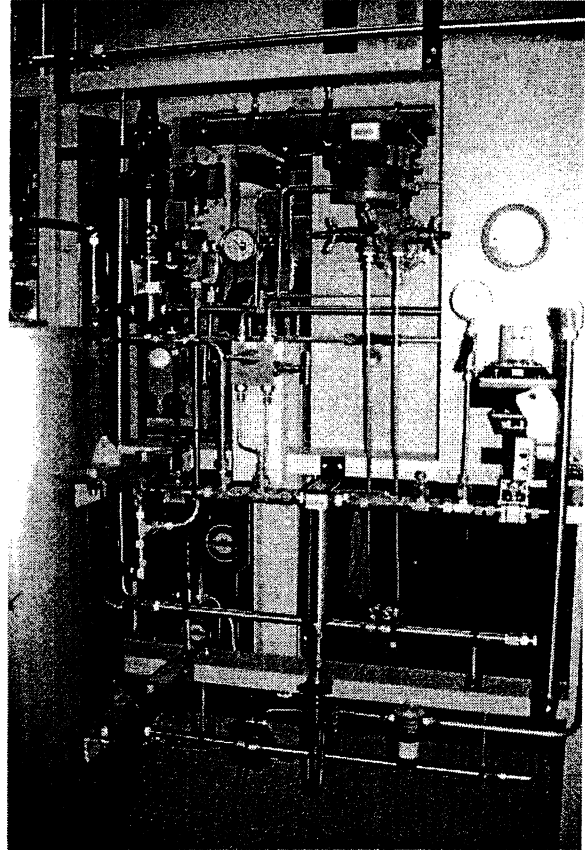
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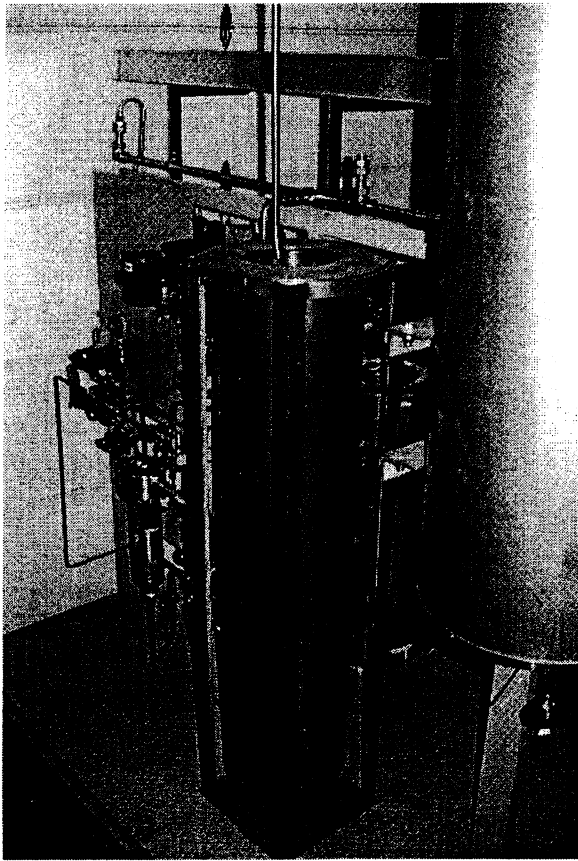
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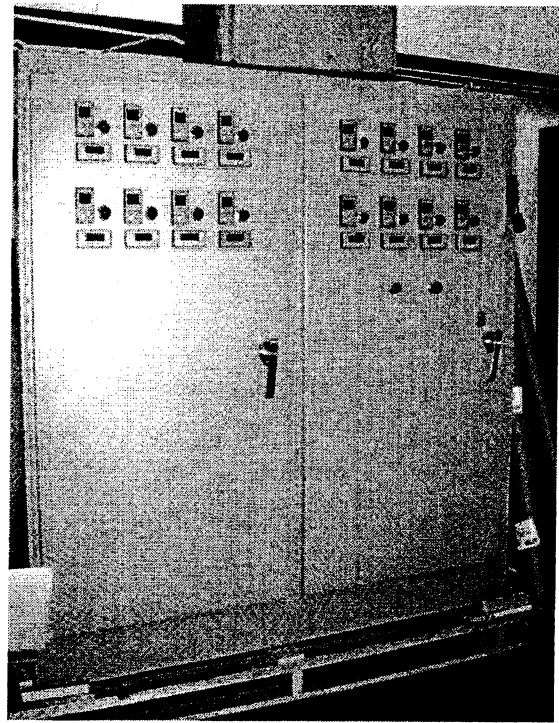
**Figure 26. Coal gas inlet flow control and filter.**



**Figure 27. Regeneration offgas inlet flow control and preheater furnace (left).**



**Figure 28. Single-stage reactor in furnace (sulfur condenser in right foreground; ROG preheater coil in rear).**



**Figure 29. Heater control panel.**

### SECTION 3 CONCLUSIONS AND FUTURE WORK

The fluidizable zinc titanate sorbent, ZT-4L, was tested in a 3-in. fluidized-bed reactor with actual coal gas and demonstrated 99+ percent removal of  $H_2S$  over three cycles, with consistent, smooth regeneration behavior. The sorbent loading capacity was up to 20 lb S/100 lb sorbent.

The integration of hot gas desulfurization/regeneration with the DSRP was demonstrated, as the bench-scale DSRP operated with actual coal gas and actual regeneration offgas. More extended operation of the DSRP was obtained using simulated regeneration offgas (by vaporizing  $LSO_2$  into nitrogen): 99+ conversion of the  $SO_2$  in the inlet gas was obtained in the first stage of the two-stage process, with 95 to 96 percent overall conversion for the two-stage system. These results suggested problems of an undesired side reaction in the second stage and led to the decision to conduct future tests with a single-stage system.

A longer duration test of the bench-scale DSRP with actual coal gas confirmed the high expected conversions using only a single reaction stage. Conversion of the total inlet sulfur compounds (both the  $SO_2$  in the regeneration gas and the  $H_2S$  in the reducing gas) to elemental sulfur was 98 percent at the beginning and at the end of 160 h of operation. Thus, there was no detrimental effect of exposure of the DSRP catalyst to actual coal gas.

Subsequent exposure of the catalyst to 200 h of a second coal gas stream showed a slight loss of activity—the best observed conversion to elemental sulfur in a laboratory bench unit (using simulated regeneration offgas and simulated coal gas) was 96 percent, compared to 98 percent previously. It was believed that the decline in conversion was caused by deposition of tars from the coal gas onto the catalyst—a unique situation caused by high-tar coal coming from an atypical fixed bed gasifier.

In expectation of additional slipstream testing, a six-fold larger, single-stage DSRP unit was designed and constructed. This unit is skid-mounted and is sized to be able to be shipped easily to a test site. Plans for testing the 6X unit with a slipstream of actual coal gas from the FETC Power Systems Development Facility (PSDF) in Wilsonville, Alabama, are under discussion. It has been proposed that the mobile laboratory constructed as part of this project be used as a control and analytical space, and that the 6X unit be positioned adjacently. The proposed test plan would include both fixed- and fluidized-bed testing of the single-stage DSRP, at varying  $SO_2$  concentrations.

The interest in the fluidized-bed DSRP, and in higher  $SO_2$  concentrations, derives from the favorable commercialization discussions that have been held with DOE and the M.W. Kellogg Company. The potential application of a scaled-up DSRP to the Sierra-Pacific Piñon Pine project has been discussed.

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