Bench-Scale Demonstration of Hot-Gas Desulfurization Technology

Topical Report

Work Performed under
Contract No.: DE-AC21-93MC30010--26

Prepared by

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Prepared for

U.S. Department of Energy
Federal Energy Technology Center
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ABSTRACT

The Direct Sulfur Recovery Process (DSRP) is a one- or two-stage catalytic reduction process for efficiently converting to elemental sulfur up to 98 percent or more of the sulfur dioxide (SO_2) contained in the regeneration offgas streams produced in advanced integrated gasification combined cycle (IGCC) power systems. The DSRP reacts the regeneration offgas with a small slipstream of coal gas to effect the desired reduction. In this project the DSRP was demonstrated with actual coal gas (as opposed to the simulated laboratory mixtures used in previous studies) in a 75-mm, 1-L size fixed-bed reactor. Integrated with this testing, a U.S. Department of Energy/Research Triangle Institute (DOE/RTI) patented zinc titanate-based fluidizable sorbent formulation was tested in a 75-mm (3-in.) diameter fluidized-bed reactor, and the regeneration offgas from that test was treated with the bench-unit DSRP. The testing was conducted at the DOE Federal Energy Technology Center (FETC)-Morgantown in conjunction with test campaigns of the pilot-scale gasifier there. The test apparatus was housed in a mobile laboratory built in a specially equipped office trailer that facilitated moving the equipment from RTI in North Carolina to the West Virginia test site. A long duration test of the DSRP using actual coal gas and simulated regeneration offgas showed no degradation in efficiency of conversion to elemental sulfur after 160 h of catalyst exposure. An additional exposure (200 h) of that same catalyst charge at the General Electric pilot gasifier showed only a small decline in performance. That problem is believed to have been caused by tar and soot deposits on the catalyst, which were caused by the high tar content of the atypical fixed-bed gasifier gas. A six-fold larger, single-stage skid-mounted DSRP apparatus was fabricated for additional, larger-scale slipstream testing.

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ACRONYMS AND ABBREVIATIONS

BPR	back-pressure regulator
COE	cost of electricity
COS	carbonyl sulfide
CRADA	Cooperative Research and Development Agreement
DCS	distributed control system
DOE	Department of Energy
DP	differential pressure
DSC	differential scanning calorimeter
DSRP	Direct Sulfur Recovery Process
EPA	U.S. Environmental Protection Agency
ES&H	Environmental Safety and Health
FCC	fluid catalytic cracking
FETC	Federal Energy Technology Center
FPD	flame photometric detector
GC	gas chromatograph
GE	General Electric
HAZOP	hazard and operability analysis
HTHP	high-temperature, high-pressure
HVAC	heating, ventilating, and air-conditioning
H ₂ S	hydrogen sulfide
IGCC	integrated gasification combined-cycle
IGT	Institute of Gas Technology
LSO ₂	liquid sulfur dioxide
MFC	mass flow controller
MGCR	modular gas cleanup rig
MS	mass spectrometer
NH ₃	ammonia
OSHA	Occupational Safety and Health Administration
P&ID	pipng and instrumentation diagram
PEL	permissible exposure level
PFD	process flow diagram
PLC	programmable logic controller
PSDF	Power Systems Development Facility
PVC	polyvinyl chloride
ROG	regeneration offgas
RTI	Research Triangle Institute
SARS	safety analysis and review system
SO ₂	sodium dioxide
SS	stainless-steel
STEL	short-term exposure level
TCD	thermal conductivity detector
TGA	thermogravimetric analysis
TiO ₂	titanium dioxide
Zn ₂ TiO ₄ or ZnTiO ₃	zinc titanate
ZnO	zinc oxide
ZTFBD	zinc titanate fluidized-bed desulfurization unit

EXECUTIVE SUMMARY

Designs for advanced integrated gasification combined cycle (IGCC) power systems call for desulfurization of coal gasifier gas at high-temperature, high-pressure (HTHP) conditions using highly efficient, regenerable metal oxides such as zinc titanate. Regeneration of the sulfided sorbent using an oxygen-containing gas stream results in a sulfur dioxide (SO_2)-containing offgas at HTHP conditions. The patented Direct Sulfur Recovery Process (DSRP) developed by the Research Triangle Institute (RTI) with Federal Energy Technology Center (FETC) support is an attractive option for treatment of this regeneration offgas. Using a slipstream of coal gas as a reducing agent, it efficiently converts the SO_2 to elemental sulfur, an essential industrial commodity that is easily stored and transported. Figure ES-1 is a schematic diagram showing a proposed commercial embodiment of DSRP.

Prior to the current contract, the development of the DSRP was done in a laboratory setting, using synthetic gas mixtures to simulate the regeneration offgas and coal gas feeds. Under this contract, the DSRP was tested using actual coal gas and actual regeneration offgas. One of the main objectives was testing the integrated system over an extended period with actual coal gas from an operating gasifier to quantify the degradative effect, if any, of the trace contaminants present in coal gas.

In order to accomplish testing with actual coal gas, RTI designed and fabricated a mobile laboratory containing a bench-scale, integrated hot-gas desulfurization/DSRP unit. The 75-mm (3-in.) fluidized-bed desulfurization reactor was used to test the U.S. Department of Energy (DOE)/RTI patented zinc titanate-based fluidizable sorbent formulation: ZT-4L, and to produce an “actual” regeneration offgas stream. The mobile lab was installed at the FETC-Morgantown site and testing was conducted with a slipstream of coal gas from the pilot-scale gasifier located there. Three separate slipstream test campaigns plus an additional exposure test took place over a period of 2 years:

Figure ES-1. Hot gas desulfurization/DSRP integration.

- September 1994 Initial shakedown test of mobile laboratory at FETC-Morgantown with integrated desulfurization reactor and two-stage DSRP
- October 1994 Test run of integrated desulfurization reactor and two-stage DSRP at FETC-Morgantown
- July 1995 Long duration run (160 h) slipstream test of single-stage DSRP at FETC-Morgantown
- March-April 1996 DSRP catalyst exposure to pure coal gas at the General Electric (GE) pilot plant in Schenectady, New York
- April-May 1996 Operation of RTI laboratory DSRP unit to test the exposed DSRP catalyst.

The 1994 slipstream testing included testing of the ZT-4L sorbent. During a run of 4 days' duration in October 1994, the ZT-4 was subjected to three sulfidations and two regenerations. The ZT-4 consistently removed H_2S from coal gas down to <20 ppmv at 873 K (1,110 °F) and 1.89 MPa (260 psig). The DSRP was very effective in converting SO_2 in actual or in synthetic regeneration offgas to elemental sulfur, achieving 95 to 99 percent conversion after the first stage of the two-stage bench unit DSRP test rig. The overall conversion of the two-stage unit was less than that achieved in the first stage alone; the undesirable "reverse Claus" reaction was believed to be the problem. The results of the initial 1994 tests were encouraging and led to the decision to refit the mobile laboratory with a single-stage DSRP unit (Figure ES-2), and with new control hardware and software to improve the stoichiometric flow control of the coal gas stream.

In the 1995 slipstream test campaign, the single-stage unit produced 98 percent conversion of SO_2 to elemental sulfur at the beginning of the run and at the end. Thus, there was no detrimental effect of 160 h of exposure of the catalyst to coal gas. The automatic coal gas flow control system, designed to maintain that coal gas at the desired stoichiometric ratio to the SO_2 in the regeneration offgas, greatly enhanced the ability to attain and maintain steady-state operation of the DSRP reaction.

In order to accelerate the exposure of the catalyst to the trace contaminants present in actual coal gas, the "used" catalyst was removed from the Mobile Laboratory at FETC-Morgantown and shipped to the GE pilot plant for placement in a coal gas line throughout a 10-day pilot plant run. This resulted in additional exposure of the catalyst to about 200 h of coal gas. The pure gas exposure of 200 h is roughly equivalent to 1,330 h of exposure at the DSRP conditions used at the Morgantown site. Thus, total exposure of the catalyst including the FETC-Morgantown testing is approximately 1,500 h. The exposed catalyst was tested in a 3-in. bench-scale reactor using synthetic mixtures of feed gases and simulated coal gas. During the laboratory testing an "induction period" was observed, as the conversion steadily improved with

Figure ES-2. New single-stage DSRP.

increasing run time. It appeared that a surface cleaning phenomenon was occurring, leading to removal of impurities and improved activity. The conversion to sulfur was 96 percent after approximately 22 h of testing, compared to 98 percent during the slipstream testing. It was hypothesized that the induction period was due to removal of tar and soot buildup on the catalyst as received from GE. Subsequent testing of the catalyst showed that the carbon content has indeed been reduced by the bench-unit test program. The overall conclusion is that the DSRP catalyst is quite rugged in the presence of tar-laden actual coal gas, even after 1,330 equivalent hours of exposure.

The second phase of this slipstream test project was the design and construction of a DSRP test unit that had six times the capacity of the bench-scale unit. Designated the 6X DSRP, this unit was initially designed for use at an industrial partner's test site, and the design was strongly influenced by the specific site requirements. Subsequent to the start of construction, the cooperative research and development agreement (CRADA) with DOE was dissolved and a non-site-specific unit was fabricated. 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 SO₂ concentrations.

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SECTION 1 INTRODUCTION AND OBJECTIVES

1.1 HOT-GAS DESULFURIZATION IN IGCC POWER SYSTEMS

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

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

The sulfidation/regeneration cycle can be carried out in fixed-, moving-, or fluidized-bed reactor configuration, and all three types of reactors are slated for demonstration in the DOE Clean Coal Technology program. The fluidized-bed reactor configuration is most attractive because of several potential advantages including faster kinetics and the ability to handle the highly exothermic regeneration to produce a regeneration offgas containing a constant concentration of SO_2 . However, a durable attrition-resistant sorbent in the 100- to 400- μm size range is needed for successful fluidized-bed operation.

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

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

RTI has also developed a durable fluidized-bed zinc titanate sorbent, ZT-4, which has shown excellent durability and reactivity over 100 cycles of testing at 750 to 780 °C. In bench-scale development tests, it consistently reduced the H₂S in simulated coal gas to <20 ppmv and demonstrated attrition resistance comparable to fluid catalytic cracking (FCC) catalysts. The sorbent is manufactured by a commercially scalable granulation technique using commercial equipment available in sizes up to 1,000 L. The raw materials used are relatively inexpensive, averaging about \$2.20/kg (\$1.00/lb). It is anticipated that the impact on cost of electricity (COE) due to sorbent replacement for attrition will be <0.5 mil/kWh. ZT-4 was tested independently by the Institute of Gas Technology (IGT) for Enviropower/Tampella Power and showed no reduction in reactivity and capacity after 10 cycles of testing at 650 °C.

1.2 THE DIRECT SULFUR RECOVERY PROCESS

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

The above reactions occur in Stage I of the process and based on previous studies (Gangwal and Chen, 1994) convert up to 96 percent of the inlet SO₂ to elemental sulfur. The sulfur is recovered by cooling the outlet gas to condense out the sulfur as another solid. Adjusting the stoichiometric ratio of coal gas to regenerator offgas to 22.0 at the inlet of the first reactor also controls the Stage I effluent stoichiometry because any H₂S and COS produced (by the reactions: $3\text{H}_2 + \text{SO}_2 \rightarrow \text{H}_2\text{S} + 2\text{H}_2\text{O}$, and $3\text{CO} + \text{SO}_2 \rightarrow \text{COS} + 2\text{CO}_2$) yield an (H₂S + COS) to SO₂ ratio of 2 to 1. The effluent stoichiometry plays an important role in the Stage II DSRP reactor (operated at 275 to 300 °C), where 80 to 90 percent of the remaining sulfur species is converted to elemental sulfur, most probably via $\text{COS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{CO}_2$ and $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow (3/n)\text{S}_n + 2\text{H}_2\text{O}$. The previously referenced work suggested that the overall sulfur recovery could be projected to be 99.5 percent.

Figure 1. Process schematic for the original two-stage DSRP design.

At the start of this project, the DSRP technology was at the bench-scale development stage with a skid-mounted system ready for field testing. The process had recently been extended to fluidized-bed operation in the Stage I reactor. Fluidized-bed operation proved to be very successful with conversions up to 94 percent at space velocities ranging from 8,000 to 15,000 $\text{std cm}^3/\text{cm}^3\cdot\text{h}$. Overall conversion in the two stages following interstage sulfur and water removal ranged up to 99 percent.

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

Through bench-scale development, it had been shown that both fluidized-bed zinc titanate and DSRP technologies are technically and economically attractive. The demonstrations prior to the start of this project, however, had only been conducted using simulated (rather than real) coal gas and simulated regeneration offgas. Thus, the effect of trace contaminants in real coal gases on the sorbent and DSRP catalyst was not known. Furthermore, the zinc titanate work had emphasized sorbent durability development rather than database development to permit design of large-scale reactors. Discussions with fluidized-bed experts prior to the start of this project indicated that data from a reactor larger than the then-current one would be required for scaleup, especially if the material does not have particle sizes similar to FCC catalysts (typically $\sim 80\ \mu\text{m}$). The fluidized-bed zinc titanate technology uses 100- to 400- μm particles. Finally, the zinc titanate desulfurization unit and DSRP had not been demonstrated in an integrated manner.

1.3 PROJECT OBJECTIVES

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

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

SECTION 2

PROJECT DESCRIPTION

The experimental aspect of this project consisted of testing fluidizable zinc titanate sorbent and the DSRP using a slipstream of actual coal gas from a working coal gasifier. There were two distinct phases:

- Design, engineering, construction, and testing of an integrated bench-scale zinc titanate fluidized-bed desulfurization unit (ZTFBD) and DSRP with a slipstream of actual coal gas
- Design and construction of a larger scale DSRP (6X) capable of handling a six-fold larger gas flow or elemental sulfur production rate.

Because RTI lacked the facilities to produce actual coal gas at its main laboratory site, the challenge of this project was to design and fabricate a portable bench-scale test apparatus that could be moved to the location of the coal gas slipstream.

2.1 DESIGN CONCEPT/FETC GASIFIER

2.1.1 Integrated Operation of ZTFBD and DSRP

In order to demonstrate the DSRP handling the offgas from regeneration of the zinc titanate sorbent, while using actual coal gas as the reducing gas, the bench-scale ZTFBD and the bench-scale DSRP had to be close together, and the control systems for the two had to be integrated. Earlier in this report, Figure 1 showed the process schematic for the two-stage DSRP. Figure 2 is a general schematic of the integrated bench-scale reactor system including the desulfurization reactor showing the main control and sampling points.

The ZTFBD/DSRP system consists of a newly constructed bench-scale skid-mounted fluidized-bed reactor system and a renovated and modified existing skid-mounted bench-scale DSRP reactor system. The bench-scale DSRP unit has been described previously (McMichael and Gangwal, 1990). It was initially configured for this project with two stages of reaction using a fixed bed of catalyst in each stage, with interstage sulfur condensation and removal. The reactor designs for both the ZTFBD and DSRP reactors are similar. A pipe cylinder, flanged at one end, is capped with a porous alumina plate to act as a gas distributor. This “Cage” holds the fluidizable sorbent or fixed-bed catalyst, as appropriate. The cages are inserted vertically into reactor shells made from 10-cm (4-in. nominal) Schedule 160 stainless-steel (SS) pipe. The sorbent and catalyst cages are made from 7.6-cm. (3-in. nominal) SS tubing. With the ZTFBD reactor utilizing a 7.6-cm (3-in.) dia sorbent cage, the size is more than a two-fold scaleup from that used for much of the previous bench-scale sorbent testing.

The ZTFBD reactor system was integrated with the existing renovated DSRP system; i.e., the regeneration offgas from the ZTFBD becomes the feed to the DSRP reactor system. Additionally, the DSRP unit can be operated independently of the ZTFBD by using simulated regeneration offgas—a mixture of nitrogen and (vaporized) liquid SO₂. In both DSRP modes of operation, the reducing gas required from the process is a slipstream of actual coal gas.

reactor, vessels F100 and V100, respectively. The particulate-free coal gas slipstream was transported through an insulated, heat-traced process line to the RTI ZTFBD/DSRP system.

2.1.4 Safety Considerations/Design Requirements

The general safety considerations for the design of the mobile laboratory were based on the determination that all general laboratory safety criteria would apply. In addition, there were specific FETC-Morgantown site requirements that had to be met relating to general laboratory design, and specifically to high-pressure, high-temperature (HTHP) processes employing toxic compounds. Thus, the design incorporated special provisions to protect the operating personnel from hazards associated with high pressure and the use of toxic gases in enclosed spaces.

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

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

The design philosophy followed was that the HTHP reactor systems would be operated semi-remotely. The equipment would be isolated in the equipment room half of the mobile lab, and operating personnel would normally stay in the control room half when the reactor systems were operating at elevated temperature and pressure. Only occasional hands-on action would be permitted (such as that action required to turn a valve or to draw liquid samples of condensate and molten sulfur). Special procedures would be followed during these occasions. Furthermore, to warn personnel that a hazardous atmosphere may be present, a toxic gas monitoring system would be installed in the mobile laboratory.

2.2 DESIGN AND CONSTRUCTION

2.2.1 Mobile Laboratory

The mobile laboratory consists of a 3.65 m (12 ft) wide × 15.24 m (50 ft) long × 2.44 m (8 ft) high (open height inside) modified office trailer. The unit was constructed with sufficient load capacity to carry the ZTFBD system equipment skid, the DSRP reactor system equipment skid, supporting equipment skid, and supporting analytical and control equipment. An artist's concept of the trailer (Figure 3) and a floor plan (Figure 4) show the equipment layout. The mobile laboratory was designed to be occupied continuously throughout any test period by rotating shifts of operators.

The trailer was partitioned into two rooms, with one room housing the reactor systems and the other acting as the control and instrumentation room. A single door provides access between the rooms. A window in the access door and another window in the partition provide visual access to the equipment from the control room. Each room has a separate personnel exit door. In addition, the equipment room was originally equipped with a roll-up door that provided access for installing the shop-fabricated, skid-mounted reactor system units. This door was subsequently blocked off with a plywood closure in which penetrations were made to pipe in the various gases, process water, and vent lines to the FETC-Morgantown stack and incinerator.

Figure 3. Artist's concept of trailer.

Figure 4. Floor plan showing equipment layout.

Shelving along one wall of the control room holds the analytical instruments, computer data acquisition system, and toxic gas alarm monitors. The analytical instruments consist of a gas chromatograph (GC) with flame photometric detector (FPD), a GC with a thermal conductivity detector (TCD), a continuous SO_2 analyzer, a continuous $\text{H}_2\text{S}/\text{SO}_2$ analyzer, and a continuous trace O_2 analyzer. On the opposite wall of the control room a counter with base cabinets provides a sink, a hot water heater, and an eyewash fountain so that simple laboratory procedures can be undertaken. Compressed gas cylinders are secured to the counters on this side of the control room. A control panel with automatic controls for the reactor systems is located on the partition wall.

Also in the control room section of the trailer is a 0.91-m (3-ft) $\times$ 0.91-m (3-ft) vented closet to house the liquid SO_2 supply system. A cylinder of liquid SO_2 was secured on the exterior of the

trailer during operation and used to fill a pressurized sample cylinder that is mounted in this closet. The sample cylinder plus some additional process equipment is used to supply a metered quantity of SO_2 ("simulated" regeneration offgas) to the DSRP system during those periods when the ZTFBD reactor is not being regenerated.

The reactor systems are located along the centerline of the equipment room section of the trailer. The ZTFBD system is built on an aluminum-framed skid that measures 1.37 m wide $\times$ 1.98 m high $\times$ 2.44 m long (4.5 ft $\times$ 6.5 ft $\times$ 8 ft). The DSRP system is built on an aluminum-framed skid that measures 1.37 m wide $\times$ 1.98 m high $\times$ 4.12 m long (4.5 ft $\times$ 6.5 ft $\times$ 13.5 ft). An electrical panel that supplies electricity to the equipment is located at one end of the DSRP skid. Power is supplied from the main trailer panel, also located in the equipment room.

City water, sewer, and electrical supply are piped through the floor of the trailer. All other FETC-Morgantown-provided lines (coal gas, high-pressure nitrogen, process water supply and return, and instrument air) are piped through a special section of the trailer wall built where the roll-up door was located (currently covered with plywood). The two process vent lines—one to the incinerator and the other to the stack—are also piped through the trailer wall where the roll-up door was located.

High-pressure air for the process is supplied from compressed gas cylinders. The cylinders are housed in a temporary storage cabinet adjacent to the trailer where the roll-up door was originally located. A pressure regulator lowers the pressure of the air from cylinder pressure of 13.75 to 2.5 MPa (2,000 to ~350 psi) for supply to the process which operates at 2.2 MPa (300 psig).

Separate heating, ventilating, and air-conditioning (HVAC) systems were provided for each of the two rooms in the trailer/mobile laboratory. One unit, with 14 kW (4 tons) of air conditioning capacity, serves the control and instrumentation room. It introduces 3.8 Nm^3/h (135 std ft^3/min) of outside air, which is enough to change the air in the control room four times per hour.

Two units, each with 17.6 kW (5 tons) of air-conditioning capacity, serve the reactor equipment room. Each unit introduces 3.4 Nm^3/h (120 std ft^3/min) of outside air, which is enough to change the air in the equipment room six times per hour. The air-conditioning capacity is based on the requirement to remove the "skin" heat load from summer weather conditions as well as remove the excess heat from the reactor system furnaces and heat tracing.

Two additional vent header systems, independent of the HVAC, were provided to minimize operator exposure to toxic and combustible gases by removing process and purge gases from the reactor systems and from the control and equipment rooms. One system, consisting of 7.5-cm (3-in.) and 10-cm (4-in.) (Schedule 40) polyvinyl chloride (PVC) pipe and a powered exhaust blower, discharges to the incinerator stack adjacent to the entrained and fluidized-bed cells situated behind FETC-Morgantown Building B-12. It receives the low-pressure gas vents from the GCs, the continuous analyzers, the vent in the liquid SO_2 closet, and gases from flexible, relocatable ducts ("elephant trunks") on the DSRP unit. This vent header operates under a slightly negative pressure. Makeup air comes from the HVAC systems that supply outside air to the two rooms.

The second system, consisting of 19-mm (3/4-in.) O.D. SS tubing discharges to the inlet of the incinerator adjacent to the entrained and fluidized-bed cells located behind Building B-12. This vent header receives the combustible gas vents from the ZTFBD and DSRP reactor systems. It operates under a small positive pressure in order to force flow to the incinerator. It is a sealed, "hard-piped" header; there is no makeup air requirement.

2.2.2 Process Equipment/Reactor Systems

A schematic of the integrated reactor system showing the main control and sampling points was shown earlier in Figure 2 in Section 2.1.1. Detailed piping and instrumentation diagrams (P&IDs) were developed for construction and permitting purposes. The slipstream of filtered hot coal gas from the FETC-Morgantown gasifier/MGCR (at 500 °C [932 °F] and in excess of 2.2 MPa [300 psig]) passes through ceramic filter F-101, mounted on the ZTFBD skid, for removal of any remaining particulate matter. The flow is then split into two lines, one feeding the ZTFBD desulfurization reactor, and a second, smaller flow feeding the DSRP Stage I reactor. Coal gas flow to the desulfurization reactor was controlled by a pneumatically operated HTHP control valve receiving a feedback signal from a downstream mass flow meter. The coal gas flow to the DSRP reactor was controlled by a pneumatic HTHP control valve that was intended to receive a feedback signal from downstream analyzers and a ratio controller with the objective of controlling the ratio of H₂S concentration to SO₂ concentration in the final DSRP effluent. This control scheme was not operational during the 1994 test campaign, and only manual control of the coal gas flow to the DSRP was used. A revised, stoichiometric coal gas flow control system was installed prior to 1995 testing.

The ZTFBD desulfurization reactor has two operating modes—sulfidation and regeneration. In the sorbent sulfidation half cycle (from 1-1/2- to 3-h long, depending on the age of the sorbent), coal gas will flow through the sorbent bed with the objective of fully sulfiding the sorbent bed. The desulfurized coal gas is cooled in a water-cooled coil to condense the steam and passes through a Drierite moisture trap and then through two stages of back-pressure regulation. The flow rate is measured continuously by an inline mass flow meter (and occasionally by a dry gas meter), and the desulfurized coal gas vents from the process through the vent header going to the FETC-Morgantown incinerator. The desulfurized coal gas will normally have very low levels of H₂S. In a commercial embodiment of this process, the operation would be controlled to maintain a low H₂S level by continuously circulating the sorbent between the sulfider and the regenerator. However, in this experimental bench-scale unit, the H₂S levels will be allowed to rise at the end of the sulfidation cycle in order to more fully sulfide the sorbent. Sulfidation will be continued up to a 500-ppm H₂S level in the desulfurized coal gas.

In the sorbent regeneration half cycle (approximately 2-h long) the sulfided sorbent is regenerated using a preheated mixture of nitrogen and air typically containing 1 to 3 percent oxygen. The flow rates of both gases are controlled by mass flow controllers (MFCs) in a feed forward control scheme. The oxygen content of the regeneration gas is controlled by the operator (by regulating the airflow), while monitoring the reactor temperature of the exothermic regeneration reaction. The H₂S adsorbed on the sorbent bed is oxidized to SO₂; the regeneration half cycle is complete when the SO₂ concentration in the offgas declines. The hot regeneration offgas, containing about 2 percent SO₂, is directed to the DSRP unit, as described below.

The DSRP reactor system has two operating modes, although the chemical reactions in both modes are the same. It can be operated in an integrated mode using the actual regeneration offgas from the ZTFBD unit, or it can be operated independently with a simulated regeneration offgas. When operating integrally with ZTFBD, the hot regeneration offgas is directed, without cooling, to the DSRP Stage I reactor. There it mixes with the hot coal gas stream and passes up through a fixed bed of catalyst. The Stage I effluent passes through a steam/hot water-heated condenser to remove elemental sulfur from the gas stream. The process gas is reheated in a furnace and passed through a second stage of sulfur condensation. The process gas then enters the bottom of the Stage II reactor and goes on to the third sulfur condenser. The outlet gas from the third condenser is cooled in a water-cooled condenser to remove steam, passes through a

Drierite moisture trap and then through two stages of back-pressure regulation, and is discharged from the system through the vent header to the FETC-Morgantown incinerator.

The molten sulfur collects in internal pots in the sulfur condensers; it is manually withdrawn periodically. Similarly, the steam condensate is collected and withdrawn manually.

Using simulated regeneration offgas, the operation of the DSRP unit is essentially the same, with the addition of operation of the equipment to generate the simulated offgas. The bulk of the simulated regeneration offgas is nitrogen that is passed through a packed pressure vessel heated by an electric furnace. Liquid SO_2 (LSO_2) from a pressurized reservoir is pressure-transferred into the preheated nitrogen stream through a rotameter, with a manual flow control needle valve. The LSO_2 reservoir is refilled occasionally from a supply cylinder during those periods of operation when the simulated regeneration offgas system is not in use. By operating alternately with a feed of actual regeneration offgas and of simulated regeneration offgas, the DSRP unit can be operated almost continuously, even though the ZTFBD is cycling between sulfidation and regeneration.

2.2.3 Process Control Scheme

This section describes the process control strategy that is independent of the remote operator control and automatic shutdown systems described in Section 2.2.4. In both reactor systems, the pressure is maintained by a pair of self-regulating back-pressure regulators (BPRs). The coal gas is supplied hot and at high pressure from the FETC-Morgantown gasifier. The flow to the ZTFBD unit during the sulfidation half cycle is regulated by a lab-scale pneumatically operated flow control valve operating at HTHP conditions. The flow rate measurement is made using a mass flow meter on the desulfurized coal gas prior to venting to the incinerator. A feed-back signal from the mass flow meter is used to adjust the control valve and maintain the flow at a desired set point. The mass flow meter operates at ambient temperature.

In the regeneration mode, the ZTFBD requires a hot nitrogen stream containing 2 percent oxygen as a feed gas. This is accomplished by blending air from compressed gas cylinders with high-pressure nitrogen supplied by FETC-Morgantown. MFCs are used to meter the flows; the composition is checked with a GC in order to verify the meter calibration. The blended gas is heated in a preheater vessel (filled with SS balls for improved heat transfer) mounted in a split tube furnace.

When the ZTFBD and DSRP are operating in the integrated mode, the DSRP is receiving actual regeneration gas (100 percent of the ZTFBD gas flow) as the feed gas. In this mode, the pressure of both systems is controlled by the BPRs on the DSRP unit. The flow through the system is controlled by the MFCs supplying the regeneration nitrogen/air mixture.

When the DSRP is operating independently of the ZTFBD, using simulated regeneration offgas, only the pressure of the DSRP is controlled by the DSRP BPRs. The flow through the DSRP is controlled by the MFC supplying nitrogen to the simulated regeneration offgas system. In this system, the nitrogen that makes up the bulk of the regeneration offgas (the " SO_2 carrier" nitrogen) is preheated and a small quantity of liquid SO_2 is mixed with it prior to the first stage reactor. The LSO_2 is pressure-transferred from a reservoir equipped with a dip tube by using a metered quantity of nitrogen flowing into the head space (the "motive" nitrogen). This arrangement was devised in order to eliminate the operating problems associated with using low boiling point

liquids in small-scale metering pumps in the laboratory. Periodic analysis of the nitrogen-SO₂ mixture using a GC will enable recalibration of flow controllers for the SO₂ carrier nitrogen and the SO₂ motive nitrogen.

An innovative scheme was conceptualized for controlling the flow of coal gas to the DSRP (for use as the reducing gas). As with the ZTFBD, the flow is adjusted by a lab-scale control valve operating at HTHP conditions. The valve position was to be set by a flow ratio controller receiving feedback signals from a continuous analysis of the composition of the exit gas. The goal was to maintain the ratio of H₂S to SO₂ at 2:1 at the exit of the DSRP reactor system. Increasing the flow of reducing gas will tend to increase the conversion of SO₂ to elemental sulfur and H₂S, thus raising the H₂S:SO₂ ratio. Similarly, decreasing the flow of reducing gas will decrease the conversion, lowering the H₂S:SO₂ ratio. The ratio controller was intended to adjust the flow of coal gas, in response to changing operation, so that composition ratio is maintained at the set point. In practice, the stand-alone, panel-mounted controller was not capable of performing the necessary calculations for this application. A more elaborate computer-based system was installed, as described below, for the 1995 field test.

In order to operate the reducing gas flow control scheme, continuous analysis of the DSRP exit gas was required. Separate analyzers were installed in the control room to measure the H₂S and SO₂ concentrations in the DSRP exit gas. A small sample stream was bled continuously off the process in order to feed these instruments. Their electrical output signals go to the flow controller.

To monitor the progress of the zinc titanate sorbent regeneration, continuous SO₂ and oxygen analyzers were installed. When the regeneration half cycle is complete, the oxygen concentration in the offgas will increase fairly rapidly and the SO₂ concentration will decrease. Because the off-gas feeds directly to the DSRP unit, it is undesirable to have oxygen in the offgas mixing with hot coal gas in Stage I. The oxygen analyzer provides the necessary safety precautions through the interlock system.

To provide a more detailed understanding of the process operation, additional gas analyses are done by GC. One objective is a complete sulfur balance around the system, so that the conversion efficiency can be tracked at optimum conditions for designated periods.

A GC with a TCD is set up to analyze for the “fixed” gases—H₂, CO, CO₂, N₂, CH₄—and for high levels of H₂S in the coal gas (raw or desulfurized). It is also set up to analyze the regeneration gas (dilute oxygen in nitrogen) and the DSRP inlet gas (either real or simulated regeneration offgases) that has percent levels of SO₂.

Another GC with a TCD is set up to measure the concentration (at high levels) of the sulfur gases—H₂S, COS, SO₂—in the outlet gases from the DSRP Stage I reactor. This analysis was to measure the Stage I conversion to sulfur. The second GC was also equipped with an FPD. That half of the machine is set up to sample and analyze H₂S and COS at low levels. The ZTFBD desulfurized coal gas during the sulfidation half cycle was analyzed at 6-min intervals in order to determine the sorbent breakthrough point.

As the test runs in this project use actual coal gas, it is expected that trace contaminants would be present. A scheme was incorporated in the design of the process equipment and the layout of the mobile laboratory to permit sampling of the process streams for heavy metals, fluoride, chlorides, and ammonia (NH₃). There are several sampling points located throughout the process to identify the input levels and potentially to identify any sequestering or removal of the trace

compounds by the sorbent, the catalyst, or the filters. The heavy metal compounds—As, Be, Cd, Co, Hg, Se, Sb, V, Zn—are analyzed using a modification of U.S. Environmental Protection Agency (EPA) Reference Method 29. The chloride and fluoride species are analyzed from 0.1 N NaOH solution through which the sample has been passed. NH_3 is captured in a 1.0 N H_2SO_4 solution.

2.2.4 Safety Equipment/Automatic Shutdown/Control Panel

A toxic gas monitoring system was installed in the mobile laboratory to warn personnel that a hazardous atmosphere may exist. There are duplicate gas monitors for H_2S and SO_2 in the equipment room, CO monitors in both the equipment room and the control room, and an SO_2 monitor in the liquid SO_2 closet. The monitors send a signal continuously to the toxic gas alarm panels. The two set points in the panel controller for each monitor correspond to the Occupational Safety and Health Administration (OSHA) 8-h permissible exposure level (PEL) for a warning alarm, and to the 15-min short-term exposure limit (STEL) value for an evacuation alarm. If the STEL value is exceeded and the alarm sounds, the operators will evacuate the trailer, shutting down the system using the emergency stop buttons, as described below.

To conduct the routine operations of the ZTFBD/DSRP reactor systems remotely, the process units were equipped with 15 pneumatically operated control and shutoff valves. The coal gas feed line from the Morgantown site was also controlled by two pneumatically operated shutoff valves on the outside of the trailer and interlocked with the RTI control system. The pneumatic valves could be operated with operator intervention from the control panel, or they could be placed in automatic mode where their operation was controlled by a programmable logic controller (PLC). The PLC will shut down part or all of the reactor system process units in response to inputs from the process pressure sensors, oxygen analyzers, and flow meters. In addition, the operators can activate one of the three emergency stop (E-stop) buttons, located at each of the two trailer exit doors and on the control panel, to shut down the process. The automatic shutdown procedure includes purging of process gases from the system by passing high-pressure nitrogen through the equipment.

The pneumatic valves were specified and ordered to be spring-operated into a “fail-safe” condition of normally open or normally closed. Thus, with a loss of air pressure or a loss of power to the PLC, the valves will automatically open or close, as appropriate, to ensure safety.

The furnaces that heat the reactor vessels have their own controllers that are independent of the process PLC. Sensing of a high-temperature limit in any zone will result in shutdown of the furnace which would be indicated on the control panel in the control room with a warning light.

For safe control of the slipstream of combustible coal gas, there is the additional administrative requirement for voice communication with the gasifier/MGCR control room. When it is determined by telephone or voice intercom with the FETC-Morgantown gasifier/MGCR operator that coal gas is available, then RTI operating personnel will remotely open the coal gas shutoff valve. This valve is interlocked with another valve that directs the coal gas through a pressure-reduction orifice and on to the incinerator. The concept is that if the RTI control panel causes the coal gas flow to be shut off, then the unneeded gas continues to flow, directed to the orifice run and from there to the incinerator. Thus, the gasifier at the Morgantown site does not experience an upset due to a sudden change in the downstream conditions. These valves are mounted on the outside of the trailer and away from the HVAC fresh air intake louvers. Thus, if a leak develops, toxic, combustible gases will not be discharged into the personnel space inside the trailer.

Communication to the FETC-Morgantown gasifier/MGCR control room from RTI is by intercom. The MGCR control room notifies the RTI operators in the trailer when startup may occur. Whenever there is an upset condition in the operation of the gasifier, the operators notify the RTI personnel in the trailer using the intercom, and, similarly, whenever an upset condition has forced the closure of the coal gas supply valve, the RTI operators notify the gasifier/MGCR control room. Also, if the RTI trailer had to be evacuated, the intercom would be used to notify the MGCR control room if emergency action is required.

As described above, the control panel that interfaces with the air-operated shutoff valves contains a PLC to provide automatic shutdown features. Table 2 presents the safety interlock strategy used to program the PLC.

The automatic shutdown logic associated with the coal gas supply is as follows:

1. When the differential pressure across the coal gas filter drops below a set point, it indicates that the coal gas flow has dropped off (due to a loss of coal gas from the gasifier at the Morgantown site, a failure of the HTHP coal gas flow control valve, or because the system pressure is too high). High differential pressure indicates that the filter element has become plugged. In either case, the PLC will cause the coal gas supply valve [YV-16] to close and the coal gas flow to be routed to the incinerator [YV-17] without entering the interior of the mobile laboratory.
2. If the system pressure decreases to below a set point, it suggests that there is a large leak in the system. In this case, the PLC will cause the coal gas supply valve system [YV-16 and YV-17] to close, and the liquid SO₂ feed line shutoff valve [YV-9] to close, thereby isolating the process equipment from toxic gases.

There are two possible shutdown scenarios associated with the use of nitrogen-diluted air as the regeneration gas:

1. To prevent the oxygen concentration from rising in the event that the diluent nitrogen supply fails, the air supply will be isolated [YV-1] if low nitrogen flow is detected.
2. Similarly, if the oxygen concentration, as measured by an online analyzer, in the regeneration gas rises above a set point (1,000 ppm), the air supply will be isolated.

To prevent the possibility of accidentally feeding air and combustible coal gas to the ZT reactor at the same time, there are features in the PLC logic:

1. The shutoff valves on the air supply [YV-1] and the coal gas [YV-5] are interlocked so that only one can be open at a time.
2. The coal gas shutoff valve [YV-5] is interlocked to stay closed at any time there is a measurable airflow in the regeneration gas system.

Finally, to limit the potential concentration of SO₂ in the simulated regeneration gas, the liquid SO₂ delivery system will be isolated [YV-9] in the event that the carrier nitrogen flow declines below a set point.

Table 2. Safety Interlock Strategy

Situation	Interlock
System pressure exceeds inlet coal gas pressure	D/P gauge digital indicator will show low alarm (indicating probable loss of flow); PLC sends signal to close coal gas valve YV-16. YV-17 will open automatically to discharge coal gas slipstream to the incinerator.
Any furnace temperature exceeds high-high-limit set temperature	High-high-limit switch in the furnace controller panel shuts off the furnace and illuminates red light on control panel indicating which furnace is off.
Oxygen concentration exceeds 1,000 ppm in regeneration offgas during sorbent regeneration	Oxygen content digital indicator will show high alarm; PLC sends signal to close air valve YV-1.
YV-5 is open (coal gas flowing to desulfurizer)	YV-1 (air valve) will be closed and cannot be opened until YV-5 is closed. (Both valves are fail-closed type.)
N₂ flow in regeneration gas lower than preset value	Digital indicator shows low flow; PLC sends signal to close air valve YV-1.
N₂ flow in liquid SO₂ delivery system lower than present value	Digital indicator shows low flow; PLC sends signal to close liquid SO ₂ valve YV-9.
Airflow in regeneration gas higher than preset value.	Digital indicator shows high flow; PLC locks out coal gas valve YV-5 in closed position.
System pressure drops below a prescribed value indicating a leak	Digital pressure indicator shows low alarm; PLC closes coal gas valve YV-16 and liquid SO ₂ valve YV-9.
CO, H₂S, or SO₂ monitors detect concentration above the level I set value	Appropriate alarm sounds to allow corrective action to be taken.
CO, H₂S, or SO₂ monitors detect concentration above the level II set value	Operators leave trailer, activating one of the emergency stop (E-stop) buttons inside the trailer. This action closes valves YV-1, YV-2, YV-4, YV-5, YV-8, YV-9, YV-10, and YV-16, thus cutting off air and coal gas supply but opens valves YV-3 and YV-7 to ensure N ₂ flow into the system, and opens YV-11, YV-12, YV-13, YV-14, YV-15, and YV-17 to dump system contents into the incinerator. Signal is sent to FETC-Morgantown MGCRC control room indicating E-stop condition.
Any other panic situation, e.g., fire or smoke alarm	Same as above.
Power failure	Same as above.

If the power fails, or the instrument air supply fails, or if one of the E-stop buttons is activated, the entire process will shut down. All shutoff valves will go to their fail state (shown in Table 3), and the following scenario will unfold:

- The slipstream of coal gas will be routed to the incinerator through a flow restricting orifice, rather than enter the mobile laboratory [YV-16 and YV-17].
- The nitrogen flows for the regeneration gas and the simulated offgas will be cut off [YV-2 and YV-8].
- The liquid SO₂ feed to the process will be cut off [YV-9].
- The air supply to the regeneration cycle will be cut off [YV-1].
- Both the ZTFBD and DSRP reactor systems will be isolated from the coal gas supply lines [YV-4 and YV-5], and the two systems will be isolated from each other [YV-10].
- The process pressure will be relieved by dumping the gas in the system to the incinerator vent header [YV-11, YV-12, YV-13, YV-14, and YV-15].

Table 3. Mechanical Fail State of Pneumatic Valves

Valve	Control panel switch label	Control panel label	Fail position
YV-1	V-1	Regen Air	Closed
YV-2	V-2	Regen N ₂	Closed
YV-3	V-3	Safety N ₂ to FBD	Open
YV-4	V-4	Coal gas to DSRP	Closed
YV-5	V-5	Coal gas to FBD	Closed
YV-7	V-7	Safety N ₂ to DSRP	Open
YV-8	V-8	N ₂ to DSRP	Closed
YV-9	V-9	Liquid SO ₂	Closed
YV-10	V-10	Regen Offgas	Closed
YV-11	V-11	FBD dump	Open
YV-12	V-12	FBD dump	Open
YV-13	V-13	De-S coal gas	Open
YV-14	V-14	DSRP dump	Open
YV-15	V-15	DSRP dump	Open
YV-16	HCV-C	Coal gas supply	Closed
YV-17	None	Coal gas dump	Open
FCV-1	FIC-101	Coal gas flow to FBD	Closed
FCV-2	AFC-201	Coal gas flow to DSRP	Closed

- In order to purge toxic and combustible gases from the process, nitrogen will be introduced into both reactor systems, bypassing any metering valves (YV-3 and YV-7) and will purge through the equipment, exiting through the dump valves into the incinerator header.

Table 3 shows the mechanical fail state (loss of instrument air, loss of electrical power) of the pneumatic valves used on the process equipment.

The electric furnaces used to heat the reactor and preheater vessels have independent control systems which are equipped with high level temperature switches that cut power to all zones if the set point is exceeded.

2.2.5 Construction Chronology

The project began in July 1993, with discussions of the proposed sites and the specific project and safety requirements of the site that was ultimately selected—FETC-Morgantown. By December 1993 the design had been finalized and formal application for safety review was made. With the design approved, a customized office trailer was ordered in January 1994.

The fabrication of the ZTFBD skid began in December 1993 and continued through March 1994, along with the remodeling of the existing DSRP skid. The custom trailer was received in April 1994 and temporarily installed at RTI. The two equipment skids were loaded inside by contract riggers, as shown in Figure 5.

With the skids in place, the outfitting of the mobile laboratory began in earnest. This activity continued through the summer of 1994.

Figure 5. Equipment skids being loaded inside.

All equipment had been installed and checked out by early August. The smaller items were disassembled and stowed in the mobile laboratory. The temporary electrical power was disconnected and the trailer left the RTI site bound for FETC in Morgantown, West Virginia on August 14, 1994. Figure 6 shows the truck leaving RTI with the trailer.

2.3 FIELD TESTING IN 1994

The conduct of the slipstream tests undertaken in the ZTFBD/DSRP mobile laboratory was coordinated with the test campaigns of the FETC-Morgantown 10-in. gasifier. A short (5-day duration) campaign was run in September, during which shakedown trials were conducted in the mobile lab. A longer (10-day duration) campaign was conducted in October during which a long duration run was made in the mobile lab.

2.3.1 Shakedown Testing/Trial Run of ZTFBD/DSRP Mobile Laboratory

Construction and preliminary checkout of the mobile laboratory unit (trailer) at RTI were completed in August 1994. The trailer weighed about 16 tons with the equipment in place. It was transported to the Morgantown site and parked in place August 15-17, 1994. A commercial crane company, assisted by FETC personnel, lifted the trailer into place near the FETC-Morgantown fluidized-bed gasifier (B-12) location. Once the trailer was in position, intense activity by FETC personnel followed to hook up the utilities (cooling water, city water, sewer, electricity, incinerator vent line, stack vent line) and the heated coal gas delivery line to the trailer. The photograph (Figure 7) shows the mobile laboratory in position at the Morgantown site.

Figure 6. Truck leaving RTI with trailer.

Figure 7. Trailer in position at FETC-Morgantown.

Preparations were made for shakedown testing of the RTI trailer in mid-September. Parallel to these preparations, the final application for the operating plan along with final design drawings was submitted. Pressure testing of the reactors at operating temperature and 1.5 times the operating pressures was conducted on site.

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

After obtaining an operating permit, the shakedown testing was ready to begin during the week of September 12, 1994. Five hundred grams (g) of sorbent was loaded in the ZTFBD reactor. One thousand cubic centimeters (cm^3) of catalyst was loaded in the Stage I DSRP reactor and 1,500 cm^3 in Stage III DSRP reactor. Nitrogen flow was established through the coal gas line and the reactors at the desired set point. Heaters and furnaces were turned on and adjusted to obtain the desired temperature in each reactor and BPRs were used to control the reactor pressures.

Two cycles, each consisting of a sulfidation and a regeneration/integrated DSRP operation, were conducted during the shakedown test. Problems were experienced in the testing due to plugging of the coal gas control valves for both sulfidation and DSRP reactors. It was discovered later that entrained sorbent particles escaped the Morgantown site MGCR and made their way to the RTI

system through the 3/8-in. coal gas line. The ceramic filter in the RTI trailer did not perform as well as expected and allowed some of these particles to get into the valves. The problem was likely caused by different thermal expansion coefficients of the alumina ceramic filter and the SS housing.

The shakedown testing was successful in that promising results were demonstrated with the sorbent and DSRP even though the integrated regeneration-DSRP operation was carried out with erratic system pressure and coal gas flow. The objective of the testing was met because problems that would be corrected prior to the formal 160-h test were identified. The main problem identified, of course, was the plugging of the coal gas control valves.

Test conditions and the main results of the two cycles of shakedown testing are shown in Tables 4 to 7 and Figures 8 to 10. Table 4 shows the conditions and results of the first sulfidation on September 13, 1994. The following points should be noted:

- Flow was erratic due to plugged control valve, and system pressure had to be reduced down to 1.2 MPa (165 psig) to maintain adequate flow (3 Nm³/h [50 std L/min]).

Table 4. Conditions and Results of First Sulfidation

Sulfidation #1 (09/13/94; 10:23–18:15)						
Reactor ID: 3.0 in.			Pressure: 165–210 psig			
Sorbent loading: ZT-4L, 500 g			Temperature 600–620 °C			
Pressure drop: 24 in. H ₂ O			Flow: 50–70 std L/min			
Inlet gas (vol%) (dry basis)						
Time	12:55 ^a	13:40	14:03	15:45	16:05	16:06
CH ₄	3.99	2.00	2.85	NA ^b	2.90	NA
H ₂ S	0.11	0.14	0.07	0.14	0.10	0.09
H ₂	17.64	15.6	17.37	NA	NA	NA
CO ₂	13.20	14.7	10.87	NA	12.00	NA
CO	10.18	9.4	10.96	NA	10.1	NA
N ₂	56.60	53.5	57.7	NA	59.0	NA
Outlet gas (vol%) (dry basis)						
Time	10:23	11:10	11:40	12:10	12:40	13:10
CH ₄	2.60	2.66	2.77	2.74	2.78	2.75
H ₂ S (ppm)	<25	<25	<25	<25	<25	<25
H ₂	16.33	17.28	17.10	18.12	18.10	17.03
CO ₂	12.80	13.36	13.20	13.05	13.03	13.12
CO	10.92	11.25	10.80	10.67	10.72	10.84
N ₂	56.46	54.76	55.72	56.30	55.54	55.53

Sulfur loading at 370 ppm H₂S = 9.7 lb S/100 lb sorbent in outlet gas.

Average vol% H₂O in gas = 11.5.

^aFETC online mass spectrometry (MS) analysis.

^bNA = Not available.

Table 5. Results of First Integrated Regeneration/DSRP Operation

Regeneration DSRP #1 (9/14/94; 15:04-15:44)			
Regeneration offgas flow = 68 std L/min		DSRP coal gas flow = erratic	
Regeneration temperature = 730 °C		O ₂ in offgas = 60 ppmv	
System pressure = 255 psig		Run terminated at O ₂ breakthrough of 500 ppmv	
SO ₂ in offgas = 13,000 ppmv (fairly stable)			
Run time (min)	Percent SO ₂ conversion	Percent SO ₂ ^a conversion to H ₂ S	Percent SO ₂ conversion to sulfur (by difference)
10	>99	2.8	97.2
14	>99	4.2	95.8
18	>99	6.2	93.8
Coal-gas valve is stuck			
22	83	0.6	82.4
26	50	0	50
30	27	0	27
34	14	0	14
38	10	0	10
42	8	0	8

^aNo COS detected.

- FETC online mass spectrometry analysis of inlet coal gas agreed with RTI's analysis except for methane.
- Inlet H₂S was quite low due to a low-S coal.

The sulfidation H₂S breakthrough is shown in Figure 8. During this cycle, water got into the sample line of RTI's sensitive GC for H₂S (Varian GC-FPD). Thus, analysis was carried out using a less sensitive TCD whose lower H₂S detection limit was 70 ppmv. The inlet H₂S ranged from about 1,000 to 1,400 ppm and the sulfidation was terminated at a breakthrough of about 400 ppm with a loading of about 10 g S/100 g sorbent (10 lb S/100 lb sorbent).

Table 5 shows the results of the first integrated regeneration/DSRP operation. High apparent sulfur conversion efficiencies were achieved initially, but then the coal gas flow control valve plugged. The regeneration of the sorbent went smoothly with no evidence of sulfate formation at 730 °C. Table 6 and Figure 9 show the results for the second sulfidation. The sulfidation inlet H₂S data, shown in Figure 9, demonstrate the high sulfur variability of the coal used by FETC. The H₂S breakthrough curve is also shown in Figure 9. Initially, nearly all the H₂S is removed even with high inlet H₂S. However, breakthrough to 200 ppm comes quickly (in just 100 min). A second breakthrough curve is seen due to the peaks and valleys in the inlet H₂S. Sulfur loading of 21 g S/100 g sorbent (21 lb S/100 lb) sorbent was achieved at 1,000 ppm H₂S in the outlet. This is close to the theoretical sorbent capacity.

Table 7 and Figure 10 show the results of the second regeneration/integrated DSRP operation. The SO₂ elution profile shows a quick rise and stabilization of the SO₂ level at the expected level

Table 6. Results of Second Sulfidation

Sulfidation #2 (9/14/94: 17:09–22:26)						
Pressure: 160 psig; flow: 51 std L/min; temperature: 625 °C						
Inlet gas (vol%) (dry basis)^a						
Time	17:42	18:00	18:32	19:00	20:00	21:30
CH ₄	3.20	3.27	2.81	3.20	3.20	3.30
H ₂ S	0.385	0.334	0.757	0.434	0.58	0.488
H ₂	16.69	16.51	16.51	16.81	17.06	16.71
CO ₂	12.63	12.61	13.24	12.79	12.96	12.96
CO	10.19	9.63	8.85	9.42	9.20	8.99
N ₂	58.57	59.23	59.43	59.11	58.79	59.23
Inlet gas (vol%) (dry basis)^b				Outlet gas (vol%) (dry basis)		
Time	18:38	17:58	19:19	20:17	21:16	21:55
CH ₄	1.92	2.15	2.18	2.30	2.28	2.31
H ₂ S	0.60	NA ^c	NA	NA	NA	0.11
H ₂	15.51	15.82	16.27	16.96	16.17	16.51
CO ₂	12.88	12.88	12.77	12.95	12.85	12.85
CO	9.76	10.44	10.67	10.37	10.34	10.324
N ₂	57.53	56.85	56.25	56.00	56.39	56.13

Sulfur loading at breakthrough = ~21 lb/100 lb sorbent (1,000 ppm H₂S in outlet).

Average percent H₂O in gas = 11.0.

^aFETC MS.

^bRTI Carle GC-TCD.

^cNA = Not available.

of about 11,000 ppm. The sulfur conversions, however, were erratic due to the problem of coal gas flow control.

The shakedown test results indicated the need for

- Better filtration
- Better coal gas flow control
- Stabilization of DSRP operation first using a simulated SO₂-actual coal gas in the appropriate ratio.

These ideas were implemented in the formal test conducted in October.

Table 7. Results of Second Regeneration/Integrated DSRP Operation

Regeneration DSRP #2 (9/15/94; 9:46-11:04)			
Regeneration offgas flow = 68 std L/min		O ₂ in regeneration gas = 1.85% (vol)	
Regeneration temperature = 725 °C		DSRP coal gas flow = erratic	
System pressure = 245 psig		O ₂ in offgas = ~60 ppmv	
SO ₂ in offgas = 12,000 ppmv (steady)		Run terminated at O ₂ breakthrough of 600 ppmv	
Run time (min)	Percent SO ₂ conversion	Percent SO ₂ conversion to H ₂ S	Percent SO ₂ conversion to sulfur (by difference)
20	87	0	87
24	46	0	46
28	33	0	33
32	69	0.3	68.7
36	99.7	19.3	78.4
40	99.6	85	14.6
44	100	100	0
48	100	100	0
52	100	43	57
56	100	25	75
60	100	12	88
64	100	4.1	95.9
68	85	0	85
72	56	0	56
76	68	0	68

2.3.2 Long-Duration Run Overview

This section summarizes the highlights and accomplishments of the October 1994 slipstream test run of the ZTFBD/DSRP mobile laboratory at FETC-Morgantown. The excellent cooperation and assistance by FETC personnel to RTI field staff contributed significantly to the success of the test. Although the run had to be shortened due to mechanical problems with gasifier at FETC-Morgantown, there was sufficient onstream time to demonstrate highly successful operation of both ZTFBD and DSRP with actual coal gas. Also, the multimetals, NH₃, and HCl/HF impinger trains were successfully used during the run to determine the level of trace contaminants. No significant effect of the contaminants was detected on either the ZTFBD or DSRP over the 70 h of the run.

The process equipment in the ZTFBD unit worked smoothly in both the sulfidation and regeneration modes. The fluidizable zinc titanate formulation ZT-4L demonstrated 99+ percent removal of hydrogen sulfide (H₂S) from actual coal gas over three cycles, and up to 20 g S/100 g sorbent (20 lb S/100 lb sorbent) loading capacity. It also demonstrated consistent, smooth regeneration behavior. For the most part the DSRP unit also ran smoothly with actual coal gas. As planned, to obtain extended operation of the DSRP, provisions were made to produce simulated regeneration offgas using LSO₂. This equipment worked very well. During periods of steady-state operation, the DSRP had concentrations of sulfur compounds in the exit gas corresponding to up

Figure 8. Sorbent sulfidation curves (9/13/94).

Figure 9. Sorbent sulfidation curves (9/14/94).

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 H₂S 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 H₂S 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 SO₂ analyzer from A-4 to A-5A (which is more suitable when DSRP is run using LSO₂). 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 LSO₂ flowing and adjusted controller by comparing with Western SO₂ analyzer.
18:43 Started coal gas flowing into DSRP for start of **DSRP/LSO₂ 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/LSO₂ 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 H₂S breakthrough of >3,000 ppm H₂S (total time: 13 h). Set up trace contaminant sampling trains.
- 16:10 Coal gas flow to DSRP started for **DSRP/LSO₂ 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 LSO₂ flowing for **DSRP/LSO₂ 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/LSO₂ Run 3. Determined that cold end train #2 had plugged. Worked to clear plugging from cold end.
- 23:19 Started LSO₂ and coal gas flowing for **DSRP/LSO₂ 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/LSO₂ 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 LSO₂ 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 SO₂. 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 H₂S 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 ₂ Run #2	1:30
Wednesday	17:00	Sulfidation Run #2	7:00	DSRP/LSO ₂ Run #3	3:40
Thursday	12:00	Regeneration Run #2	1:15	DSRP/LSO ₂ Run #4	6:00
Friday	10:00	DSRP/LSO ₂ Run #1	6:00	Total	39.5
Total	70:20				

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

Under these conditions, an H₂S breakthrough curve during Cycle 3 is shown in Figure 11. The sorbent exhibited excellent removal efficiency and capacity even with highly variable inlet H₂S values. Sorbent regeneration, which went very smoothly, is shown in Figure 12. Note that with 2.25 percent O₂ in the inlet, nearly two-thirds, i.e. ~1.5 percent SO₂ 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.

Table 9. FETC Gasifier Coal Gas Composition (vol%)

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

Table 10. ZT-4 Reactor Conditions^a

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

^a3.0-in. Reactor; 600 g sorbent loaded.

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) (N₂ + SO₂)-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 SO₂-DSRP tests were highly successful. One of the simulated SO₂-DSRP tests was not successful due to plugging of the coal gas line from 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 H₂S is seen in later runs, although even in these tests a 96 percent sulfur conversion level is achieved.

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 ² /g)	3.2	7.56
Pore volume (cm ³ /g)	0.234	0.11
Pore diameter (Å)	2,500	1,800
Particle size (µm)	112	95
Air-jet attrition (%)		
5-h loss	16	1.4
20-h loss	36	6.2
Compacted density (lb/ft ³)	91.6	107
Zn/Ti	1.35 ± 0.05	1.42 ± 0.05
TGA capacity (g/100 g)	21.0	20.5
As (µg/g)	NM ^a	<10
Se (µg/g)	NM	15
Cl (µg/g)	NM	38

^aNM = Not measured.

Table 12. DSRP Stage I Reactor Conditions

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:

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

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 MGCR 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).

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 O₂ 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 H₂S and metal vapor addition are needed to ascertain this. The estimated gaseous concentrations based on the measurements are about 100 µg/m³ for As and 10 to 40 µg/m³ 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 AsH₃ or H₂Se) 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 ₂ conversion (%)	SO ₂ conversion to H ₂ S (%)	SO ₂ conversion to sulfur (%)
Run No. 1			
32	99.4	0.0	99.4
36	99.4	0.0	99.4
40	99.5	0.0	99.5
44	99.7	0.0	99.7
48	99.5	0.0	99.5
52	98.5	0.0	98.5
56	98.0	0.0	98.0
Run No. 3			
117	99.6	1.2	98.4
121	100.0	4.1	95.9
125	100.0	4.9	95.1
129	100.0	2.4	97.6
Run No. 4			
175	100.0	4.9	95.1
179	100.0	4.1	95.9
183	100.0	4.9	95.1
199	100.0	4.7	95.3

Table 14. DSRP Stage I Catalyst

	Fresh	Used
Size (in.)	1/8	1/8
Crush strength (lb _f /mm)	2.0	2.5
Surface area (m ² /g)	208	158
Exposure (h)	0	Coal gas (20); 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 (µg/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 ^a
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

^aNA = 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 NH_3 decomposition at 850 °C and 1.1 MPa (150 psia).

The ZTFBD system was modified for the 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 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 SO_2 with actual coal gas.
- Temperature/pressure corrected orifice flow meter for coal gas
- Process control computer to input 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 H_2 , 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 μm).
  - 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 Nm³/h (70 std L/min) of synthetic regeneration offgas with 1.4 to 4.9 percent SO₂
  - 0.45 Nm³/h to 0.96 Nm³/h (7.5 to 16 std L/min) of actual coal gas
  - Space velocity of 5,100 std cm³/cm³·h.
- ZTFBD unit operated at
  - 1.1 MPa (150 psig)
  - 780 °C
  - 4.1 Nm³/h (68 std L/min) of actual coal gas
  - Space velocity of 5,000 std cm³/cm³·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 (LSO₂ flowing; producing molten sulfur) for nine periods during run, totaling 44 h.
- NH₃ 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 NH₃ decomposition ranged from 85 to 95 percent (depending on analytical technique).
- No effect of exposure time on NH₃ 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 LSO₂). 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 LSO₂ 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 LSO₂ 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 LSO₂ 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. LSO₂ 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 SO₂ analyzer appeared to be at odds with the reading on the LSO₂ rotameter. A brief experiment in which the automatic valve on the LSO₂ 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 LSO₂ 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 LSO₂ 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 SO₂ 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 SO₂ 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 LSO₂ 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 CO₂. 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 SO₂ 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 SO₂ 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 LSO₂ 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.
- LSO₂ 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® 3.1 was not rugged enough for continuous operation; “General Protection Faults” and other Windows®-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® 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 SO₂ inlet concentration.
- The SO₂ 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 SO₂ in the mixture of nitrogen and vaporized LSO₂ was measured by a continuous SO₂ analyzer, so that the molar flow rate of SO₂ 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:

$$(\text{H}_2\text{S})_{\text{Ametek}} = [\text{H}_2\text{S}] + [\text{COS}]/2 .$$

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 ₂ on		4.0	6.40	3.82	6.57	5.30	4.70	2.90	5.0	4.75		
Cum. time @ end of run		4.0	10.57	15.68	22.35	28.92	52.64	76.40	112.1	153.5	154.1	155.6
RXTR Temp. (°C)	Top TE-204	602	601-603	613	576	609	596	601	607	605	606	605
	Middle TE-203	610	611-613	621	584	616	605	611	616	614	615	616
	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 (212-202) ^a	260-250 (252) ^a	258	250	250	265	265
SO ₂ concentration in simulated regenerated offgas (ROG) (%)		3.1-3.2	2.8	2.5-2.7	2.5-2.7	2.8	4.0 ^b	2.4 ^c	3.6	3.4-3.5	3.56	4.9
LSO ₂ rotameter reading (cm ³ /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 ^d	94.8	97.8	97.7-98.1	97.5	96.6 (avg'd)

^aSystem pressure when steady-state.

^bProbably false high value from SO₂ analyzer. Based on LSO₂ rotameter, the concentration was probably actually about 1.4%.

^cAdditional heat tape added to LSO₂ line for this and subsequent runs. SO₂ analyzer values should be more reliable.

^dCalculated percent reduction of sulfur compounds in 96% based on inlet SO₂ concentration of 1.4%.

their effect on the DSRP reactions. Table 16 summarizes the operating conditions during all of the times that 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
- 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 H_2S and 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 SO₂ 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 SO₂ 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 SO₂ 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 SO₂ that lie below this value were taken at lower pressures. Conversion at 5 percent inlet SO₂ 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 SO₂ concentration, a variable suspected of influencing COS formation. It can be seen that the higher reactor temperatures are associated with higher SO₂ 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 SO₂ concentration on COS concentration in the offgas. This is the clearest trend observed in this series of parametric studies, with COS increasing with increasing SO₂. This trend is consistent with the understanding of the chemistry

Figure 21. Relationship of inlet SO₂ concentration to catalyst bed temperature.

of the DSRP where COS is produced from the reaction of SO₂ 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 @FETC	After 200 h additional @GE	After testing in DSRP
As ^a	<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 ^a	<0.5	<0.5	<0.5	<0.5

^aAs 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 SO₂ 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 LSO₂ under pressure. The continuous H₂S/SO₂ 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 SO₂ 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 ³ /cm ³ ·h)	5,100	2,700–8,200
Reactor diameter (in.)	3.0	3.0
Catalyst volume (cm ³)	1,000	600
Inlet SO ₂ (%)	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_2 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 ⁻¹)	Inlet SO ₂ Conc'n (vol%)	Outlet gas composition (dry)			Conv. to sulfur (%)
					H ₂ S (ppmv)	SO ₂ (ppmv)	SO ₂ (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

	1X “Bench-scale”	6X “Pilot” unit
Flow rate (ROG + CG), stdL/min (std ft ³ /h)	75 (170)	460 (1,050)
Catalyst volume	1L	6L
Space velocity (std cm ³ /cm ³ ·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 ₂ 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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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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