Appendix A

Bench-Scale Demonstration of Hot-Gas Desulfurization Technology: Topical Report

RESEARCH TRIANGLE INSTITUTE

Bench-Scale Demonstration of Hot-Gas Desulfurization Technology

Topical Report

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

Prepared by

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Prepared for

U.S. Department of Energy
Federal Energy Technology Center
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Morgantown, WV 26507-0880

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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_2S	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	piping 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_2TiO_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:

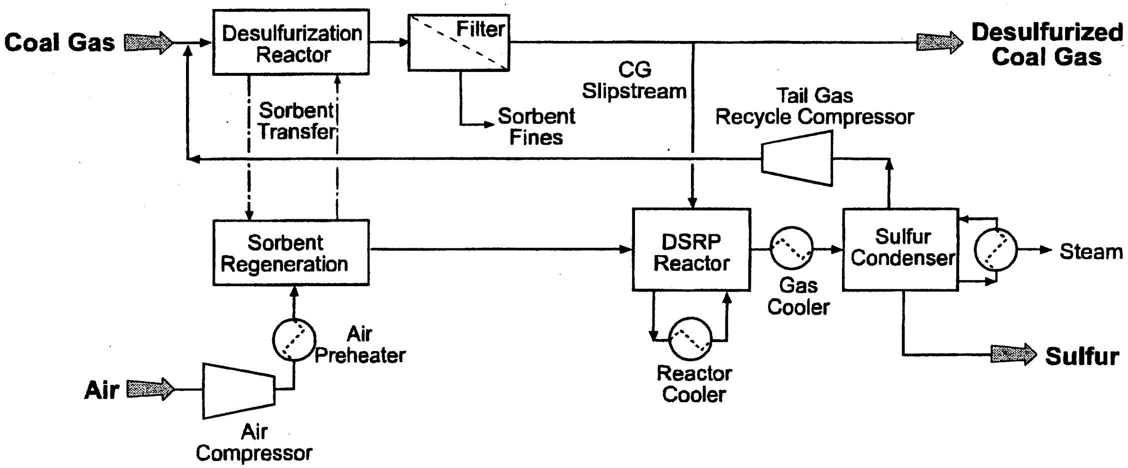

Figure ES-1. Hot gas desulfurization/DSRP integration.

• 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

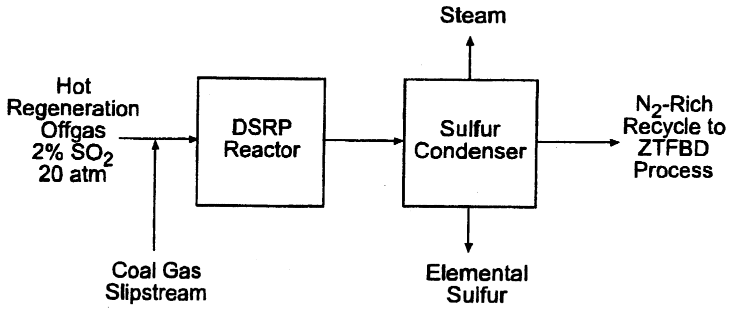

Figure ES-2. New single-stage DSRP.

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 SO_2 concentrations.

ACKNOWLEDGMENTS

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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:

$$Zn_2TiO_4 + 2H_2S \rightarrow 2ZnS + TiO_2 + 2H_2O \qquad \text{Sulfidation}$$

$$2ZnS + TiO_2 + 3O_2 \rightarrow Zn_2TiO_4 + 2SO_2 . \qquad \text{Regeneration}$$

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 H_2S 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) SO_2 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 SO_2) reacts in the presence of a selective catalyst to produce elemental sulfur directly:

$$\begin{aligned} 2H_2 + SO_2 &\rightarrow (1/n)S_n + 2H_2O \\ 2CO + SO_2 &\rightarrow (1/n)S_n + 2CO_2 \\ CO + H_2O &\rightarrow CO_2 + H_2 . \end{aligned}$$

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 SO_2 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 H_2S and COS produced (by the reactions: $3H_2 + SO_2 \rightarrow H_2S + 2H_2O$, and $3CO + SO_2 \rightarrow COS + 2CO_2$) yield an ($H_2S$ + COS) to SO_2 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 $COS + H_2O \rightarrow H_2S + CO_2$ and $2H_2S + SO_2 \rightarrow (3/n)Sn + 2H_2O$. The previously referenced work suggested that the overall sulfur recovery could be projected to be 99.5 percent.

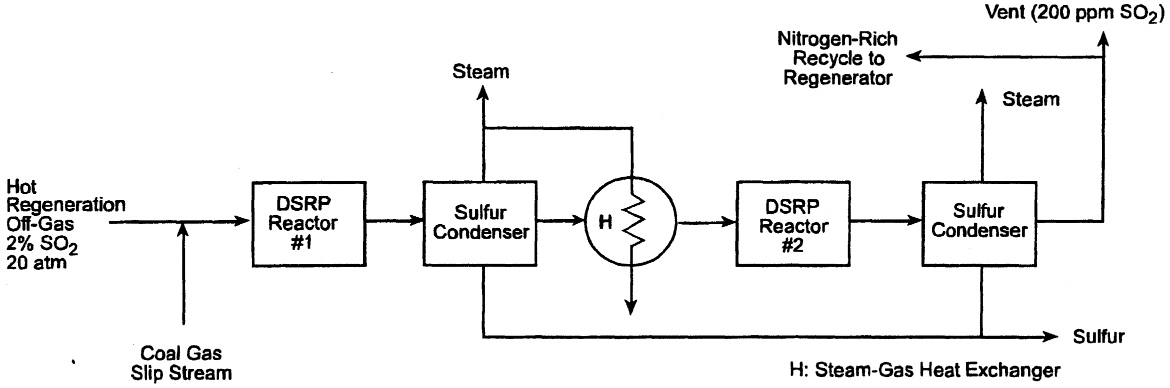

Figure 1. Process schematic for the original two-stage DSRP design.

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 std $cm^3/cm^3 \cdot h$. 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 ~80 µm). 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 SO_2. In both DSRP modes of operation, the reducing gas required from the process is a slipstream of actual coal gas.

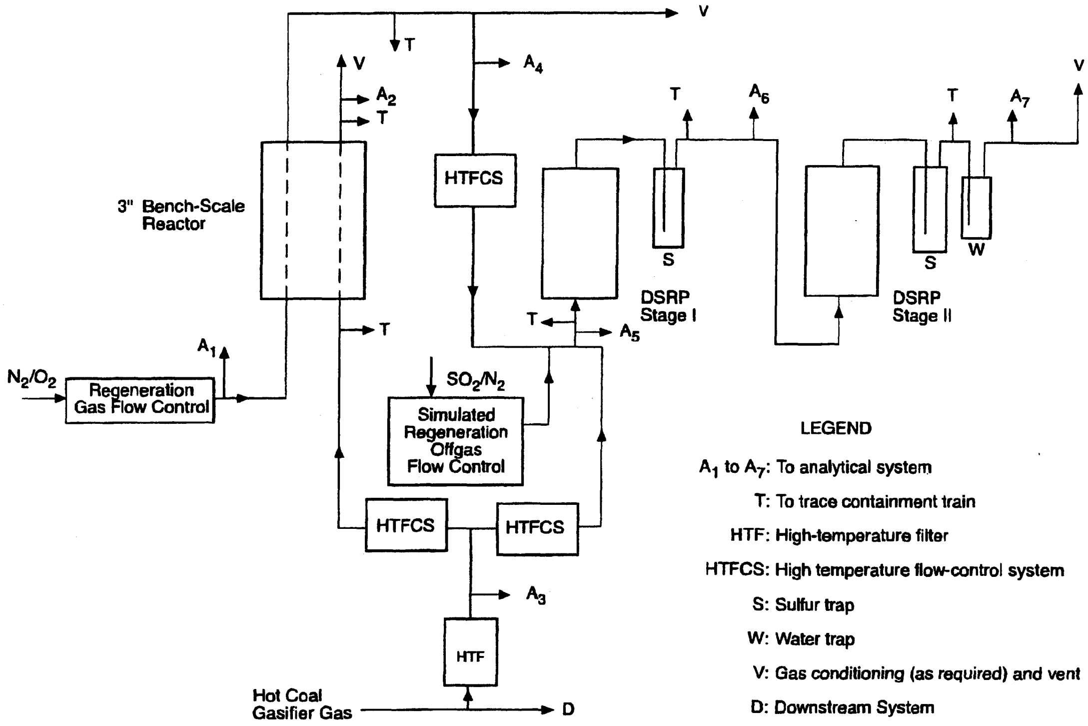

Figure 2. Integrated zinc titanate and DSRP reactor system.

2.1.2 Mobile Laboratory

The innovative concept that was crucial to the success of this project was the idea of putting the bench-scale process equipment into a "mobile laboratory." All of the process equipment, control equipment, and sampling and analysis equipment for field testing would be housed in a specially modified office trailer. The experimental apparatus would be fabricated, assembled, installed, and commissioned in the mobile laboratory while it was conveniently located at an RTI site. Then the completed mobile lab would be moved to the source of the coal gas slipstream and be temporarily installed.

2.1.3 Site Selection

Of several possibilities investigated, the FETC-Morgantown site was chosen for the bench-scale slipstream testing. The Morgantown site operates an air-blown, fluidized-bed gasifier capable of providing ~136 kg/h (300 lb/h)—~127 Nm^3/h (4,750 std ft^3/h)—of low-Btu coal gas from a nominal charge rate of 36 kg/h (80 lb/h) of coal. Table 1 shows the typical coal gas composition following gasification of a medium-sulfur coal. The raw coal gas is supplied at 538 °C (1,000 °F) and 3.0 MPa (425 psig) pressure to downstream cleanup devices. The system includes several particulate removal stages that provide the capability to tailor the particle loading to the cleanup section. The cleanup test section consists of a closely coupled modular gas cleanup rig (MGCR). To supply the ZTFBD and DSRP test apparatus, a coal gas slipstream of ~4.95 Nm^3/h (185 std ft^3/h) (equivalent to 3.9 percent of the gasifier flow) at 538 °C (1,000 °F) and 2.5 MPa to 2.8 MPa (350 to 400 psig) was taken from the MGCR section between the filter vessel and MGCR sorbent 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_2O	11.0
H_2S	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.

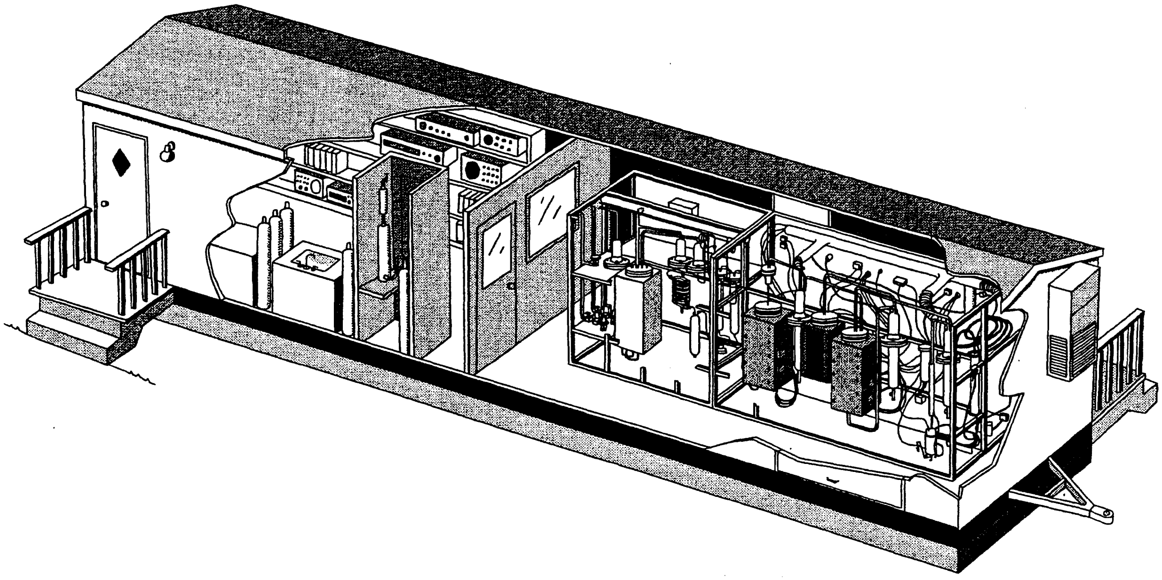

Figure 3. Artist's concept of trailer.

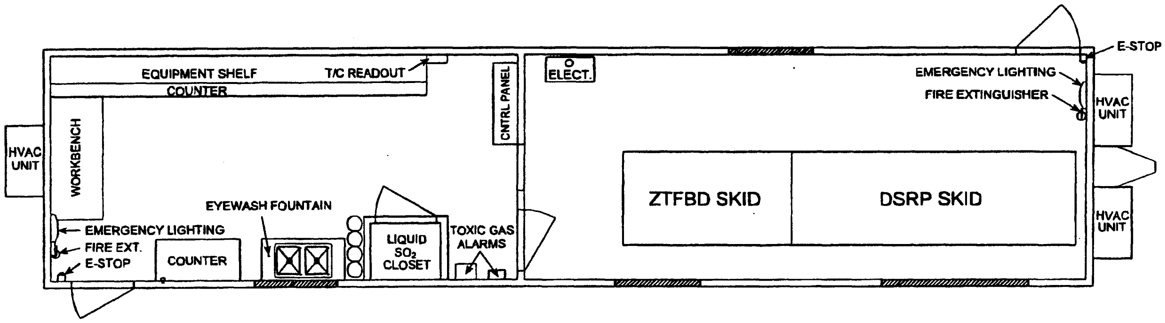

Figure 4. Floor plan showing equipment layout.

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 H_2S/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) × 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 × 1.98 m high × 2.44 m long (4.5 ft × 6.5 ft × 8 ft). The DSRP system is built on an aluminum-framed skid that measures 1.37 m wide × 1.98 m high × 4.12 m long (4.5 ft × 6.5 ft × 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 H_2S concentration to SO_2 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 H_2S. In a commercial embodiment of this process, the operation would be controlled to maintain a low H_2S level by continuously circulating the sorbent between the sulfider and the regenerator. However, in this experimental bench-scale unit, the H_2S 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 H_2S 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 H_2S adsorbed on the sorbent bed is oxidized to SO_2; the regeneration half cycle is complete when the SO_2 concentration in the offgas declines. The hot regeneration offgas, containing about 2 percent SO_2, 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-SO_2 mixture using a GC will enable recalibration of flow controllers for the SO_2 carrier nitrogen and the SO_2 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 H_2S to SO_2 at 2:1 at the exit of the DSRP reactor system. Increasing the flow of reducing gas will tend to increase the conversion of SO_2 to elemental sulfur and H_2S, thus raising the H_2S:SO_2 ratio. Similarly, decreasing the flow of reducing gas will decrease the conversion, lowering the H_2S:SO_2 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 H_2S and SO_2 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 SO_2 and oxygen analyzers were installed. When the regeneration half cycle is complete, the oxygen concentration in the offgas will increase fairly rapidly and the SO_2 concentration will decrease. Because the offgas 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—H_2, CO, CO_2, N_2, CH_4—and for high levels of H_2S 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 SO_2.

Another GC with a TCD is set up to measure the concentration (at high levels) of the sulfur gases—H_2S, COS, SO_2—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 H_2S 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 (NH_3). 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 SO_2 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 SO_2 in the simulated regeneration gas, the liquid SO_2 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.)
• N_2 flow in regeneration gas lower than preset value	Digital indicator shows low flow; PLC sends signal to close air valve YV-1.
• N_2 flow in liquid SO_2 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, H_2S, or SO_2 monitors detect concentration above the level I set value	Appropriate alarm sounds to allow corrective action to be taken.
• CO, H_2S, or SO_2 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 MGCR 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 SO_2 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.

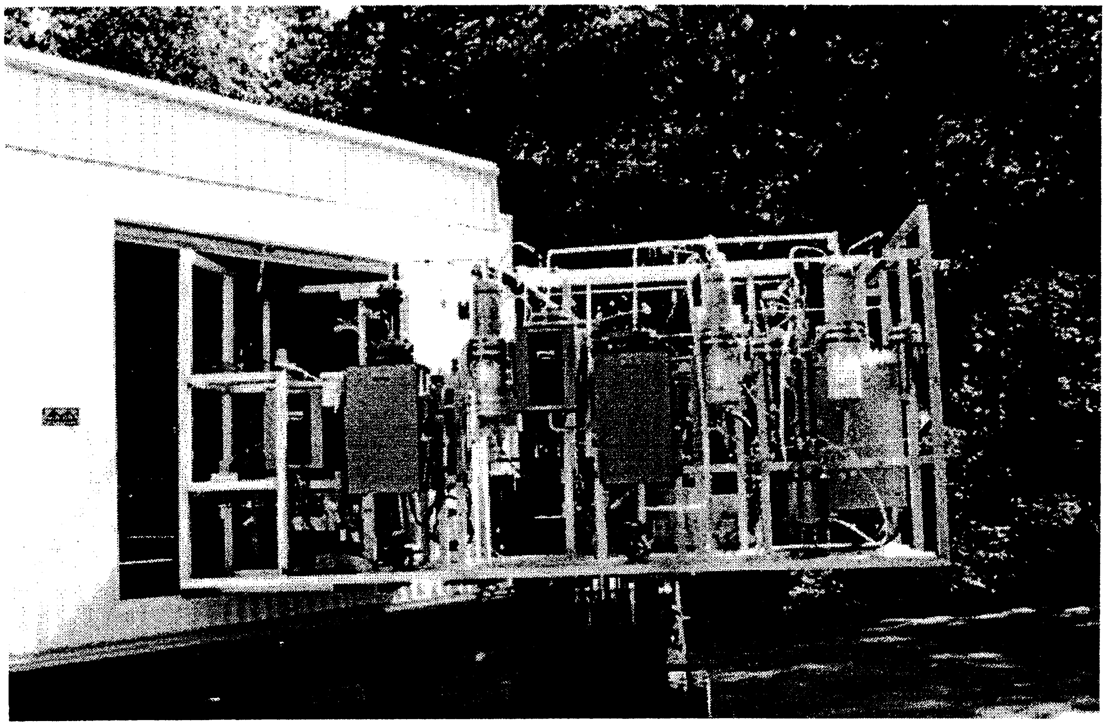

Figure 5. Equipment skids being loaded inside.

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.

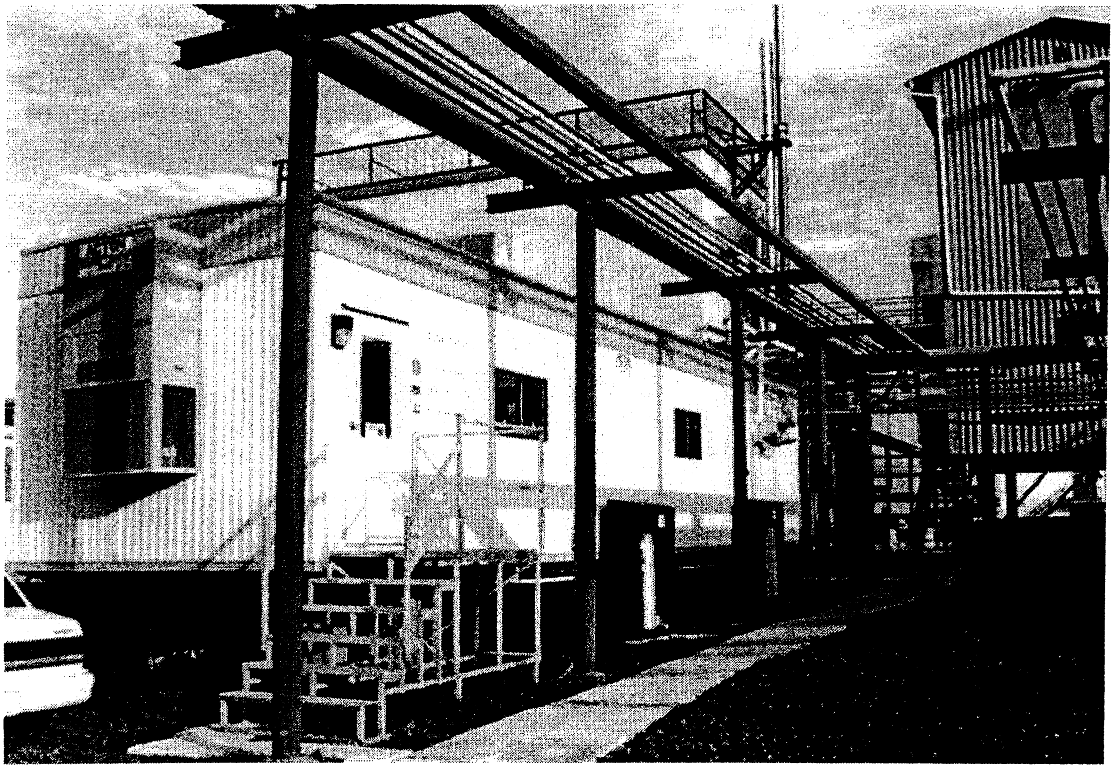

Figure 7. Trailer in position at FETC-Morgantown.

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 Nm^3/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_2O				**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_2S	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_2S (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 H_2S = 9.7 lb S/100 lb sorbent in outlet gas.
Average vol% H_2O in gas = 11.5.
[a] FETC online mass spectrometry (MS) analysis.
[b] NA = 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
Regeneration temperature = 730 °C
System pressure = 255 psig
SO_2 in offgas = 13,000 ppmv (fairly stable)
DSRP coal gas flow = erratic
O_2 in offgas = 60 ppmv
Run terminated at O_2 breakthrough of 500 ppmv

Run time (min)	Percent SO_2 conversion	Percent SO_2[a] conversion to H_2S	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

[a] No COS detected.

- FETC online mass spectrometry analysis of inlet coal gas agreed with RTI's analysis except for methane.
- Inlet H_2S was quite low due to a low-S coal.

The sulfidation H_2S breakthrough is shown in Figure 8. During this cycle, water got into the sample line of RTI's sensitive GC for H_2S (Varian GC-FPD). Thus, analysis was carried out using a less sensitive TCD whose lower H_2S detection limit was 70 ppmv. The inlet H_2S 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 H_2S data, shown in Figure 9, demonstrate the high sulfur variability of the coal used by FETC. The H_2S breakthrough curve is also shown in Figure 9. Initially, nearly all the H_2S is removed even with high inlet H_2S. 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 H_2S. Sulfur loading of 21 g S/100 g sorbent (21 lb S/100 lb) sorbent was achieved at 1,000 ppm H_2S 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 SO_2 elusion profile shows a quick rise and stabilization of the SO_2 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_2S	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_2S	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 H_2S in outlet).
Average percent H_2O in gas = 11.0.
[a] FETC MS.
[b] RTI Carle GC-TCD.
[c] NA = 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 SO_2-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
Regeneration temperature = 725 °C
System pressure = 245 psig
SO_2 in offgas = 12,000 ppmv (steady)

O_2 in regeneration gas = 1.85% (vol)
DSRP coal gas flow = erratic
O_2 in offgas = ~60 ppmv
Run terminated at O_2 breakthrough of 600 ppmv

Run time (min)	Percent SO_2 conversion	Percent SO_2 conversion to H_2S	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, NH_3, 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 (H_2S) 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 LSO_2. 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

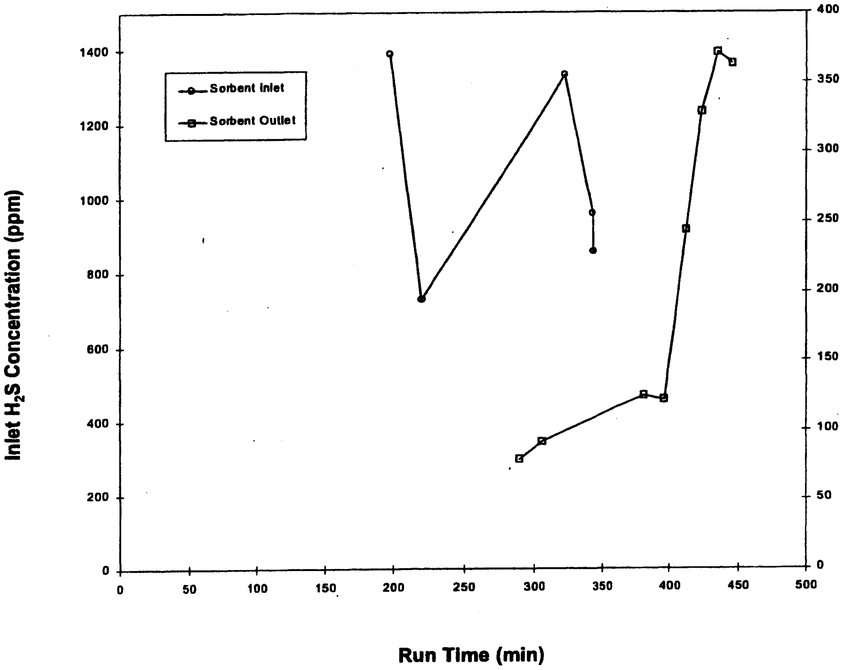

Figure 8. Sorbent sulfidation curves (9/13/94).

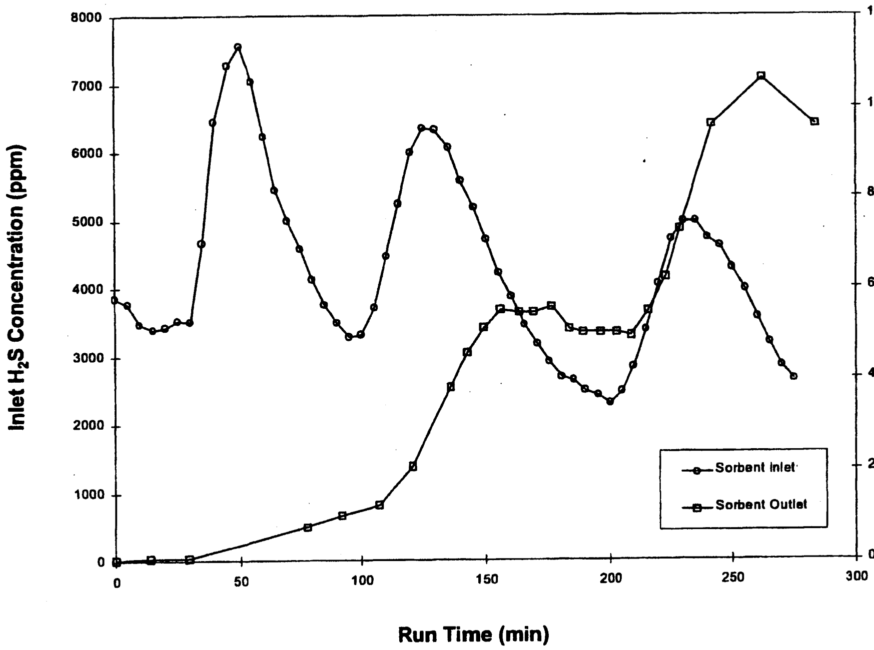

Figure 9. Sorbent sulfidation curves (9/14/94).