Bench-Scale Demonstration of Hot-Gas Desulfurization Technology

Final Report

SUBMITTED TO:

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

PREPARED BY:

S.K. Gangwal
J.W. Portzer
RTI
3040 Cornwallis Road
P.O. Box 12194
Research Triangle Park, NC 27709-2194

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

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ABSTRACT

Designs for advanced integrated gasification combined cycle (IGCC) power systems call for desulfurization of carbonaceous fuel-derived synthesis gas (syngas) using regenerable sorbents at high-temperature, high pressure (HTHP) conditions. Regeneration of the sulfided sorbent using an oxygen-containing gas stream or air results in a sulfur dioxide (SO_2)-containing offgas at HTHP conditions. The patented Direct Sulfur Recovery Process (DSRP) developed by RTI with support from the National Energy Technology Laboratory (NETL) and its precursor organizations [Federal Energy Technology Center (FETC) and Morgantown Energy Technology Center (METC)] efficiently converts the SO_2 in this offgas to elemental sulfur. Under development since 1988, the original work was conducted in a laboratory with simulated laboratory gas mixtures.

The Direct Sulfur Recovery Process is a catalytic reduction process for efficiently converting to elemental sulfur up to 98% 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 syngas to effect the desired reduction. In this project, the DSRP was demonstrated with actual coal-derived syngas (as opposed to the simulated laboratory mixtures used in previous projects for the original development work) in 75-mm (3-in) and 125-mm (5-in) fixed- and fluid-bed reactors.

This report focuses primarily on the slipstream testing of a skid-mounted DSRP field-test unit that utilized the 125 mm (5-in) fluid-bed reactor. This slipstream testing was conducted at the U.S. Department of Energy's (DOE's) Power System Development Facility (PSDF) in Wilsonville, Alabama in conjunction with their coal gasification tests. The earlier work with 75 mm (3-in) reactors has been previously reported in detail. Thus, only the highlights of this earlier work will be reported in the main body of this report. Previous reports will be included in the Appendices for reference.

The field testing of DSRP at DOE's Morgantown site used a bench-scale (75-mm) reactor installed inside RTI's Mobile Laboratory. These tests were conducted in conjunction with METC fluidized-bed gasifier tests that supplied actual coal gas to the RTI's Mobile laboratory. The testing was highly successful with SO_2 conversion in a regeneration off-gas at 98% at the beginning and end of the 160 hour slip-stream test.

The logical path to potential commercialization of the process led to the construction of a larger DSRP unit to demonstrate longer on-stream times, higher inlet SO_2 concentrations, and effective automatic process control to maintain the optimal reactor feed stoichiometry. Originally designed and fabricated in 1995 for Enviropower's European test site, the skid-mounted DSRP field-test unit was later substantially modified and enhanced (over the period 1997-2000) for the test at PSDF. The fixed-bed reactor was modified to operate also in a fluid-bed mode, and the Mobile Laboratory was remodeled to serve as the control room and analytical support facility for the adjacent, outdoor equipment skid. Equipment was added to the skid to generate a simulated regeneration offgas of any desired concentration by vaporizing liquid SO_2 into a heated nitrogen stream.

During the commissioning activities in March 2001, the skid-mounted DSRP at PSDF received coal gas for 53.5 hours, during which time liquid SO_2 was charged for 30 hours. Major accomplishments were successfully transferred coal gas through a long, heat-traced line; successfully measuring the flow rate and composition of the actual syngas; safely generating a flow of simulated regeneration offgas by vaporizing liquid SO_2; and controlling the DSRP unit remotely using computer-based process control hardware and software that included automatic control of the reactor feed stoichiometry.

The commissioning run accomplished an important objective of a “shakedown” run—identifying needed improvements for future operation, including eliminating of plugging of sample and impulse lines caused by “tars” (primarily naphthalene) present in the coal gas, improving heat tracing to eliminate cold spots and sulfur plugging, fine-tuning of control system instrument parameters to smooth out responses, and improving collection efficiency of the elemental sulfur.

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ACRONYMS AND ABBREVIATIONS

°C	degrees Celsius
cc	cubic centimeters
CG	coal gas
CRADA	cooperative research and development agreement
DHR	design hazard review
DOE	U.S. Department of Energy
DSRP	Direct Sulfur Recovery Process
°F	degrees Fahrenheit
FETC	Federal Energy Technology Center
GC	gas chromatograph
GE	General Electric
h	hour
HTHP	high temperature, high pressure
IGCC	integrated gasification combined cycle
in.	inch
IR	infrared
K	kelvin
lb/hr	pounds per hour
LSO_2	liquid sulfur dioxide
METC	Morgantown Energy Technology Center
mm	millimeter
MPa	megapascal
NETL	National Energy Technology Laboratory
OSHA	Occupational Health and Safety Administration
P&IDs	Piping and instrumentation diagrams
PCD	particulate control device
PFD	process flow diagram
PLC	programmable logic controller
ppmv	parts per million by volume
PSDF	Power Systems Development Facility
psig	pounds per square inch gauge
PSV	pressure relief valve
PV	process value
ROG	regeneration offgas
RTI	Research Triangle Institute
SCADA	Supervisory Control and Data Acquisition
scc	standard cubic centimeters
SCS	Southern Company Services
SimROG	simulated ROG
TCD	thermal conductivity detector
ZTFBD	zinc titanate fluidized-bed desulfurization

ACKNOWLEDGEMENTS

RTI gratefully acknowledges the assistance and guidance of the current NETL contracting officer's representative (COR) on this project, Mr. Suresh Jain, and that of the former COR, Mr. Thomas P. Dorchak. RTI also wishes to thank the staff of the PSDF for their support during the slipstream testing. In particular, RTI wishes to acknowledge SCS employees Mr. Doug Maxwell, Mr. Brandon Russell, and Ms. Roxann Leonard. Mr. Gary B. Howe, Dr. Brian S. Turk, Mr. Daryl D. Smith, Mr. K. David Carter, Mr. Curtis E. Moore, Mr. Martin Lee, and many others at RTI provided valuable contributions to the work.

EXECUTIVE SUMMARY

BACKGROUND

Designs for advanced integrated gasification combined cycle (IGCC) power systems call for desulfurization of carbonaceous fuel-derived synthesis gas (syngas) using regenerable sorbents at high-temperature, high-pressure (HTHP) conditions. Regeneration of the sulfided sorbent using an oxygen-containing gas stream or air results in a sulfur dioxide (SO_2)-containing off-gas at HTHP conditions. The patented Direct Sulfur Recovery Process (DSRP) developed by RTI with support from the National Energy Technology Laboratory (NETL) and its precursor organizations uses a slipstream of syngas as a reducing agent to convert the SO_2 to elemental sulfur. Under development since 1988, the original work for DSRP was conducted in a laboratory using simulated laboratory gas mixtures. It has now moved to the field with a slipstream of syngas from a demonstration-scale coal gasifier.

SUMMARY OF PRIOR WORK

The Direct Sulfur Recovery Process (DSRP) is a catalytic reduction process for efficiently converting to sulfur up to 98% or more of the sulfur dioxide (SO_2) contained in the regeneration off-gas streams produced in advanced IGCC power systems. The DSRP reacts the regeneration off-gas with a small slipstream of syngas to effect the desired reduction.

In the original work (DOE Contract No. DE-AC21-80MC23260) the DSRP was demonstrated with simulated syngas and off-gas using 25 to 50 cc of catalyst in a 1-in diameter fixed-bed reactor. More than 50 tests were conducted with 7 different catalysts. Effect of space velocity, temperature, steam content and pressure was evaluated. These results showed that 99.2 to 99.9% sulfur recovery could be obtained in a 2-stage DSRP reactor system. An economic study using these results showed that the DSRP had the potential to produce sulfur at costs about 10 to 13% of conventional processes (such as Wellman-Lord/Augmented Claus) from regeneration off-gas.

Based on these encouraging results, the DSRP was scaled up to a 2-stage 3-in reactor system with 1 liter of catalyst in each reactor and demonstrated with up to 13% SO_2 containing off-gas (Contract NO. DE-AC21-MC27224). Thermal degradation of DSRP catalyst was not observed at these high concentrations. It was shown that reversal of sulfur conversion could occur in the second stage of reaction if sulfur is not effectively removed in interstage condensers. By removing additional sulfur with the water at the interstage level, sulfur conversion did increase to 98.5% to 99.1%.

FIELD TEST CONDUCTED IN MORGANTOWN, WV

Detailed description of the work during the first five tasks of this project is provided in Appendices A and B. Under these tasks, RTI designed and fabricated a Mobile Laboratory, using a modified office trailer, containing an integrated hot-gas desulfurization/ DSRP unit. The trailer was moved to Morgantown, West Virginia, and temporarily installed at the DOE facility there (the former Morgantown Energy Technology Center [METC]) in order to receive a slipstream of actual coal gas from a pilot-scale gasifier.

In field testing in 1994, the 3-in diameter, fluidized-bed, desulfurization reactor was used to test a zinc titanate-based sorbent formulation and to produce a regeneration offgas (ROG) stream that was fed to the two-stage, 3-in diameter, fixed-bed DSRP reactors. The DSRP achieved 95% to 99% conversion of the SO_2 to elemental sulfur after the first stage. For the 1995 testing, the DSRP apparatus was modified to be a single-stage unit; testing was conducted with a synthesized ROG and actual gasifier gas. The conversion of SO_2 to elemental sulfur was 98% at both the beginning and the end of a 160-hour run.

The fixed-bed catalyst used in the 1995 test was removed from the reactor in the Mobile Laboratory and subsequently exposed for another 10 days to tar-containing coal gas in a General Electric pilot gasifier. Further testing of the exposed catalyst in a bench-scale DSRP unit in RTI's laboratory (using synthetic gas mixtures) demonstrated 96% conversion to elemental sulfur.

PLANNING FOR FIELD TEST AT WILSONVILLE, AL

The main body of this report is devoted to Task 6 which called for DSRP to be demonstrated at a larger scale and with actual coal gas. In 1995, RTI designed and fabricated a fixed-bed, single-stage unit with 6 times the capacity of the reactor in the Mobile Laboratory (hence, the designation "6X DSRP") for integration and testing at Enviropower's European pilot plant. However, that test program never took place. The test site was changed to DOE's facility in Wilsonville, Alabama—the Power Systems Development Facility (PSDF). The main attraction at that site is a commercial demonstration-scale, air-blown, transport reactor coal gasifier. The objectives of the DSRP field test were to conduct an extended run with actual coal gas and high concentrations of SO_2 in the field.

Previous DSRP development efforts had focused on a process to treat the low concentration ROG (1-3% SO_2) that results from diluted-air regeneration. With a growing interest in regenerating hot-gas desulfurization sorbents using pure air, the DSRP development focus was directed toward processing higher concentrations. Up to 14% SO_2 is contained in ROG from "neat" air regeneration. Because of its potential for greater heat transfer, a fluid-bed reactor is more suited for the high heats of reaction that result from processing a concentrated feed stream. Thus the 6-in fixed-bed reactor on the "6X" unit was rebuilt to accommodate a 5-in diameter fluid-bed sorbent cage. Reflecting this change in design capability, the apparatus was renamed the "Skid-Mounted DSRP Field-Test Unit."

In parallel, testing was carried out in RTI's 3-in reactor system and an active and attrition-resistant fluid-bed catalyst was developed. The details of this testing and catalyst development are provided in Appendix B with a summary in Section 5.

For testing at the PSDF site, the scope of RTI's efforts included refitting the Mobile Laboratory (trailer) for use as a control room and analytical space. As the skid-mounted DSRP field-test unit was too large to be mounted inside the trailer, it was set up outdoors (under a carport-type shed roof) with the trailer adjacent. A simulated ROG stream was synthesized by vaporizing liquid SO_2 into a heated nitrogen stream. Planning for this test started in earnest in 1997; construction of the modified, skid-mounted DSRP and remodeling of the Mobile Laboratory took place from 1998 to 2000. The trailer and skid were moved to the PSDF site in December of 2000 for an early 2001 commissioning and "shakedown" run.

An important aspect of the design of the skid-mounted DSRP field-test unit was the inclusion of an automatic process control system to maintain the reactor feed stoichiometry. The control system monitors the composition and flow rate of both the coal gas and the simulated ROG so that the reducing components can be kept in the precise 2:1 stoichiometric ratio with the SO_2 content.

COMMISSIONING OF SKID-MOUNTED DSRP FIELD-TEST UNIT AT PSDF

The commissioning of the skid-mounted DSRP field-test unit took place in March 2001 in conjunction with the scheduled PSDF gasifier run identified as GTC-4. After several false starts earlier in the month, the PSDF gasifier was lined-out on coal feed, and the heated slipstream line was also operational. In the course of a 4-day "shakedown" run, the DSRP unit received coal gas for 53.5 hours and processed SO_2 for 30 hours. At the end of that time, the field crew discovered that only a small amount of elemental sulfur had been formed. The causes of the shortfall are not completely understood, but the unstable operation during much of the shakedown period is at least partly responsible. The important results from the commissioning experience were as follows:

- successfully transferred coal gas through a long, heat-traced line that PSDF provided.
- successfully measured the flow rate and composition of the coal gas that was received at the RTI skid and Mobile Laboratory control room/analyzer room.
- safely generated a flow of simulated ROG by vaporizing liquid SO_2.
- controlled the DSRP unit remotely using computer-based process control hardware and software that included automatic control of the reactor feed stoichiometry.

The commissioning run demonstrated aspects of the design and construction of the DSRP field-test unit that will need to be improved for future operation:

- eliminating the plugging of sample and impulse lines caused by "tars" (primarily naphthalene) that are present in the coal gas.
- improving heat tracing to eliminate cold spots and sulfur plugging.
- fine-tuning control system instrument parameters to smooth out responses.
- improving collection efficiency of the elemental sulfur.

CATALYST CANISTER EXPOSURE TESTING

In parallel with the field test of the skid-mounted DSRP field-test unit (equipped with a fluid-bed reactor), two samples of fixed-bed catalyst were placed in perforated canisters inside the Westinghouse candle filter in PSDF gasifier main train. After approximately 1000 hours of exposure to the rugged PSDF conditions— both oxidizing and reducing at high temperatures 600°C (1100+°F), the canisters were removed and shipped to RTI. Testing of the catalyst at RTI indicated that the catalyst converted approximately 90% of the SO_2 to elemental sulfur, which was lower than normal DSRP catalyst performance of 98% conversion. Characterization of the PSDF-exposed catalyst indicated that its reduced activity may have been caused by its lower surface area, lower pore volume, and lower level of active ingredient. It is believed that this was due to exposure of the catalyst to oxygen at high temperature.

CONCLUSIONS AND RECOMMENDATIONS

DSRP is an efficient regeneration off-gas treatment process for sorbent based treatment processes that remove H_2S and COS from coal gasifier gas. In this project, the process has been developed to a small pilot-scale. Sulfur conversions as high as 98% have been demonstrated with a single-stage reactor with simulated and actual coal gases in both fixed-bed and fluidized-bed modes. Catalyst durability has been verified by canister exposure tests of over 1,000 hours.

As DSRP is a tail-end process, its further scale-up and demonstration needs to be carried out in parallel to the development of the front-end hot-gas desulfurization process. To this end, discussions are currently ongoing with ChevronTexaco to demonstrate the DSRP in conjunction with their gasifier-quench system that is to be coupled to a hot-gas desulfurization process at 250°C (482°F).

SECTION 1
BACKGROUND AND PRIOR WORK

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) (USP 5,366,717 and USP 5,798,088) developed by the Research Triangle Institute (RTI) with support from the National Energy Technology Laboratory (NETL) and its precursor organizations (Morgantown Energy Technology Center [METC] and Federal Energy Technology Center [FETC]), is an attractive option for treating this regeneration offgas (ROG). 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 1 is a schematic diagram showing a proposed commercial embodiment of DSRP.

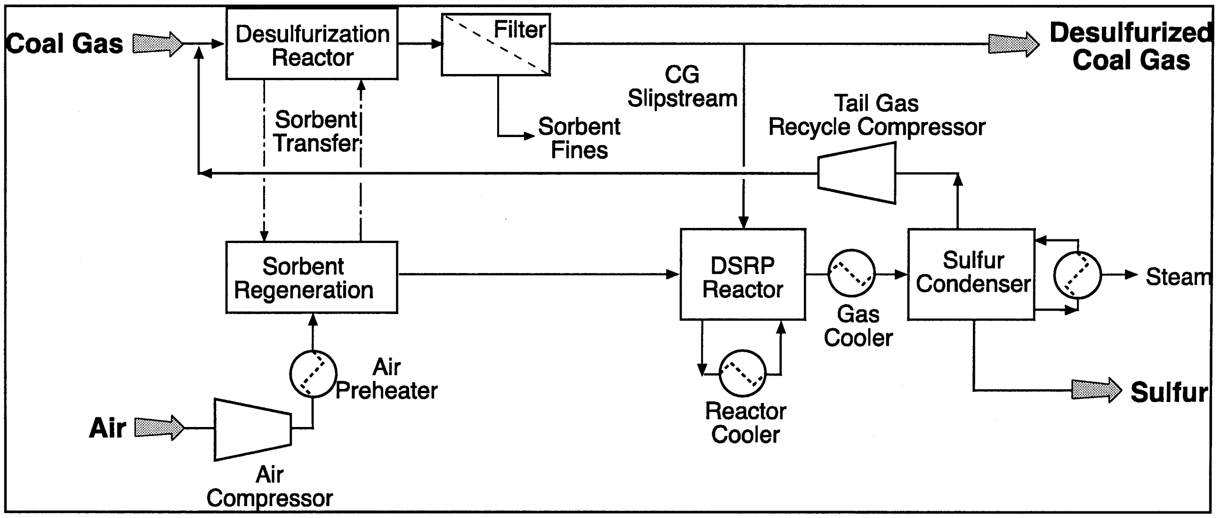

Figure 1. Hot-Gas Desulfurization/DSRP Integration

Prior to the current contract, the DSRP was developed in a laboratory setting, using synthetic gas mixtures to simulate the ROG and coal gas feeds (See McMichael & Gangwal, 1991; Gangwal & Chen, 1994). Work done in the first five tasks for this contract is described in detail in Appendices A and B. Under these tasks, the DSRP was tested using actual coal gas and actual ROG. One of the main objectives was to test 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 test 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" ROG stream. The mobile lab was installed at the NETL-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 two years:

September 1994:	Initial shakedown test of mobile laboratory at Morgantown with integrated desulfurization reactor and two-stage DSRP
October 1994:	Test run of integrated desulfurization reactor and two-stage DSRP at Morgantown
July 1995:	Long-duration run (160 h) slipstream test of single-stage DSRP at 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-4L was subjected to three sulfidations and two regenerations. The ZT-4L consistently removed H_2S from coal gas down to <20 ppmv at 873 K (1110 °F) and 21.89 MPa (260 psig). The DSRP was very effective in converting SO_2 in actual or in synthetic ROG to elemental sulfur, achieving 95% to 99% 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 2) and with new control hardware and software to improve the stoichiometric flow control of the coal gas stream.

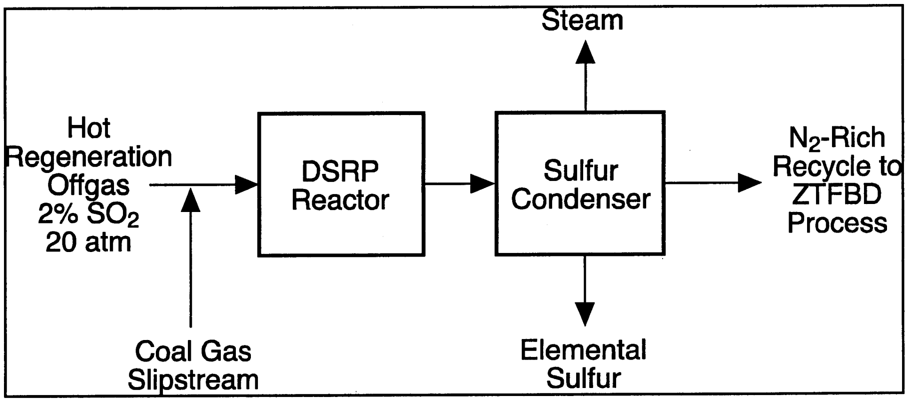

Figure 2. Single-Stage DSRP

In the 1995 slipstream test campaign, the single-stage unit produced 98% conversion of SO_2 to elemental sulfur at both the beginning and end of the run. Thus, 160 h of exposure of the catalyst to coal gas resulted in no detrimental effect. The apparatus used in that field test included a "first generation" automatic coal gas flow control system, designed to maintain the coal gas at the desired stoichiometric ratio to the SO_2 in the ROG. Though insufficiently rugged for long-term use, that scheme greatly enhanced the operators' ability to attain and maintain steady-state operation of the DSRP reaction.

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 (then at Morgantown) and shipped to the GE pilot plant for placement in a coal gas line throughout a 10-day pilot plant run. This action resulted in additional exposure of the catalyst during March-April, 1996 to about 200 h of coal gas, 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 Morgantown testing was approximately 1,500 h.

The exposed catalyst was tested in April-May, 1996 in a 75-mm (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 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% after approximately 22 h of testing, compared to 98% 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 bench-unit test program had indeed reduced the carbon content. 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.

Task 6 of this contract involved 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 Enviropower's European test site, and the design was strongly influenced by the specific site requirements. Subsequent to the start of construction, the partner's cooperative research and development agreement (CRADA) with DOE dissolved; a search for an alternate test site commenced.

As originally conceived, the 6X DSRP was skid-mounted and sized to accommodate shipping in a standard overseas shipping container. When it became clear that the DOE/NETL Power Systems Development Facility (PSDF) in Wilsonville, Alabama, would be the chosen test site and that over-the-road shipping would be possible, design changes had to be incorporated. The major impact was that the Mobile Laboratory (described above) would be remodeled to be used as a control and analytical space and the 6X DSRP would be positioned adjacently, but outdoors. With these design changes, the nomenclature for the apparatus also changed, from 6X DSRP to "skid-mounted DSRP field-test unit."

This report describes the completion of fabrication of the skid-mounted DSRP field-test unit and its subsequent commissioning at PSDF.

SECTION 2
OBJECTIVES

The overall goal of the DSRP development program was to operate a “pilot” unit at a large enough scale and for long enough duration to establish commercial credibility of the process. Furthermore, additional, confirming data on the effects, if any, of trace components in coal gas were desired. The overall contract objectives are summarized below:

- Develop and test an integrated, skid-mounted, bench-scale zinc titanate fluidized-bed desulfurization (ZTFBD)/DSRP reactor system with a slipstream of actual coal gas.
- Test the bench-scale DSRP over an extended period with a slipstream of actual coal gas to quantify the degradation in performance, if any, caused by the trace contaminants present in coal gas (including heavy metals, chlorides, fluorides, and ammonia).
- Expose the DSRP catalyst to actual coal gas for extended periods (about 400 hours) and then test its activity in a laboratory reactor to quantify the degradation in performance, if any, caused by static exposure to the trace contaminants in coal gas.
- Design and fabricate a six-fold-larger-scale DSRP reactor system for future slipstream testing.
- Further develop the fluidized-bed DSRP to handle high concentrations (up to 14%) of SO_2 that are likely to be encountered when pure air is used for regeneration of desulfurization sorbents.
- Expose the DSRP catalyst further (about 1,000 hours) and then test its activity in a laboratory reactor to quantify the degradation in performance, if any.
- Conduct an extended field test of the 6X DSRP reactor with actual coal gas and high concentrations of SO_2.

The work to satisfactorily meet the first three objectives is covered in detail in Appendices A and B. The main body of this report details the work towards the last four objectives.

SECTION 3
FIELD TESTING OF THE SKID-MOUNTED DSRP UNIT AT PSDF

3.1 CHRONOLOGY OF EVENTS LEADING UP TO THE PSDF TESTING

The concept of testing the skid-mounted DSRP unit at DOE's PSDF was first seriously discussed at a meeting at the PSDF site in July 1996. This was the first visit by RTI personnel to that location, and several options for establishing a working arrangement were proposed and discussed. The idea of canister exposure testing of the fixed-bed catalyst pellets was also considered and scheduled for immediate implementation.

PSDF and RTI staff worked out the specifics of the exposure test plan from February to April 1997. RTI staff fabricated the two canisters that would be placed inside the Westinghouse particulate control device (PCD) on the downstream (clean) side. Two batches of fixed-bed DSRP catalyst were pre-sulfided, following two different protocols, and stored in evacuated, sealed containers in preparation for placing in the gasifier later that year.

In September 1997, RTI conducted bench-scale, laboratory tests of several formulations of fluid-bed catalysts. Using a simulated coal gas mixture and a simulated ROG with 14% SO_2 content, the testing identified one particular material—Catalyst B, as referenced in the paper presented at the Advanced Coal-Based Power and Environmental Systems '98 Conference, included as Appendix A.

The planned August 1997 startup of the PSDF gasifier did not take place as scheduled, causing installation of the exposure canisters to be postponed. However, plans for the field test of the DSRP skid did proceed. The kick-off meeting for that activity took place in December 1997 at the PSDF site, at which the requirements for field test equipment at that site were defined.

Because the gasifier startup schedule was delayed, the DSRP skid modifications to accommodate the PSDF field test proceeded at a modest pace. In April 1999, a rigging contractor moved the process equipment skid out of the RTI shop, into the parking lot. The crew joined the heater control panel (previously intended to be installed at a remote location) to the equipment skid to make a single, larger skid.

With the initial startup of the gasifier finally scheduled for the fall of 1999, RTI shipped the canisters and sealed containers of catalyst in July 1999. On August 16, 1999, PSDF loaded the canisters and placed them on the support ring of the opened Westinghouse PCD. Several days later, that unit was closed up in preparation for the gasifier run.

A second field test kick-off meeting took place in February 2000 at PSDF. The construction of the supporting infrastructure was accelerated to accommodate commissioning schedule for November-December. The exact requirements for the field test were discussed, and the safety standards to be met were more carefully delineated. To meet those requirements, RTI scheduled a design hazard review (DHR) of the RTI-supplied equipment, to be facilitated by an outside consultant. This DHR was conducted during July-August 2000 in coordination with the DHR activities at PSDF. An intensive fabrication and construction effort ensued in order to incorporate the required design changes and still meet the proposed project schedule.

Finally, in November 2000, contract haulers moved the trailer and the DSRP skid to the PSDF site. December 2000 to March 2001 marked an intensive period of field work, during which RTI personnel made multiple trips to Alabama to set up the equipment for the field test. The commissioning ("shakedown") of the unit took place in March 2001. At the end of the gasifier run, the exposure test canisters were removed from the PCD, and the catalyst pellets were taken out of the perforated exposure canisters and returned to RTI.

3.2 FEATURES OF THE PSDF FACILITY

The major attraction of the PSDF site in relation to DSRP testing is the "demonstration" scale transport reactor gasifier. This air-blown gasifier has a coal feed rate of approximately 2.5 tons per hour, and a syngas production rate of 15,000-20,000 lb/hr. This gasifier is much larger than the one at Morgantown and has the potential for longer campaigns and, thus, longer on-stream time for the DSRP test unit.

On the other hand, there is no hot-gas desulfurization equipment at the PSDF; therefore, there is no stream of ROG available to feed to the DSRP. A simulated ROG stream (SimROG) had to be provided as part of the DSRP test skid. This was accomplished by including equipment to vaporize liquid sulfur dioxide (LSO_2) into a heated nitrogen stream.

3.3 LIAISON AND SCOPES OF RESPONSIBILITY FOR PSDF AND RTI

RTI personnel interfaced primarily with Southern Company Services (SCS) personnel at the PSDF site, although other organizations were present. The basic philosophy established for the field test was that SCS (and other entities, as required) would provide a place for RTI to set up the equipment, and would provide a heated slipstream of coal gas. RTI would provide all the test equipment, support equipment (Mobile Laboratory), and personnel to operate the equipment.

Figure 3 shows the proposed concept, including the routing of the slipstream line from the fifth floor of the gasifier structure down to the ground-level DSRP skid.

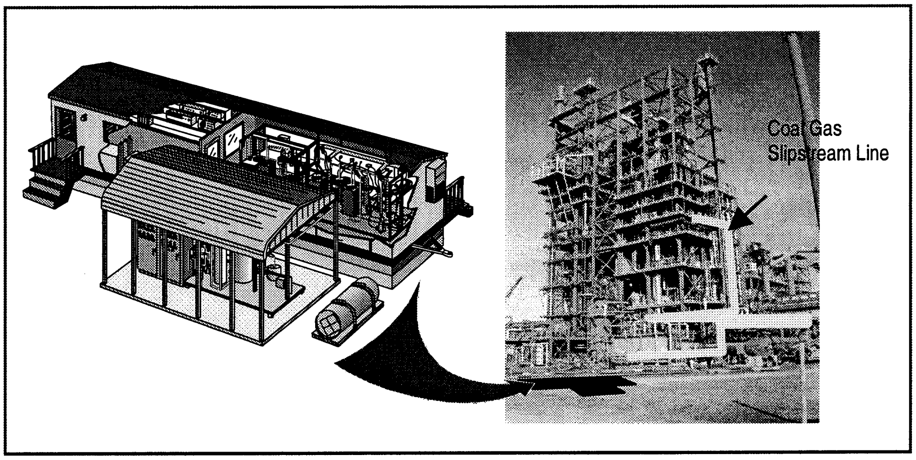

Figure 3. Slipstream Route

Figure 4 shows the final definition of the scopes of responsibility in some detail. In addition to the coal gas line, SCS also provided:

- heated process vent line back to the thermal oxidizer
- cooling water supply and return
- medium pressure nitrogen
- instrument air
- construction assistance to assemble the carport-type roof and to install the trailer and skid
- telephone line
- computer network connection (including e-mail and Internet access)
- access to the gasifier process control system (for monitoring-only of process conditions)
- electrical hookups of the skid and trailer.

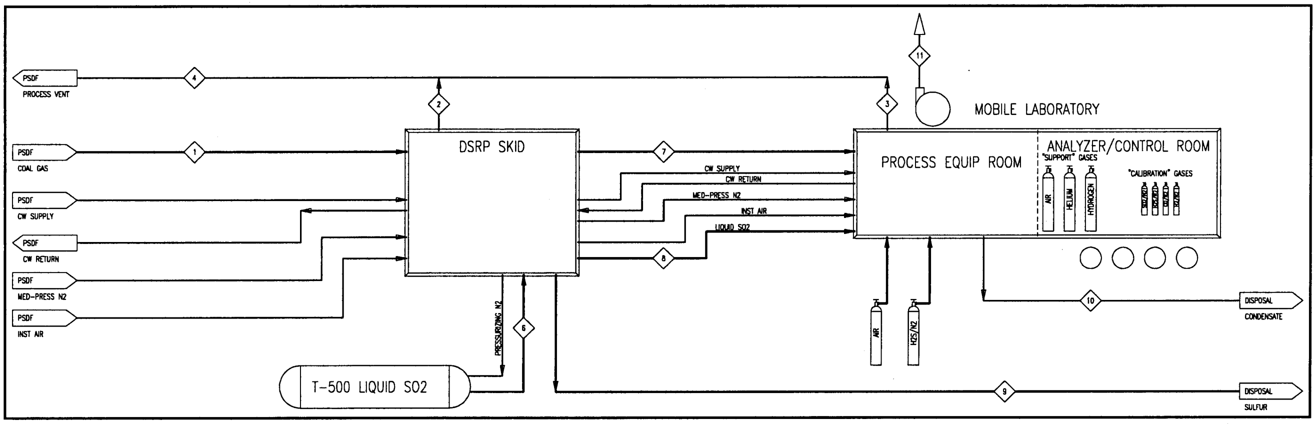

Figure 4. Scope Definition Diagram

In addition to providing the DSRP skid and the Mobile Laboratory, RTI was responsible for

- carport/shed parts
- interconnections between the skid and the trailer
- unpacking and re-assembly of all equipment at the site
- all work on the skid and/or in the trailer
- operating staff.

During the planning and liaison meetings, the possibility of exposing canisters of fixed-bed DSRP catalyst to the PSDF gasifier coal gas was discussed. All parties agreed that it would be fairly straightforward to provide that service, and informal arrangements were made to do so. Section 4, Catalyst Canister Exposure Testing, describes this activity more fully.

3.4 MODIFICATIONS TO DSRP FIELD-TEST UNIT REQUIRED FOR PSDF SITE TESTING

The decision to test the DSRP skid at PSDF meant that the equipment had to be modified considerably from its original design. As initially fabricated for the European site test, the DSRP process equipment skid was a stand-alone device without process control equipment. The heater control panel was to be located remotely from the process equipment, and process control was to be provided by the site's distributed control system. Furthermore, at that site, both actual coal gas and actual ROG were to be provided. Because the ROG was expected to have a low concentration of SO_2 (1-3%), a fixed-bed DSRP reactor was designed and fabricated.

As described in Section 3.3 above, RTI was responsible for the complete operation of the DSRP at PSDF and for providing a SimROG stream. Also at this time (1996-97), greater interest lay with testing ROG streams with higher SO_2 concentrations (up to 14%). As a fluid-bed reactor was expected to be better able to handle the higher heat of reaction of the more concentrated feed stream, the reactor on the skid-mounted DSRP field-test unit had to be rebuilt for use in the fluid-bed mode. Table 1 shows the design material balance for the PSDF testing. The flow rates were specified to achieve the optimum fluidization velocity with a 5-in diameter fluid bed inside the 6-in diameter reactor vessel.

As ROG was not available from PSDF, a system for generating a SimROG stream at high SO_2 concentrations (up to 14%) was incorporated into the skid-mounted equipment using the technique that was used successfully during the Morgantown field tests—vaporization of pressurized liquid SO_2 into a preheated nitrogen stream. An additional furnace, preheater coil, and liquid flow metering controls had to be added, and the relatively large inventory of LSO_2 that would be required caused some safety concerns (described below).

Figure 5 is a process flow diagram showing the final configuration of the skid-mounted DSRP field-test unit tested at PSDF. This diagram includes the changes made to the process (described above) as well as the changes made due to safety-related issues described in the following section.

Table 1. Design Material Balance for DSRP Field Test at PSDF

		Stream								
Compound	Molar Weight (MW)	1 CG Slip-stream	2 Liquid SO_2	3 Nitro-gen	4 Sim-ROG	5 Feed to DSRP	5A Reactor Make	5B Cond. Outlet	6 Sulfur Make	7 DSRP Tail Gas
COMPOSITION IN MOLE FRACTION										
CH_4	16.043	0.0000								
CO	28.0134	0.1850				0.0812				
CO_2	44.01	0.0800				0.0351	0.1163	0.1163		0.1258
H_2O	18	0.0800				0.0351	0.0966	0.0966		0.1044
H_2	2.016	0.1400				0.0614				0.0000
H_2S	34.08	0.0005				0.0002	0.0021	0.0021		0.002274
SO_2	64.063		1.0000		0.1401	0.0786	0.0011	0.0011		0.001137
S	32.064					0.0000	0.0755	0.0755	1.0000	0.0000
O_2	31.9988									
N_2	28.0134	0.5145		1.0000	0.8599	0.7083	0.7085	0.7085		0.7663
Total		1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
MW of mixture		24.86	64.06	28.01	33.06	29.46	29.26	29.26	32.06	29.03
FLOW RATE IN GRAMS PER HOUR										
CH_4	16.043	0				0	0	0		0
CO	28.0134	576				576	0	0		0
CO_2	44.01	391				391	1296	1296		1296
H_2O	18	160				160	440	440		440
H_2	2.016	31				31	0	0		0
H_2S	34.08	2				2	18	18		18
SO_2	64.063		1275		1275	1275	17	17		17
S	32.064						613	613	613	0
O_2	31.9988						0	0		0
N_2	28.0134	1,601		3423	3423	5024	5024	5024		5024
Flow rate (kg/h)		2.761	1.275	3.42	4.70	7.46	7.41	7.41	0.613	6.79
Flow rate (g/s)		0.77	0.35	0.95	1.30	2.07	2.06	2.06	0.17	1.89
Flow rate (lb/hr)		6.09	2.81	7.55	10.36	16.45	16.33	16.33	1.35	14.98
FLOW RATE IN VOLUMETRIC UNITS										
SLPM		41		46	53	95	94	94		87
SCFH		94		104	120	215	215	215		198
SCFM		1.57		1.73	2.01	3.58	3.58	3.58		3.31
gal/hr			0.25						0.091	
gal/day									2.18	
cc/min			15.41						5.66	
Temperature (°C)		538	21	21.	599.	599.	427.	135.	21.	204.
Temperature (°F)		1000	70	70	1110	1110	800	275	70	400
Pressure, atm, abs	19.98	24.82	21.41	19.98	19.98	19.71	19.51	1.00	2.02	
Pressure, psig		279	350	300	279	279	275	272	0	15
Density, g/cc			1.379	0.02486	0.00924	0.00823	0.0101	0.0171	1.80	
Density, lb/ft³				1.5581	0.5794	0.5163	0.6303	1.0692		
ALPM				2.29	8.47	15.10	12.28	7.24		
ACFH				4.84	17.88	31.86	25.91	15.28		

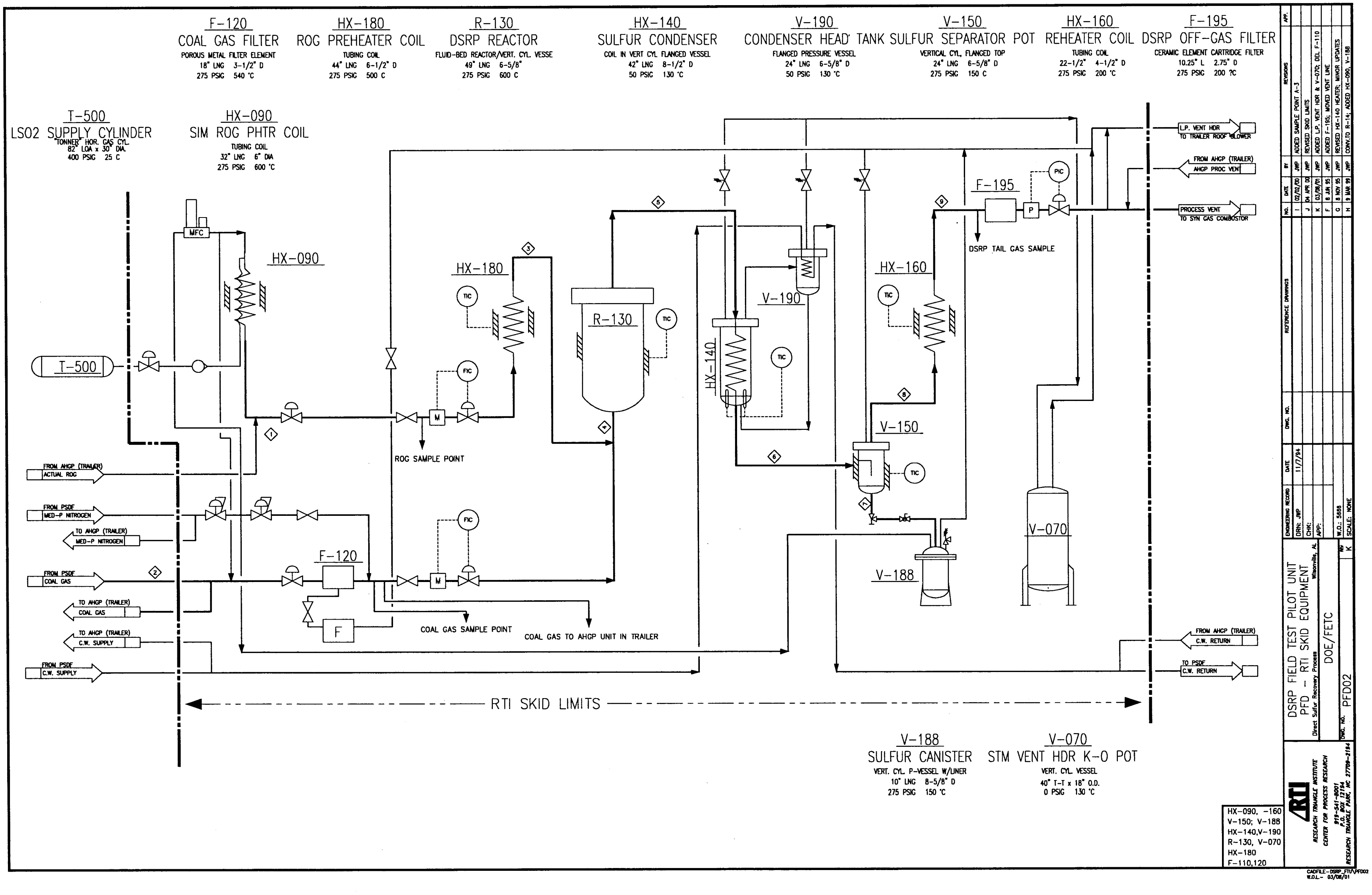

Figure 5. Process Flow Diagram for the Skid-Mounted DSRP Field-Test Unit

3.5 DESIGN HAZARD REVIEW (DHR)

At the request of the SCS personnel at PSDF charged with insuring its safe operation, RTI conducted a detailed DHR of the DSRP field-test unit and the Mobile Laboratory. A rigorous approach was used, such as might be followed for a full-scale process plant. Although research units are legally exempt from the process safety requirement contained in the Occupational Safety and Health Administration (OSHA) rules, SCS personnel felt it prudent to take a detailed look at this relatively unknown equipment to be operated on their site. Thus, RTI was held to the same safety standards as their own personnel. Appendix C reproduces the final report that was generated from the review process.

As a result of the analysis, a number of equipment modifications had to be incorporated for the RTI equipment to be approved for operation at PSDF. The main items are summarized as follows:

1. The pressure relief valves (PSVs) were required to vent to a safe location; therefore, a low-pressure vent header, ducted to trailer roof blower, was added.
2. PSVs on the steam side of the heat exchangers (which might contain water during a pressure relief) were directed to a separate vent header, in which a knockout pot was incorporated.
3. The total height of the test skid was sufficient that OSHA rules governing elevated work platforms came into play, and scaffolding-type permanent platforms with railings were added.
4. The back-pressure in the process vent (to syngas combustor) required additional isolation valves to protect RTI personnel during set-up and maintenance operations.
5. The potential for excessively high pressure in the medium-pressure N_2 supplied from PSDF to RTI meant that additional safety relief valves had to be added in several locations.
6. The potential for exposure to toxic gases from the unit resulted in the need for additional sensor heads to be added to the existing alarm system in the trailer.
7. PSVs had to be added to the analytical system inside the trailer to protect the plastic sample tubing lines.

With these required process and equipment changes, the need for which was only made clear as the dates for field testing approached, RTI staff had to exert a concerted effort to meet the schedule. Appendix D contains the final Piping and Instrumentation Diagrams (P&IDs) for the DSRP field-test unit, including the analytical equipment that was installed inside the Mobile Laboratory trailer. Figure 6 shows the final fabricated DSRP skid with the canopy removed during packing for shipment, and Figure 7 shows the skid and trailer in place at the PSDF in Wilsonville, Alabama.

3.6 DSRP PROCESS CONTROL

As stated above and as described in the 1998 Topical Report (Appendix D), the 6X DSRP test unit did not include process control equipment (hardware and software); for the PSDF testing, a complete, self-contained system was needed. RTI staff spent considerable effort designing and fabricating (including supervising vendor-supplied labor and materials) a control system for the skid-mounted DSRP field-test unit. The core of the system is a programmable logic controller (PLC) with National Instruments' Lookout^{TM} software on a connected personal computer to provide the human-machine interface (HMI). This hardware-software combination is commonly referred to in the process control industry as a Supervisory Control and Data Acquisition (SCADA) system.

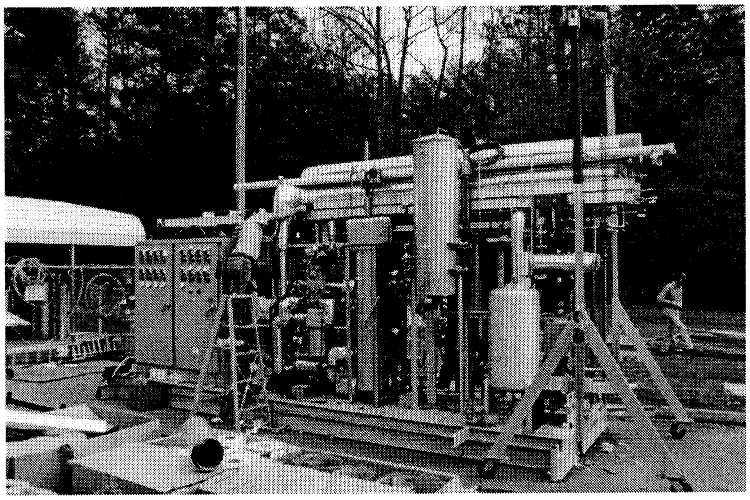

Figure 6. DSRP Skid Without Canopy

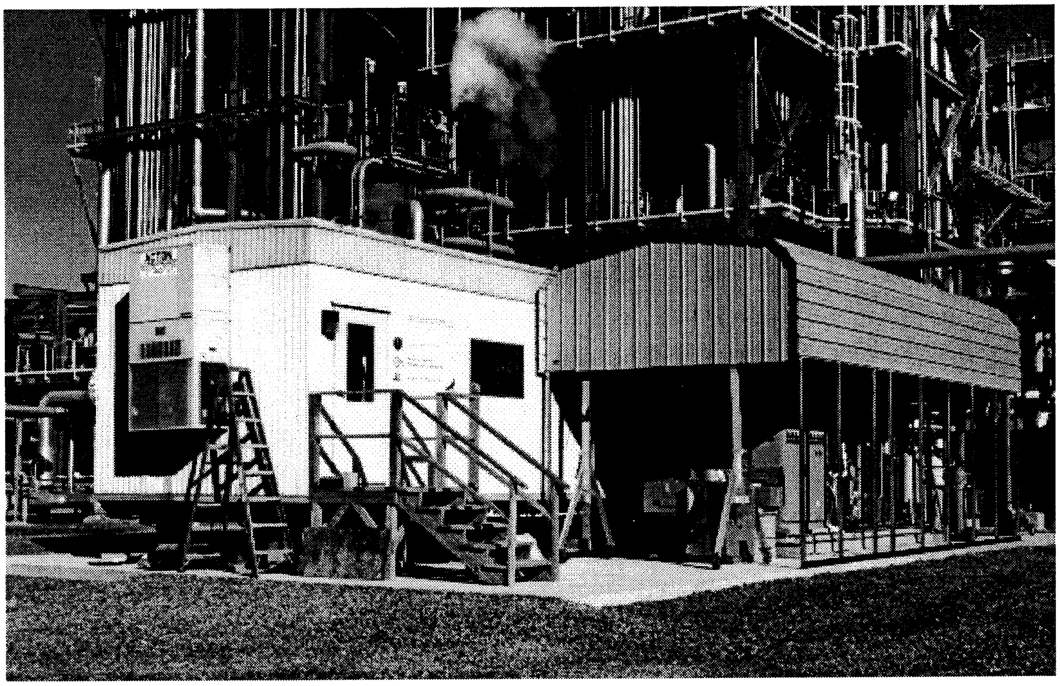

Figure 7. Trailer and Canopy at the PSDF in Wilsonville, AL

The field-test unit SCADA system performs the following functions:

- monitoring (and alarming) of process temperatures and pressures
- remote actuation of three air-operated shutoff valves for ROG, CG, and LSO_2
- modulation of the flow of two streams, ROG and coal gas (CG), through two air-operated flow control valves
- stoichiometric ratio flow control.

The separate heater control panel, mounted on the skid, controls the temperature set points of the furnaces and the heat tracing.

The trickiest control function is that the CG mass flow going to the DSRP reactor must be maintained in precise stoichiometric ratio (*i.e.*, ratio of the chemical components) with the ROG mass flow, taking into account changing chemical composition of both, as well as changing pressure and temperature at the orifice flow meters.

3.6.1 Need for Control of Reaction Stoichiometry

In the early stages of DSRP development, the researchers recognized the need to maintain the reactants in the proper stoichiometric ratio of 2.0. The final report on the bench-scale unit project (DOE Contract No. DE-AC21-90MC27224) makes this point graphically (Gangwal & Chen, p. 17, Figure 6). For example, the percent conversion to sulfur at 14.6 atm was 90% at a H_2S to SO_2 ratio of 1.87 and 84.5% when this ratio was reduced to 1.77.

From an apparatus design standpoint, achieving the correct feed stoichiometry with actual process streams (both ROG and CG), rather than synthetic mixtures prepared from compressed gas cylinders, is challenging. One expects a fair degree of natural fluctuation in composition, temperature, and pressure of actual process streams. Thus, a control system that automatically compensates for these changes (without active operator intervention) is required. As fabricated, the control scheme on the DSRP field-test unit achieves the desired functionality:

- When the operator increases the ROG flow rate, the control system automatically increases the CG flow rate in proportion.
- When the SO_2 content of the ROG decreases randomly, the CG flow rate decreases in proportion.
- When the CO or H_2 content of the coal gas decreases randomly, the CG flow rate increases.
- When the tail gas composition shows less than optimum composition, the operator can change the stoichiometric ratio to change the ratio of CG to ROG flow rate.
- When the temperature and/or pressure of the ROG or CG streams flowing through their respective orifice flow meters change, the flow control valves modulate automatically to maintain the set points based on a mass flow rate value.

3.6.2 Automatic Stoichiometric Ratio Control

The design of the automatic stoichiometric ratio flow control scheme provides the desired functionality by achieving three objectives:

- continuous measurement and control of the mass flow of SO_2 in the ROG (either simulated or actual) to the DSRP reactor
- continuous measurement of the concentration of the reactants in the coal gas (H_2 and CO)
- continuous, automatic adjustment of the mass flow of the coal gas so that the reactants will be introduced into the DSRP reactor in the desired ratio (2:1 mole ratio of reducing components to SO_2) for maximum conversion. This mass flow rate control compensates for any fluctuations in the concentrations of the SO_2, CO, and H_2, as well as fluctuations in the flow rate.

Figure 8 graphically shows the stoichiometric control system logic in a simplified P&ID format.

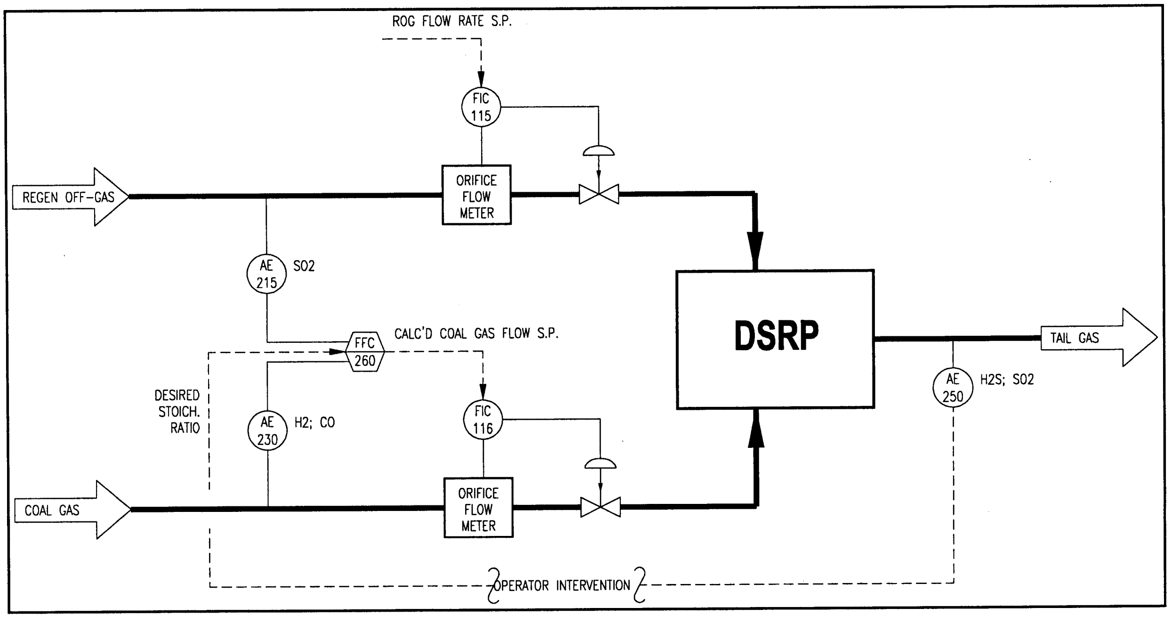

Figure 8. Stoichiometric Ratio PFD

For the purposes of programming the SCADA system, the control system logic can be described stepwise, as follows:

1. Measure the pressure drop across an orifice flow meter in the ROG line.
2. Measure the gas temperature and pressure at the orifice.
3. Based on an approximate molecular weight (keyboard entry by the operator) and pre-defined coefficients for the orifice plate, calculate the mass flow rate of the ROG.
4. Control the mass flow rate of the ROG to the set point value.
5. Measure the volumetric concentration of SO_2 in the ROG.

6. From the mass flow rate and concentration values, calculate the molar flow rate of SO_2.
7. Calculate the required molar flow of reducing components to achieve the desired stoichiometric ratio. (Nominally this value is 2.0, but the operator can input a different value to fine tune the reactor performance.)
8. Measure the volumetric concentrations of H_2 and CO in the coal gas.
9. Calculate the required mass flow rate of coal gas (using a keyboard input value of the approximate molecular weight) to achieve the required molar flow. This value becomes the set point.
10. Measure the pressure drop across an orifice flow meter in the coal gas line.
11. Measure the gas temperature and pressure at the orifice.
12. Calculate coal gas mass flow rate. This value becomes the "process value" or PV input to a proportional control algorithm.
13. Use the control algorithm to modulate the coal gas flow control valve to change the PV in order to satisfy the set point.

Fine-tuning the process control scheme requires operator intervention; in order to determine if the optimum reactant ratio in the reactor feed has been achieved, the operator monitors the composition of the sulfur components in the tail gas.

Appendix E describes in detail the calculations and logic that were programmed into the PLC and HMI of the SCADA system.

3.6.3 Analytical Equipment

The analytical equipment installed in the trailer serves two functions: Process control and process evaluation. In terms of process control, the stoichiometric flow ratio control system (as explained above) requires composition data of the reactor feed streams in order to set the flow rates. The operator needs information on the tail gas composition to fine-tune the stoichiometric ratio.

Determination of the composition of the reducing components of the coal gas requires both a continuous analyzer and a gas chromatograph (GC). The infrared (IR) continuous analyzer measures the CO content, a reducing component, and feeds a continuous analog input signal to the PLC. The IR analyzer also measures the CO_2 content, but that is for interest only; it is not required for process control.

A GC equipped with a thermal conductivity detector (TCD) measures the hydrogen content of the coal gas. This measurement is intermittent (~15-minute cycle); additional software and hardware in the GC's control computer convert the data point into a continuous (but stepwise) analog input.

Another IR-based analyzer measures the concentration of SO_2 in the SimROG and supplies a continuous analog input to the PLC. This is the third analysis input to the process control scheme.

Two separate instruments monitor the tail gas from the DSRP, but neither is directly connected to the process control logic. An ultraviolet-based analyzer continuously measures the H_2S and SO_2 content. This measurement is very useful for observing trends and catching process upsets, but the absolute accuracy is low because the COS present in the tail gas causes an interference. For accurate measurement of all the sulfur species in the tail gas, a GC equipped with a TCD monitors H_2S, COS, and SO_2 on a 10-minute cycle.

3.6.4 Chronology of the Shakedown/Commissioning Test

The test campaign of the PSDF gasifier, designated as GCT-4, was anticipated to start in early March 2001. This date had been rescheduled several times, but by mid-February it was considered fairly firm. In addition to a lined-out gasifier operating on coal feed, the RTI test program also required that the heated slipstream line be functioning properly. Several false starts occurred during March before both of these requirements were satisfied. Finally, on March 24 the coal feed was started for the beginning of a period of several days of gasification. RTI staff immediately traveled to the site and commenced the start-up procedure.

On Monday, March 26, 2001, the field crew attempted to flow coal gas through the slipstream line. After a few start-up glitches, flow was achieved 4 hours later and checkout of the RTI coal gas analytical equipment commenced. Twelve hours later, in the early morning of March 27, the coal gas sample regulator had to be replaced due to plugging.

Following several hours of successful flow control and analysis of the coal gas slipstream, the crew started up the SimROG flow. The DSRP reaction could not be lined out, apparently due to coal gas flow control problems that surfaced. That afternoon it was discovered that the impulse lines on the coal gas flow orifice meter had become plugged; naphthalene was suspected. Both coal gas and SimROG flows were restarted late that afternoon and the process was run continuously but with erratic tail gas compositions.

In an effort to smooth out the composition changes of the SimROG, a design change was incorporated: During the early morning of March 28, the night shift staff relocated the LSO_2 needle valve flow controller to be downstream of the rotameter. They took the opportunity to unplug the coal gas sample regulator again at this time, and restarted the process after only a few hours of downtime. Control of the process definitely improved.

Later in the morning of March 28, the process tail gas sample line became plugged, presumably with elemental sulfur. That line was re-routed and better analyses of the tail gas ensued. At this time, the best period of operation began.

By late morning of March 28, it seemed that enough LSO_2 had run into the process that a sizeable quantity of elemental sulfur should have collected. The collection canister was isolated and opened to reveal only a very small quantity of elemental sulfur. Apparently, the sulfur condenser and separator pot, as designed, had failed to capture the sulfur mist. One hypothesis was that the vessel heat tracing temperature was too high, causing the condensed sulfur to be re-vaporized. Therefore, after reassembly of the collection canister, the set point was lowered.

The unit continued to operate smoothly during the afternoon, until problems developed in controlling the coal gas flow and the LSO_2 flow had to be shut off as the orifice flow meter was worked on. LSO_2 flow was restarted that evening, but had to be shut down because the coal gas differential pressure transmitter impulse lines were once again completely plugged with naphthalene.

The decision earlier in the day to adjust the set point of the heat tracing had an unintended consequence. Around 02:00 on March 29, it became apparent that the outlet piping of the whole system had become plugged. The field crew worked most of that day to disassemble parts of the apparatus to find the plugs, and no LSO_2 feed was permitted that day due to stack testing of the main PSDF stack. The efforts to unplug the system were unsuccessful. As March 30 was the scheduled end of the gasifier run, no further attempts were made to operate the DSRP.

3.6.5 Observed Performance of the DSRP Reactor During Shakedown

For the shakedown/ commissioning test, a generic fluid-bed catalyst was charged to the reactor. Because it was anticipated that potential upsets in operation during the initial runs might cause the loss of some or all of the catalyst charge, an optimized formulation of a fluid-bed DSRP catalyst was not used. Thus, low conversion efficiencies of around 80% were not unexpected.

The longest period of continuous operation was on March 28, 2001, with 13.5 hours of LSO_2 feed. The best performance of the DSRP reaction was during the period from 11:00 to 14:00; Table 2 summarizes the operating conditions.

Table 2. Operating Conditions on March 28, 2001, During Period of Best Performance

General Operating Conditions	
Reactor pressure	202 psig
Reactor temperature	
Bottom of reactor (inlet)	275 ºC
Catalyst bed (1" above frit)	570 ºC
Catalyst bed (7" above frit)	515 ºC
Catalyst bed (14" above frit)	515 ºC
SimROG	
Flow rate	37 SLPM
SO_2 concentration	10 vol%
Coal Gas	
Flow rate	34 SLPM
CO concentration	9-10 vol %
H_2 concentration	approx. 8 vol%

During this time period, the tail gas composition showed H_2S to SO_2 in the preferred 2:1 ratio, indicating that the optimum 2:1 ratio of reducing gas to SO_2 had been achieved in the feed. As Figure 9 shows, the tail gas sulfur compound concentrations were somewhat high, however, indicating that the SO_2 conversion was lower than expected. As calculated from the gas analyses, approximately 79-82% of the SO_2 in the inlet was converted to elemental sulfur in the 11:00-14:00 time period.

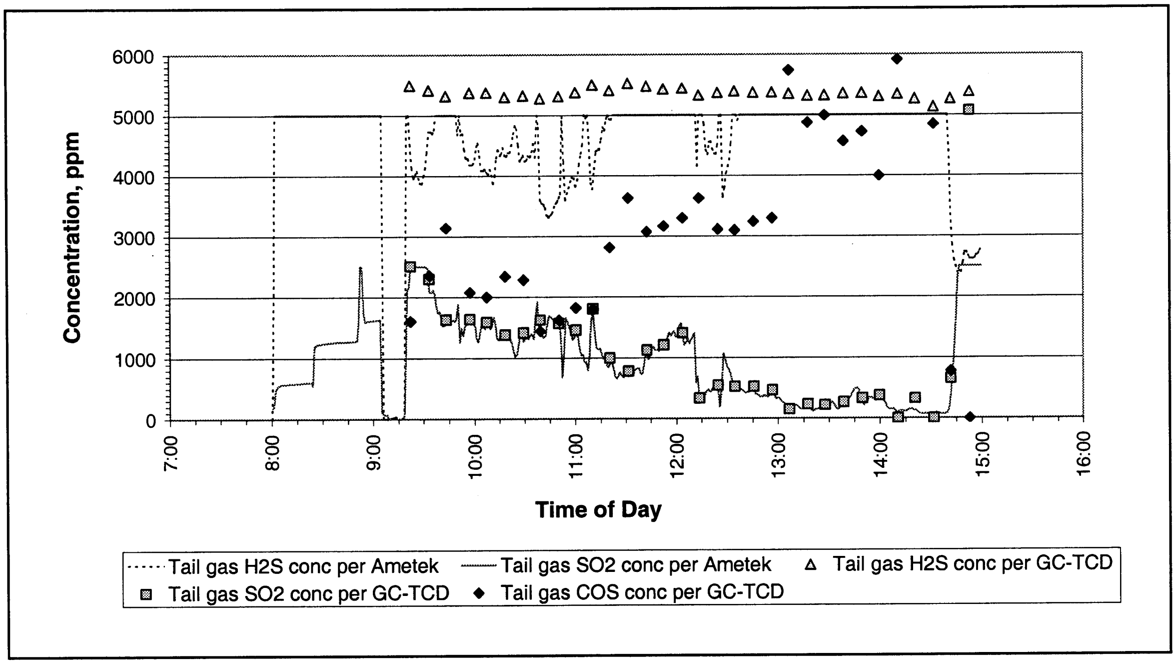

Figure 9. Tail Gas Composition, March 28, 2001

Table 3 presents the material balance derived (in part) from the observed performance of the field-test unit. The measured syngas compositions are used at the actual operating pressure, which was lower than design (202 psig [1.39 MPa] compared to 279 psig [1.92 MPa]). The content of the reducing components in the coal gas, H_2 and CO, was also much lower. To calculate the material balance, the extent of the reaction was inferred from the measured tail gas composition and was used to calculate the reactor outlet stream. The overall effect is that the expected yield of elemental sulfur in this material balance (201 g/h) is considerably lower than the design value (613 g/h).

Because the DSRP reaction is highly exothermic, a significant rise in catalyst bed temperature is expected when LSO_2 feed is started. Figure 10 plots the temperatures logged by the SCADA system for the four thermocouples on the inside of the reactor. A bed temperature rise of 150 °C (over a period of approximately 3 hours) occurred when the LSO_2 feed was re-started at 02:42. Similarly, a 150 °C-drop occurred over a period of about 4 hours when the LSO_2 feed was cut off at 16:13. Calculations performed during the DHR suggested that a catalyst bed temperature rise of over 300 °C should be expected, based on full conversion of the feed SO_2 and minimal heat leak from the reactor. The less-than-expected temperature rise is confirming evidence of the low conversion.

An interesting observation with this test run is the importance of the COS in the tail gas, which accounted for 6 to 7 percentage points of the 20% of the sulfur in the feed that remained in the tail gas.

Table 3. Approximate Material Balance During Operation on March 28, 2001

Compound	Molar Weight (MW)	Stream 1 CG Slip-stream	2 Liquid SO_2	3 Nitro-gen	4 Sim-ROG	5 Feed to DSRP	5A Reactor Make	5B Cond. Outlet	6 Sulfur Make	7 DSRP Tail Gas
COMPOSITION IN MOLE FRACTION										
CH_4	16.043	0.0000								
CO	28.0134	0.1100				0.0579	0.0058	0.0058		0.0060
CO_2	44.01	0.0800				0.0421	0.0927	0.0927		0.0963
H_2O	18	0.0800				0.0421	0.0744	0.0744		0.0773
H_2	2.016	0.0700				0.0369	0.0037	0.0037		0.0038
H_2S	34.08	0.0005				0.0003	0.0003	0.0003		0.000275
SO_2	64.063		1.0000		0.1001	0.0474	0.0063	0.0063		0.006593
S	32.064					0.0000	0.0381	0.0381	1.0000	0.0008
COS	60						0.0019	0.0019		0.002015
O_2	31.9988									
N_2	28.0134	0.6595		1.0000	0.8999	0.7733	0.7767	0.7767		0.8068
Total		1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
MW of mixture		26.68	64.06	28.01	31.62	29.02	28.99	28.99	32.06	28.87
FLOW RATE IN GRAMS PER HOUR										
CH_4	16.043	0				0	0	0		0
CO	28.0134	274				274	27	27		27
CO_2	44.01	313				313	687	687		687
H_2O	18	128				128	225	225		225
H_2	2.016	13				13	1	1		1
H_2S	34.08	2				2	2	2		2
SO_2	64.063		513		513	513	68	68		68
S	32.064						205	205	201	4
COS	60						20	20		20
O_2	31.9988						0	0		0
N_2	28.0134	1,644		2017	2017	3661	3661	3661		3661
Flow rate (kg/h)		2.374	0.513	2.02	2.53	4.90	4.90	4.90	0.201	4.70
Flow rate (g/s)		0.66	0.14	0.56	0.70	1.36	1.36	1.36	0.06	1.30
Flow rate (lb/hr)		5.23	1.13	4.45	5.58	10.81	10.80	10.80	0.44	10.35
FLOW RATE IN VOLUMETRIC UNITS										
SLPM		33		27	30	63	63	63		60
SCFH		75		61	68	143	143	143		137
SCFM		1.26		1.02	1.13	2.39	2.38	2.38		2.29
gal/hr			0.10						0.030	
gal/day									0.72	
cc/min			6.20						1.86	
Temperature (°C)		538	21	21.	599.	599.	427.	135.	21.	204.
Temperature (°F)		1000	70	70	1110	1110	800	275	70	400
Pressure, atm, abs		15.29	24.82	21.41	15.29	15.29	14.95	14.75	1.00	2.02
Pressure, psig		210	350	300	210	210	205	202	0	15
Density, g/cc			1.379	0.02486	0.00676	0.00620	0.0076	0.0128	1.80	
Density, lb/ft^3				1.5581	0.4239	0.3890	0.4734	0.8005		
ALPM				1.35	6.24	13.17	10.77	6.37		
ACFH				2.85	13.16	27.80	22.81	13.49		

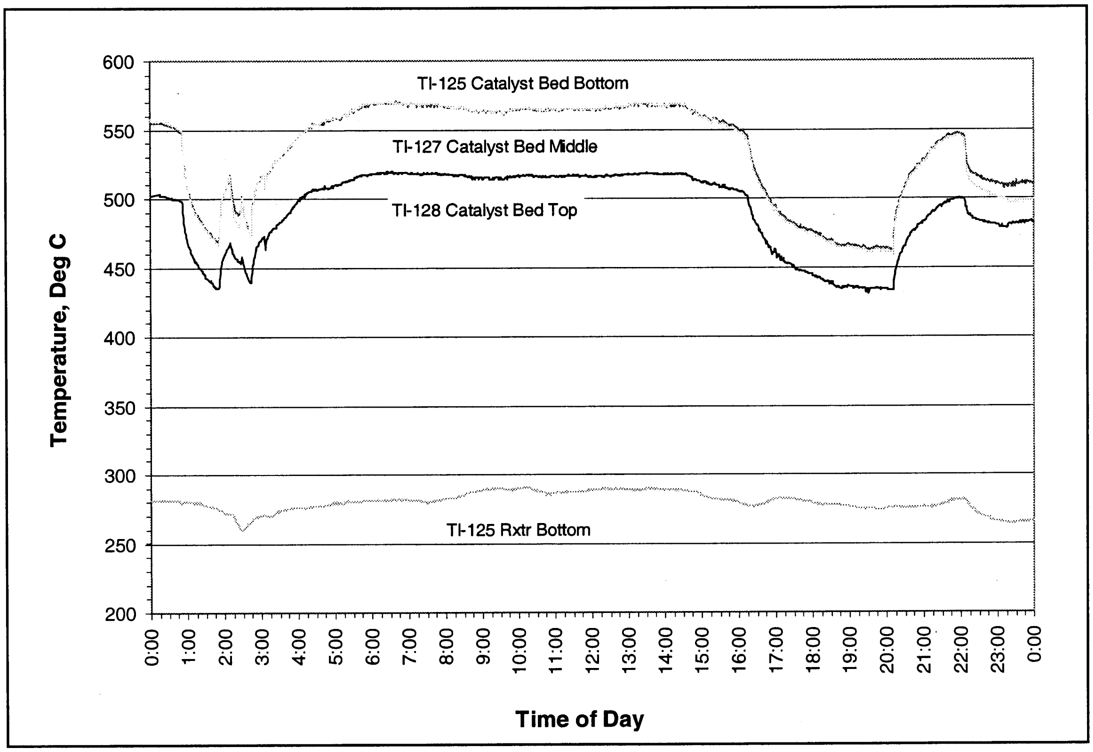

Figure 10. Reactor Temperatures, March 28, 2001

3.6.6 Lessons Learned from the Shakedown/Commissioning

Table 4 summarizes the on-stream time for the shakedown test. Syngas was passed through the fluid-bed reactor in the field-test unit for a total of 54 hours. During that time, SimROG (from vaporization of liquid SO_2) was being fed for 30 hours.

Although the skid-mounted DSRP field-test unit was operated for only a relatively brief period of time, a great deal of valuable information was gathered. That the unit was able to be run at all represents the accomplishment of many significant project milestones by both RTI and Southern Company Services at PSDF:

- completed construction of the skid-mounted DSRP field-test unit at RTI
- completed modification of the Mobile Laboratory (trailer) for use as the control room for the skid-mounted DSRP
- designed and fabricated a PLC-based SCADA-type process control system
- constructed both the skid and the trailer to meet the requirements of the designated test site, PSDF, in terms of safety and interface/operability
- shipped the skid and trailer to the PSDF site in Wilsonville, Alabama
- installed the skid and trailer at the PSDF site
- connected the systems to the PSDF-supplied process and utility lines
- passed coal gas through a long, heat-traced slipstream line and successfully measured its flow and composition

Table 4. Summary of On-Stream Times

Time	Syngas			LSO$_2$		
	On	**Off**	**Elapsed**	**On**	**Off**	**Elapsed**
3/26/01 14:05	√					
3/26/01 16:15		√	2:10:00			
3/26/01 17:00	√					
3/27/01 5:25		√	12:25:00			
3/27/01 6:00	√					
3/27/01 7:52				√		
3/27/01 13:17					√	5:25:00
3/27/01 13:30		√	7:30:00			
3/27/01 15:50	√					
3/27/01 16:25				√		
3/28/01 0:35					√	8:10:00
3/28/01 1:50				√		
3/28/01 2:24					√	0:34:00
3/28/01 2:42				√		
3/28/01 16:13					√	13:31:00
3/28/01 20:10				√		
3/28/01 23:15					√	3:05:00
3/28/01 23:15		√	31:25:00			
TOTAL			**53:30:00**			**30:45:00**

- generated a simulated ROG by safely vaporizing LSO$_2$
- controlled the skid-mounted DSRP field-test unit remotely using the SCADA system, and logged useful process monitoring data.
- demonstrated that the process control system could continuously monitor the reactor inlet streams and adjust the coal gas flow rate automatically to maintain the required feed stoichiometry.

The shakedown test achieved its intended purpose of identifying areas of improvement as follows:

- The major issue to be resolved will be elimination of naphthalene plugging of the sample and impulse lines.
- The heat tracing in several locations needs to be improved in order to eliminate cold spots and sulfur plugging.
- The main reactor furnace needs to be changed so that the desired reaction temperature of 600-630°C can be achieved.
- The control system instrument parameters need fine-tuning to smooth out the responses.
- The sulfur collection system needs to be improved so that the sulfur mist can be captured effectively.

SECTION 4
CATALYST CANISTER EXPOSURE TESTING

As described in Section 1, field testing based on simple exposure of the catalyst to the coal gas can be an economical means of determining the possible deleterious effects of trace contaminants. The technique is limited to fixed-bed pellets, however, as the much smaller particles of the fluid-bed catalyst cannot be contained in a perforated canister.

The primary focus of this phase of the DSRP research program was fluid-bed reactors. However, the anticipated longer duration operation of the PSDF gasifier presented a good opportunity to obtain additional exposure data on fixed-bed material.

4.1 CANISTER EXPOSURE

The plan, as with the Morgantown/GE tests described previously to determine if the catalyst had been degraded, was to test the exposed catalyst pellets in the bench unit in the RTI lab with SimROG and simulated coal gas. The key performance parameter is the 1-stage efficiency of conversion of SO_2 to elemental S, with the following variables:

- Exposed vs. non-exposed
- Pretreatment technique used (A vs. B).

Two canisters of catalyst pellets were prepared following two different pre-treatment techniques. These pretreatment techniques are not described here because they are proprietary.

The canisters were fabricated from perforated stainless steel, as Figure 11 shows, and placed on an interior support ring on the "clean" side of the Westinghouse PCD (candle-filter type particulate control device in the PSDF gasifier main train). Figure 12 is a photograph taken during a shutdown of one canister in place in the partially disassembled PCD.

Based on information supplied by SCS (Figure 13), the canisters saw 876 hours of coal gas flow over the course of two years (August 1999 to April 2001).

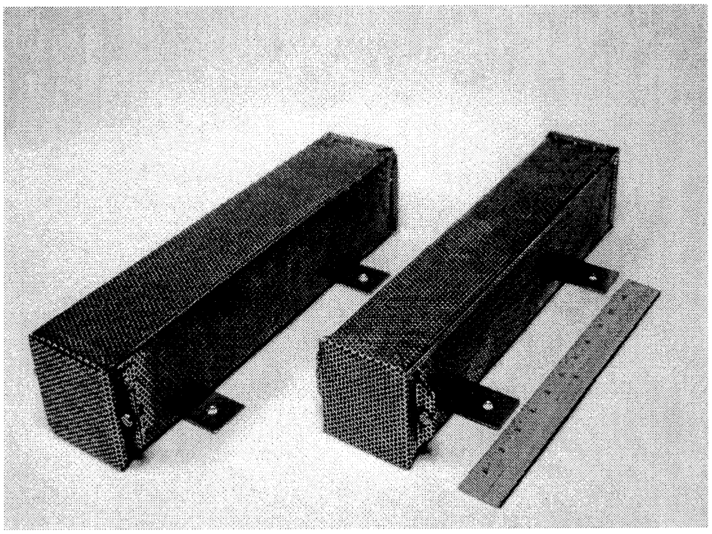

Figure 11. Perforated, Stainless Steel Canister

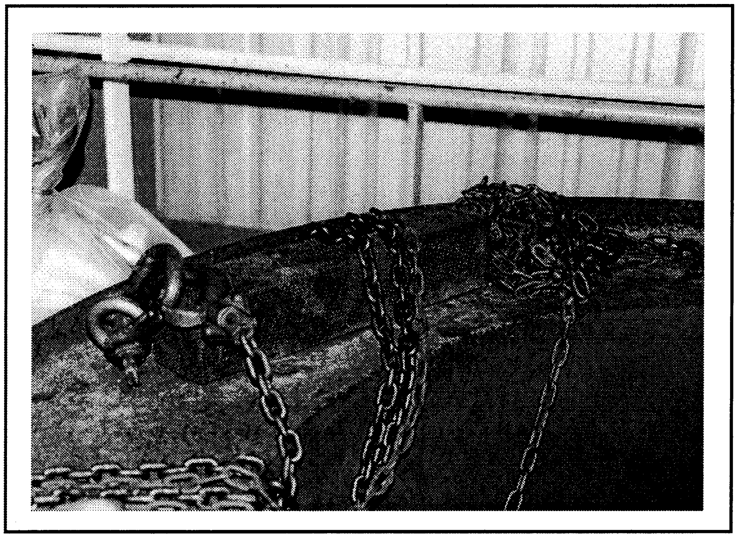

Figure 12. Canister and Westinghouse PCD

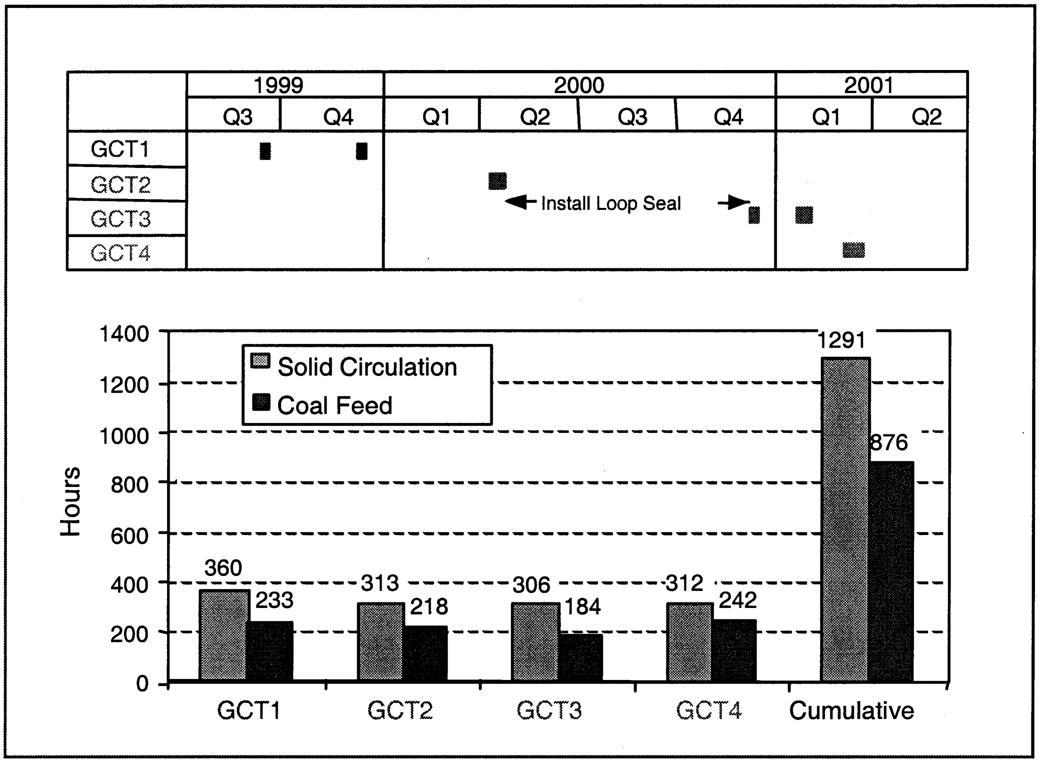

Figure 13. Transport Reactor Gasification Operations

4.2 BENCH UNIT TEST RESULTS

A 36-h bench-scale test of the PSDF-exposed canister catalyst was conducted using RTI's HTHP bench-scale unit. One liter of the catalyst was placed in a 3.0-in i.d. cage and loaded in the reactor. The catalyst was tested for DSRP efficiency at 280 psig, 600°C (1112°F), and 2000 scc/(cc.h) with a SO_2-coal gas mixture containing 2.5 vol% SO_2, 2 vol% H_2, 3 vol% CO, 5 vol% steam, 0.1 vol% H_2S, and the balance N_2. The conversion of the inlet sulfur compounds to elemental sulfur was 85-90%—as compared to the 98% conversion performance of freshly activated catalyst—and remained at this level throughout the 36-h test, indicating negligible carbon burn-off during the test.

Table 5. Analysis of DSRP Catalysts

	Fresh, unactivated	Freshly activated	PSDF exposed
Active ingredient (wt%)	0.04	3.03	1.06
Surface area (M2/g)	188.5	168.3	80.8
Pore volume (cm3/g)	0.59	0.52	0.26

To explain the lower performance of the PSDF-exposed catalyst, fresh catalyst, freshly activated catalyst, and PSDF-exposed catalyst were analyzed as shown in Table 5. The surface area and pore volume of the PSDF-exposed catalyst were lower by about 50% each. In addition, the PSDF-exposed catalyst contained nearly 67% less active ingredient than the freshly activated catalyst. The results indicated sintering and removal of active ingredient from the PSDF-exposed catalyst due to oxygen exposure at PSDF, offering a possible explanation for the lower performance of the PSDF-exposed catalyst as compared to freshly activated catalyst. The oxygen exposure at PSDF occurred during startup and in between gasification runs.

SECTION 5
FLUID-BED CATALYST DEVELOPMENT

In order to operate the DSRP field-test unit in the fluid-bed mode, it was essential to obtain a sufficient quantity of a suitable catalyst material. RTI conducted catalyst development studies during FY98 in preparation for the field test; using synthetic gas mixtures several candidate fluid-bed catalysts were tested in the bench-scale DSRP unit in the Research Triangle Park laboratory. Appendix B contains the full report describing the catalyst development program.

Two candidate catalysts were developed, Catalyst A with an alumina support and Catalyst C with a proprietary support. Catalyst A was more active than Catalyst C, but had a lower attrition resistance. Catalyst A achieved 98% single-stage sulfur conversion whereas Catalyst C achieved only around 90%. The attrition of Catalyst A in a 20 hour ASTM attrition test was 7.2% whereas that of Catalyst C was estimated to be only around 1%. Although the higher conversion with Catalyst A is attractive, it needs further development to increase attrition resistance, thereby reducing catalyst losses in commercial application.

SECTION 6
CONCLUSIONS AND RECOMMENDATIONS

DSRP is an efficient regeneration off-gas treatment process for sorbent based treatment processes that remove H_2S and COS from coal gasifier gas. In this project, the process has been developed to a small pilot-scale. Sulfur conversions as high as 98% have been demonstrated with a single-stage reactor with simulated and actual coal gases in both fixed-bed and fluidized-bed modes. Catalyst durability has been verified by canister exposure tests of over 1,000 hours.

As DSRP is a tail-end process, its further scale-up and demonstration needs to be carried out in parallel to the development of the front-end hot-gas desulfurization process. To this end, discussions are currently ongoing with ChevronTexaco to demonstrate the DSRP in conjunction with their gasifier-quench system that is to be coupled to a hot-gas desulfurization process at 250°C (482°F).

SECTION 7
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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

S.K. Gangwal
J.W. Portzer
Research Triangle Institute
P.O. Box 12194
Research Triangle Park, NC 27709

Prepared for

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

May 1998

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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:

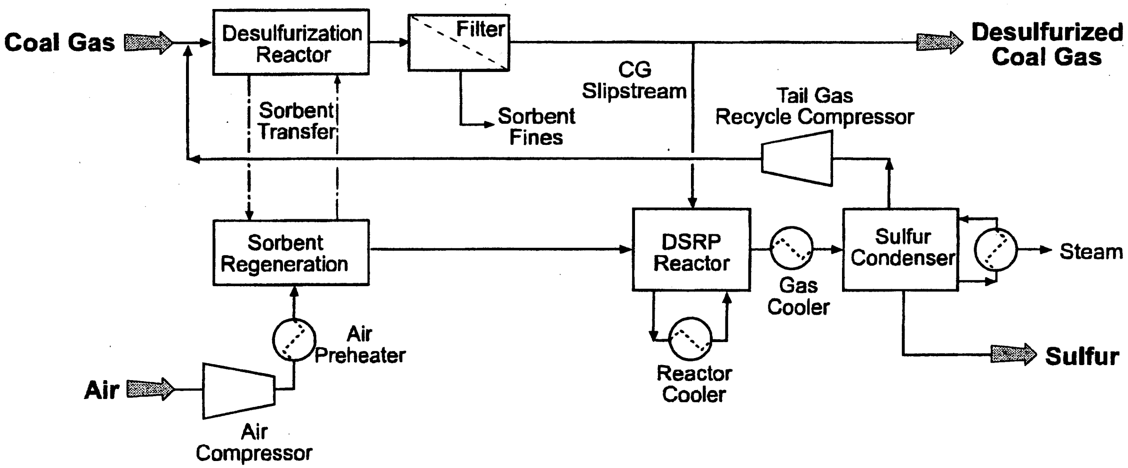

Figure ES-1. Hot gas desulfurization/DSRP integration.

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

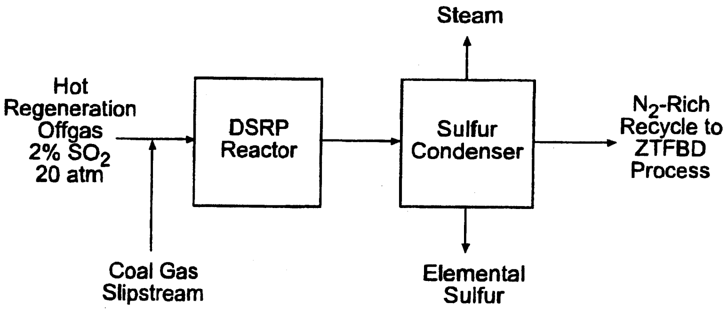

Figure ES-2. New single-stage DSRP.

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

The Research Triangle Institute (RTI) gratefully acknowledges the assistance and guidance of the current FETC contracting officer's representative (COR) on this project, Mr. Thomas P. Dorchak, and that of the former CORs, Mr. Daniel C. Cicero and Dr. Suresh Jain. RTI also wishes to thank the FETC-Morgantown in-house staff for their enthusiastic support during the slipstream test campaign, and Dr. Raul Ayala at General Electric Corporate Research and Development, Schenectady, New York, for conducting the operations to expose the Direct Sulfur Recovery Process (DSRP) catalyst to the pilot plant coal gas. Valuable contributions to the work were provided by Dr. Brian S. Turk, Mr. Gary B. Howe, Mr. Peter M. Grohse, Mr. K. David Carter, Mr. Daryl D. Smith, Mr. Dan A. Ward, and many others at RTI.

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.

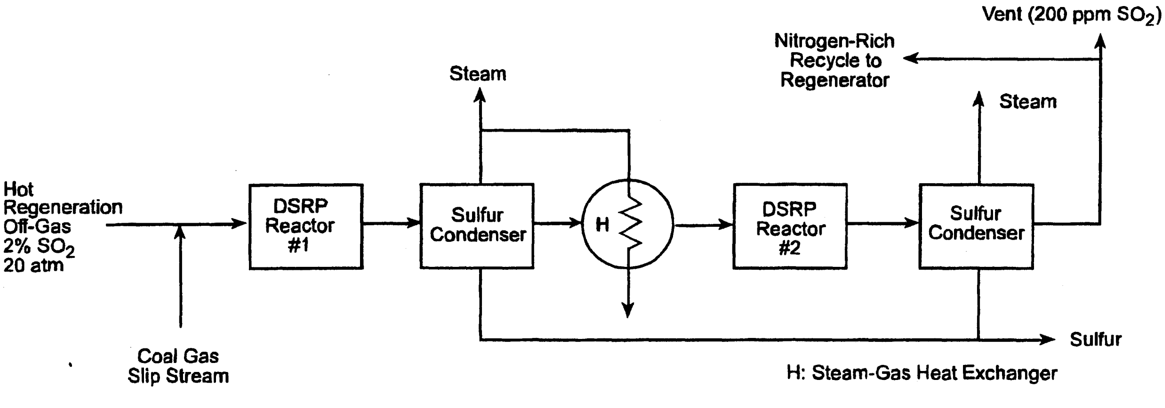

Figure 1. Process schematic for the original two-stage DSRP design.

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.

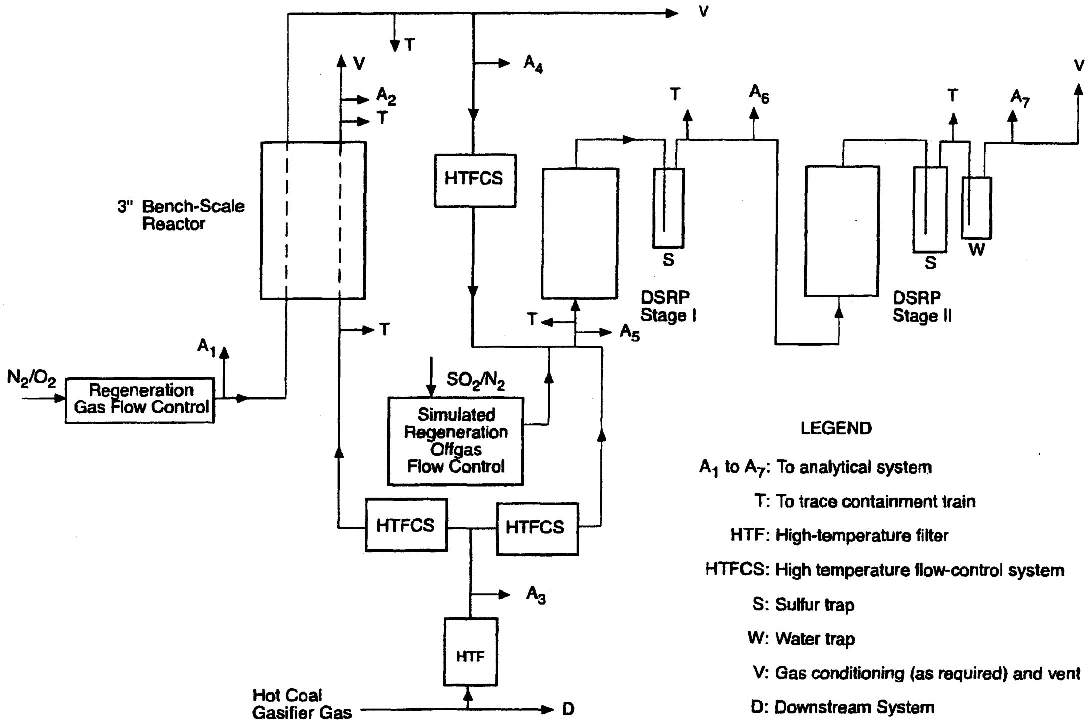

Figure 2. Integrated zinc titanate and DSRP reactor system.

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	$<10\ \mu g/m^3$
Se	$<16\ \mu g/m^3$
Hg	$<2\ \mu g/m^3$
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.

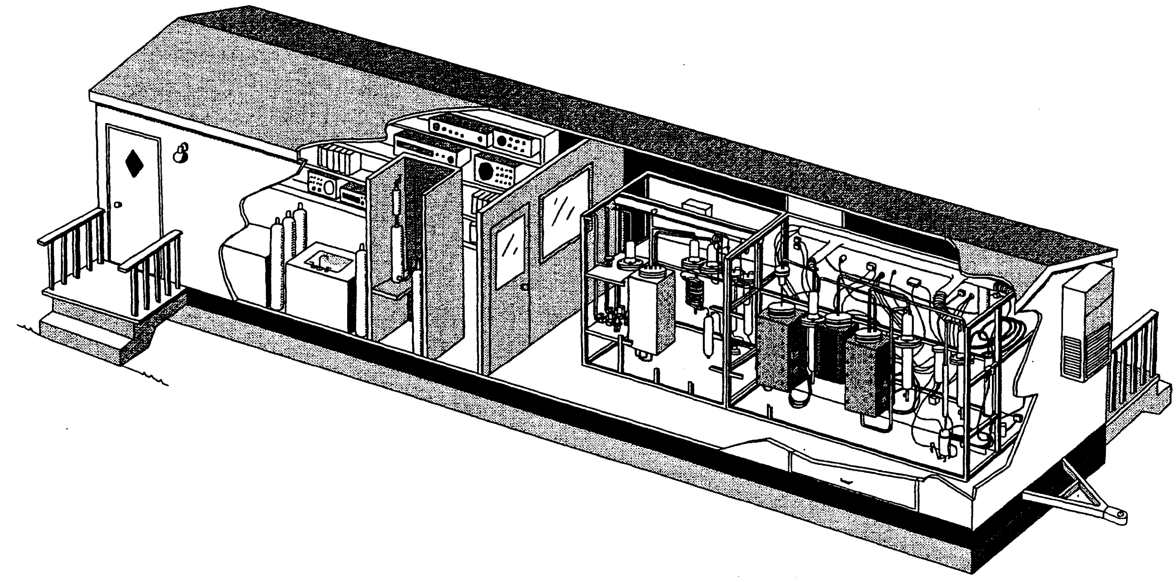

Figure 3. Artist's concept of trailer.

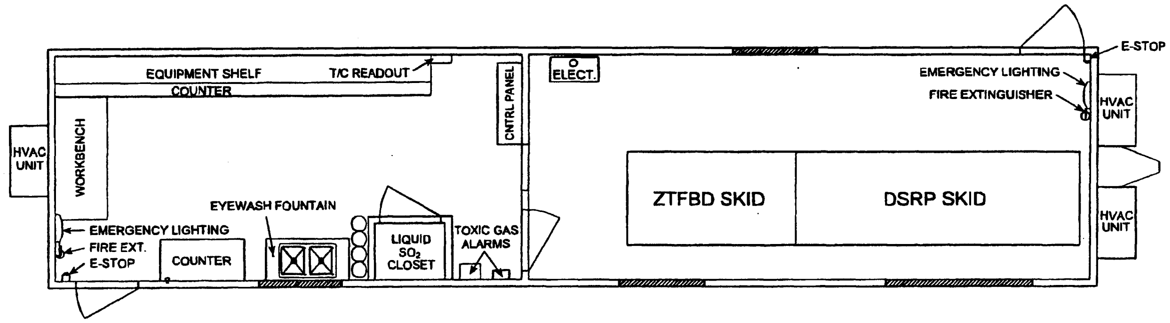

Figure 4. Floor plan showing equipment layout.

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.

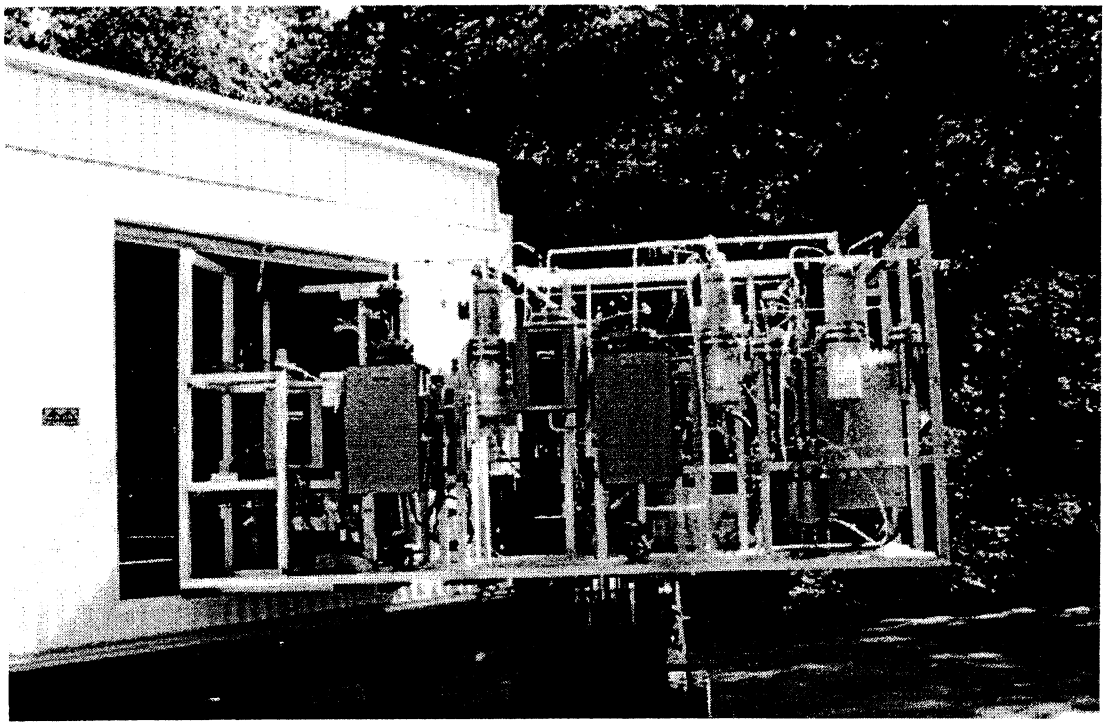

Figure 5. Equipment skids being loaded inside.

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.

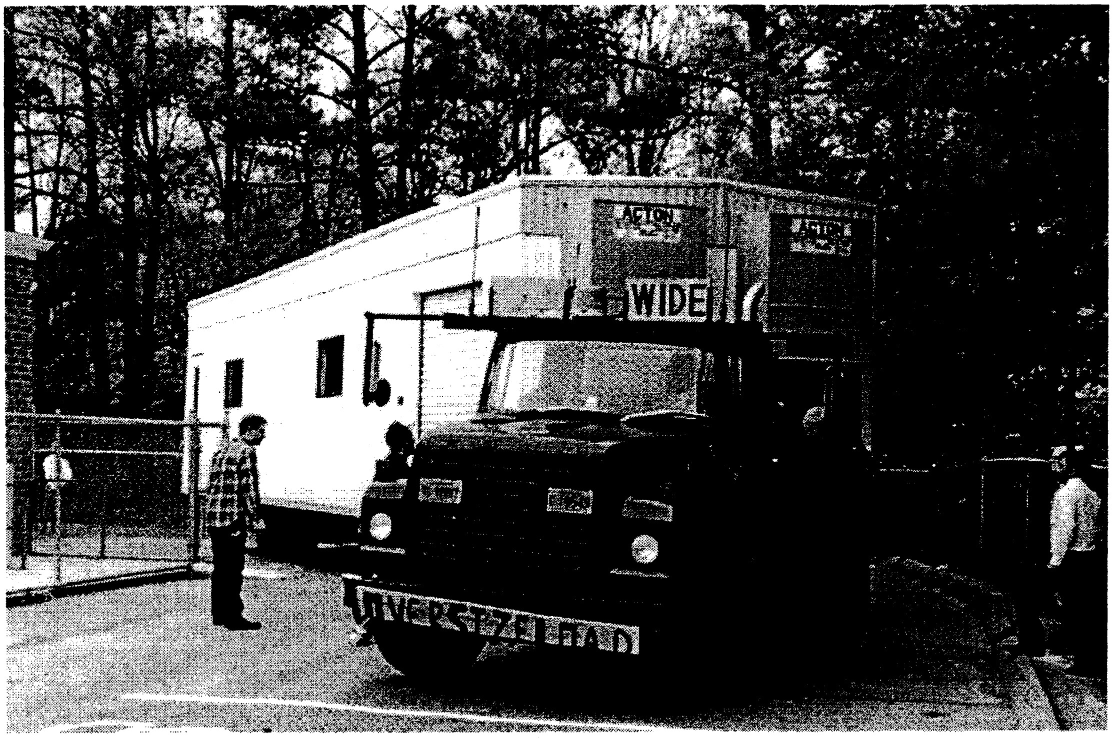

Figure 6. Truck leaving RTI with trailer.

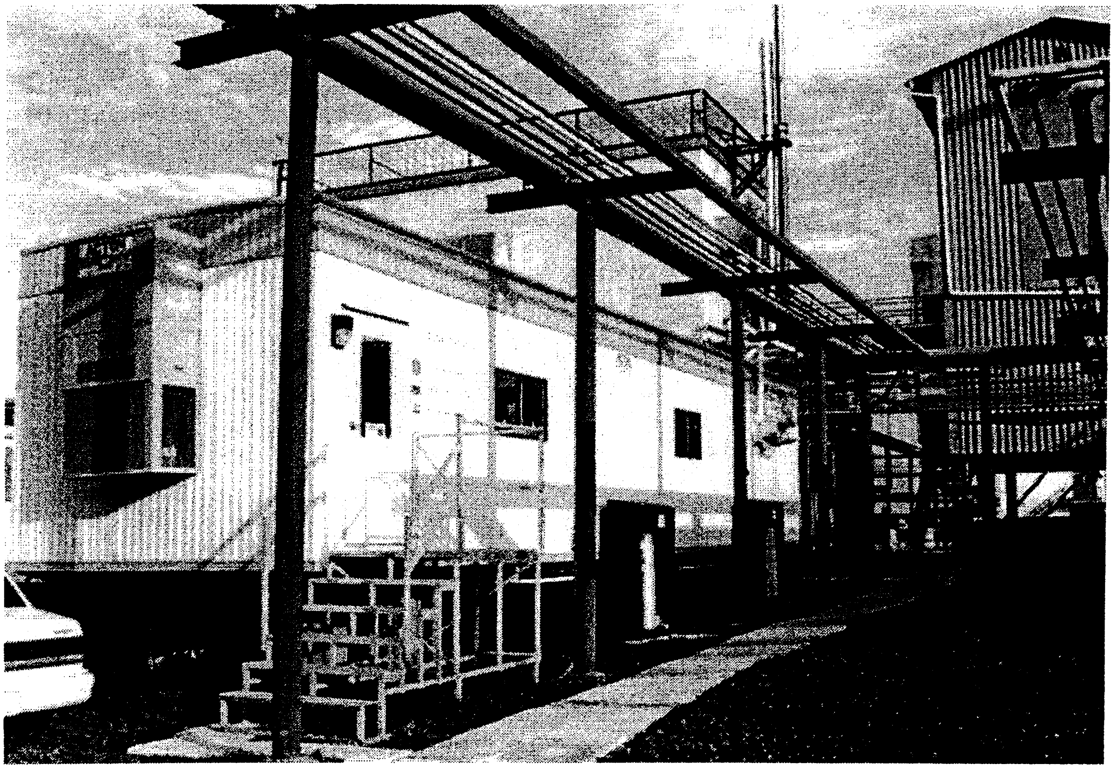

Figure 7. Trailer in position at FETC-Morgantown.

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	**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_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

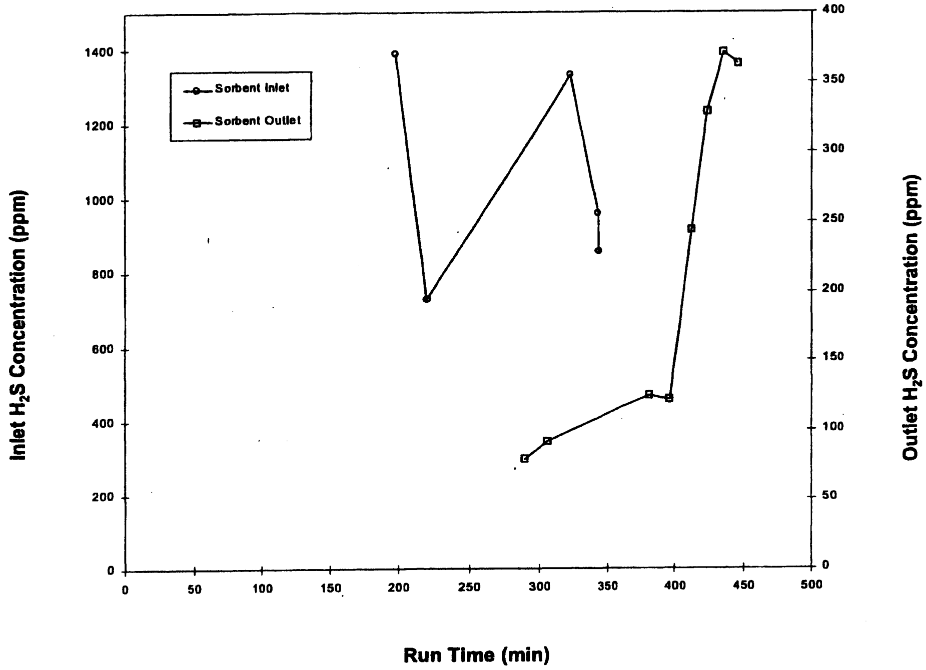

Figure 8. Sorbent sulfidation curves (9/13/94).

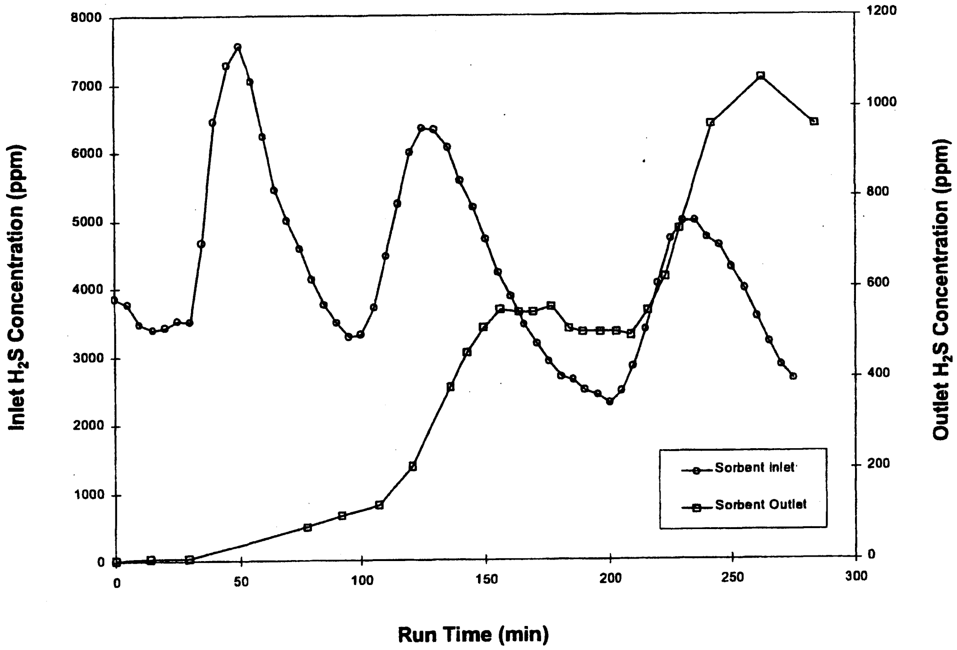

Figure 9. Sorbent sulfidation curves (9/14/94).

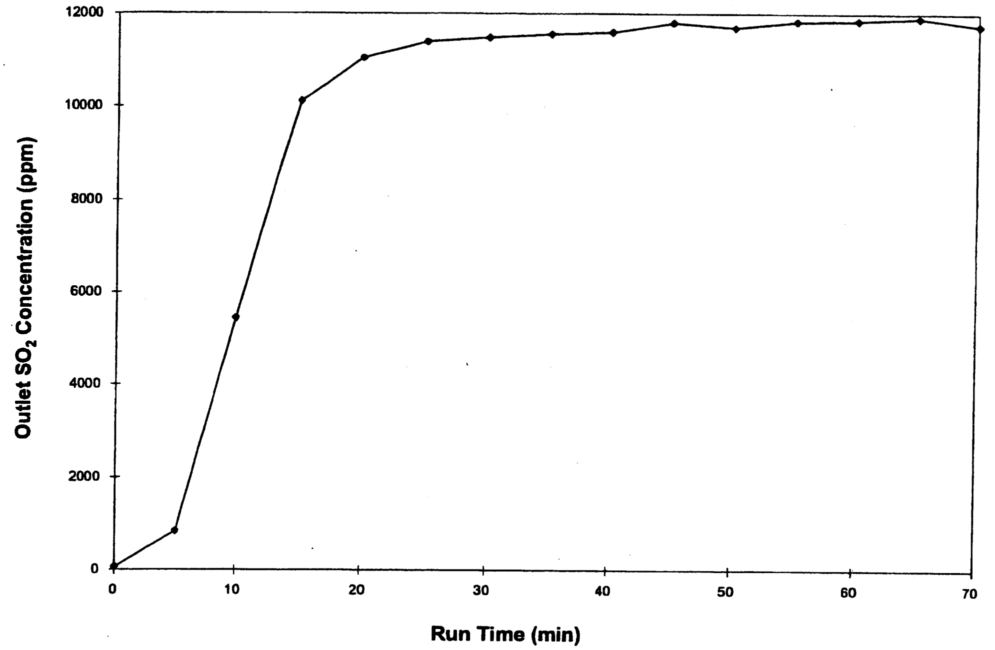

Figure 10. Sorbent sulfidation curves (9/15/94).

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

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

The DSRP unit did experience some plugging problems that resulted in unscheduled outages. The very small flow of coal gas used by the DSRP means that the HTHP control valve that is required is very small. It tended to plug if there were any particulate matter in the coal gas. The high-temperature ceramic filter on the RTI equipment was apparently not completely effective and suggests that for small equipment a SS filter may be better. There were also some problems with sulfur plugging in the cold end of the unit that required depressurization and disassembly to unblock, suggesting that keeping the exit gases hot will be necessary for continuous operation, free of plugs.

There was one time period when it appeared that the "RTI Interface Line" that FETC-Morgantown had installed between the MGCR and the RTI trailer had become plugged. Efforts to clear the line while maintaining system pressures were not effective. Subsequently, the line was taken out of service and some particulates were removed from the line when it was depressurized and disassembled. Because this cleanup did not reveal any large amount of solids, it remains unclear as to why there was apparently no flow for awhile.

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

2.3.3 Chronology of Run

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

Monday, October 24,1994

00:01 Startup sequence initiated by FETC-Morgantown.
08:45 RTI personnel started heating up furnaces, etc., in RTI trailer.
16:00 The operators for the MGCR started hot nitrogen flowing through their unit, and also into the RTI Interface line connected to the RTI trailer. Hot nitrogen began flowing into RTI's ZTFBD unit.
16:40 Coal gas started flowing into the MGCR and simultaneously into the interface line. Started **Sulfidation Run #1.**
22:30 H_2S breakthrough at 1,100 ppm (according to the Carle GC on sample point A-2). Stopped Sulfidation Run #1 (total time was 5:50).
23:14 Started **Regeneration Run #1** with ***integrated operation of the DSRP.***

Tuesday, October 25,1994

00:32 End of Regeneration Run #1 (total time 1:18).
02:05 Began **Sulfidation Run #2.**
09:08 H_2S breakthrough at approximately 1,000 ppm. End Sulfidation Run #2 (total time was 7:03). Set up trace contaminant sampling trains.
12:20 Started coal gas flowing for **Regeneration Run #2.**
12:30 Started air flowing for Regeneration Run #2. The acid gas trace contaminant sampling train was used on Stage I offgas (TCT-5) and the multimetals sampling train was used on the regeneration offgas (TCT-3).
13:46 End of Regeneration Run #2 (total time 1:16). At this point, the DSRP was depressurized and hardware modifications were made to move the sample point for the Western SO_2 analyzer from A-4 to A-5A (which is more suitable when DSRP is run using LSO_2). In order that both sample points would be available in the future without depressurization again, sample conditioning equipment was cannibalized from sample point A-5 for use with A-5A. During this time period it was also determined that the Omega MFC (being used as a flow meter) installed on the DSRP (designated FT-240 on the P&ID) was no longer functioning properly and it was removed from the system.
18:13 Started LSO_2 flowing and adjusted controller by comparing with Western SO_2 analyzer.
18:43 Started coal gas flowing into DSRP for start of **DSRP/LSO_2 Run #1.**
23:30 Problems with maintaining coal gas flow were noted; assumed problem was plugging of Badger control valve FCV-2.

Wednesday, October 26, 1994

00:12 Stopped coal gas flow; took nitrogen through interface line. End of DSRP/LSO_2 Run #1 (total time 6 h).

01:15 Started **Sulfidation Run #3.**

10:10 Continuing Sulfidation Run #3; some irregularity noted in automatic control of Badger valve FCV-1. Coincident with plugging problems noted by MGCR operators. Nitrogen was substituted for coal gas in MGCR (and, hence, in interface line) for approximately 1 h. During this time the multimetals trace contaminant sampling train was running on raw coal gas (TCT-1), and the acid gas train was running on the Stage I offgas (TCT-5).

11:10 MGCR advised RTI that coal gas was flowing in MGCR again, and that the gasifier had started taking chloride-doped coal.

11:30 Coal gas flow through the interface line was interrupted at RTI's request so that maintenance could be performed on FCV-2 (DSRP).

12:11 Coal gas flow to sulfidation run restarted.

14:10 End of Sulfidation Run #3 with H_2S breakthrough of >3,000 ppm H_2S (total time: 13 h). Set up trace contaminant sampling trains.

16:10 Coal gas flow to DSRP started for **DSRP/LSO_2 Run #2.** The ammonia trace contaminant sampling train was run on Stage I offgas (TCT-5), and the acid gas train was run on Stage II offgas (TCT-6).

17:49 Run was stopped when it was determined that little or no coal gas was actually flowing. Various means were attempted to clear the line; evidence suggested that the FETC-Morgantown interface line (or orifice) was plugged. DSRP was left hot with 67 std L/min of nitrogen flowing through it.

Thursday, October 27,1994

AM FETC at the Morgantown site and EG&G staff worked to clear the Interface Line. RTI worked to re-install sample conditioning equipment at Sample Point A-5 (cannibalized from Point A-3) in order to run Carle GC on mixture of regeneration gas and coal gas as an additional aid to determination of coal gas flow rate.

12:00 Coal gas was available again, through the interface line. RTI could not operate DSRP, however, due to sulfur plugging in cold end. Attempted to clear the plug; eventually switched to alternative flow path in cold end train #2. Drained sulfur condenser #1. No sulfur was collected in condensers #2 and #3.

16:26 Started LSO_2 flowing for **DSRP/LSO_2 Run 3.**

16:27 Started coal gas flowing. The multimetals trace contaminant sampling train was run on the first stage offgas (TCT-5).

20:10 Plugging in DSRP noted; stopped DSRP/LSO_2 Run 3. Determined that cold end train #2 had plugged. Worked to clear plugging from cold end.

23:19 Started LSO_2 and coal gas flowing for **DSRP/LSO_2 Run 4**.

Friday, October 28, 1994

05:12 Safety relief valve on Sulfur Condenser #1 popped. Coal gas released to equipment room; detected by toxic gas monitoring system. Coal gas flow stopped; end of DSRP/LSO_2 Run 4.

10:00 MGCR advised that they were going off coal gas for approximately 24 h. Also, gasifier operators decided to stop feeding coal and go into a "hot hold" with no coal gas production for approximately 24 h. RTI determined that the #1 sulfur condenser was leaking process gas into the water jacket. The condenser was drained of sulfur, removed from service, and disassembled. The leak was determined to be in the coil; a new coil was fabricated and the condenser was reassembled and reinstalled by 18:00. Sulfur was also drained from condenser #3; none was collected in condenser #2.

21:00 FETC-Morgantown advised RTI that the gasifier team had decided to stop the run due to the discovery of a heat-deformed pipe in the ash-removal system. RTI turned off heat to furnaces and heat tracing. Left a small nitrogen purge through the equipment. Bled off the unused LSO_2 to the incinerator stack.

Saturday, October 29, 1994

All Day FETC operating crews at Morgantown had finished up during the night. RTI staff cleaned up and put away equipment. Finished purging SO_2. Diluted reagents from the trace sampling project were disposed of. Sorbent, catalyst, and recovered sulfur samples were removed and packed for transport back to RTI. Some instruments and tools were removed and packed for transport. Cooling water was removed from the system. All equipment was depressurized; cylinders were capped, power to the control panel and the equipment skids was shut off. The HVAC units were left on with set points of 55 and 80 °F for heating and cooling, respectively.

Table 8 shows the summary of total hours.

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

2.3.4 Results

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

Points to note in Table 9 are that H_2S 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 H_2S breakthrough curve during Cycle 3 is shown in Figure 11. The sorbent exhibited excellent removal efficiency and capacity even with highly variable inlet H_2S values. Sorbent regeneration, which went very smoothly, is shown in Figure 12. Note that with 2.25 percent O_2 in the inlet, nearly two-thirds, i.e. ~1.5 percent SO_2 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_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

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

[a] 3.0-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) (N_2 + SO_2)-DSRP tests were conducted using the FETC gasifier coal gas. During the integrated tests, it was not possible to obtain steady-state operation in the short duration of the regeneration half-cycle due to the larger time constant (~2 h) of the DSRP. However, three of the simulated SO_2-DSRP tests were highly successful. One of the simulated SO_2-DSRP tests was not successful due to plugging of the coal gas line from FETC's gasifier. The results of the successful DSRP tests are shown in Table 13. Note that in Run 1, with fresh catalyst, an extremely high sulfur conversion (up to 99.7 percent) is achieved. Some selectivity toward H_2S is seen in later runs, although even in these tests a 96 percent sulfur conversion level is achieved.

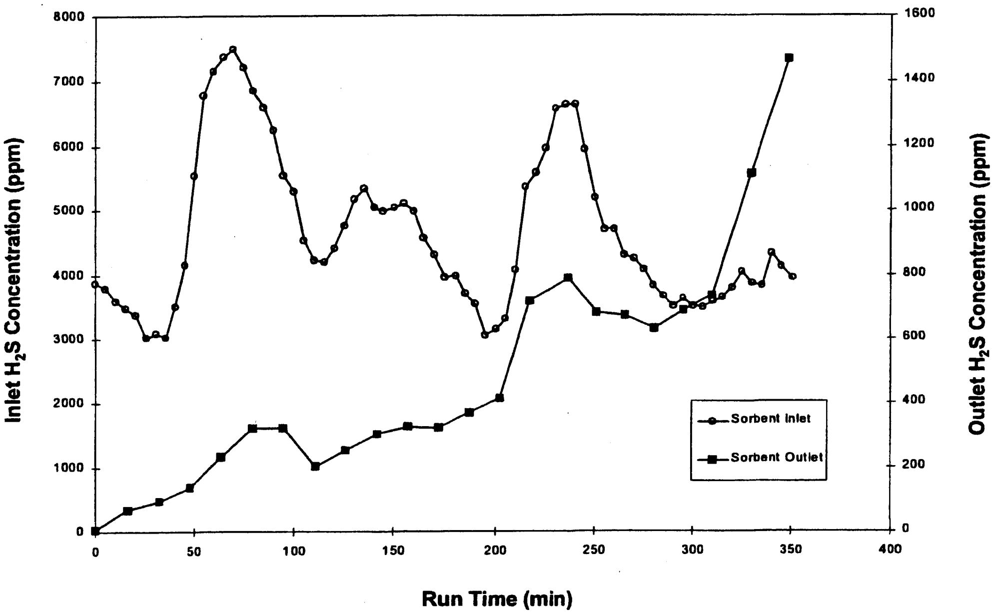

Figure 11. Sorbent sulfidation curves (10/24/94).

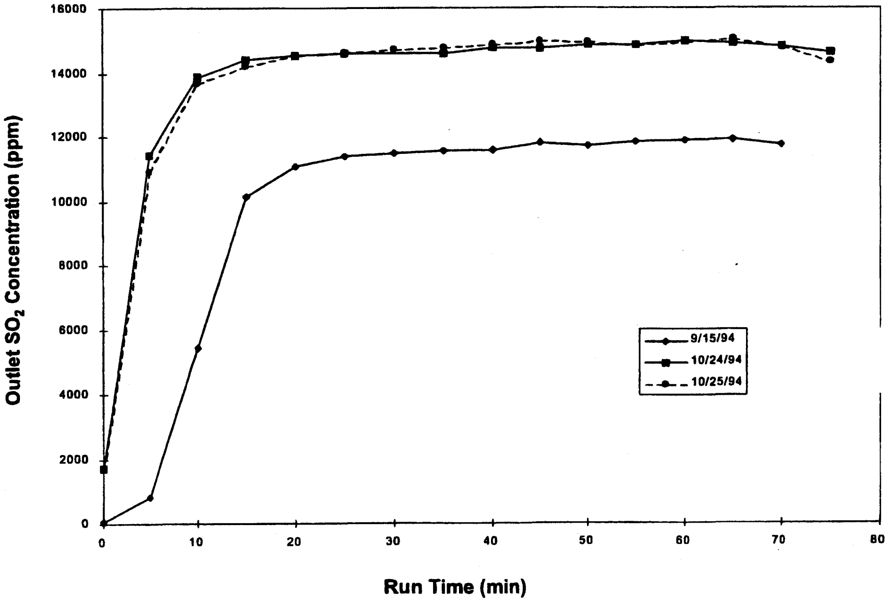

Figure 12. Sorbent regeneration curves.

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

[a] NM = Not measured.

Table 12. DSRP Stage I Reactor Conditions

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

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:

$$2H_2O + (3/n)S_n \rightarrow 2H_2S + SO_2 .$$

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 O_2 at 650 °C in an atmospheric pressure TGA. Compared to a typical ZT-4L, sulfided using simulated coal gas, it appeared that the mobile lab ZT-4L, sulfided using actual coal gas, regenerated slower. Some poisoning of the regeneration active sites due to trace contaminants was suspected. Several trace contaminants were measured on the sulfided ZT-4L and the results are compared in Table 15.

The increase in concentration of As, Pb, or other metals in the sulfided materials is noteworthy and could have contributed to the slower regenerability. However, controlled tests on ZT-4L with H_2S and metal vapor addition are needed to ascertain this. The estimated gaseous concentrations based on the measurements are about 100 μg/m^3 for As and 10 to 40 μg/m^3 for Se. No Hg was detected in the gas or sorbents.

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_2S (%)	SO_2 conversion to sulfur (%)
Run No. 1			
32	99.4	0.0	99.4
36	99.4	0.0	99.4
40	99.5	0.0	99.5
44	99.7	0.0	99.7
48	99.5	0.0	99.5
52	98.5	0.0	98.5
56	98.0	0.0	98.0
Run No. 3			
117	99.6	1.2	98.4
121	100.0	4.1	95.9
125	100.0	4.9	95.1
129	100.0	2.4	97.6
Run No. 4			
175	100.0	4.9	95.1
179	100.0	4.1	95.9
183	100.0	4.9	95.1
199	100.0	4.7	95.3

Table 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

2.3.4.2 Sulfur Purity

The sulfur purity of the DSRP sulfur was examined using a DSC. Figure 13 compares the DSC profile of pure sulfur obtained from the drugstore with that of sulfur obtained from the DSRP condensers. There are three phase transitions that are typical of sulfur. The middle transition, due to melting, occurs at the same temperature for all samples. There is a slight shift in the other two transitions for the "DSRP" sulfur versus the "drugstore" sulfur. This could be due to small amounts of undissolved metal impurities in the DSRP sulfur caused by corrosion of the SS vessel or due to metal vapor in the coal gas (such as AsH_3 or H_2Se) 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 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

[a] NA = Not available.

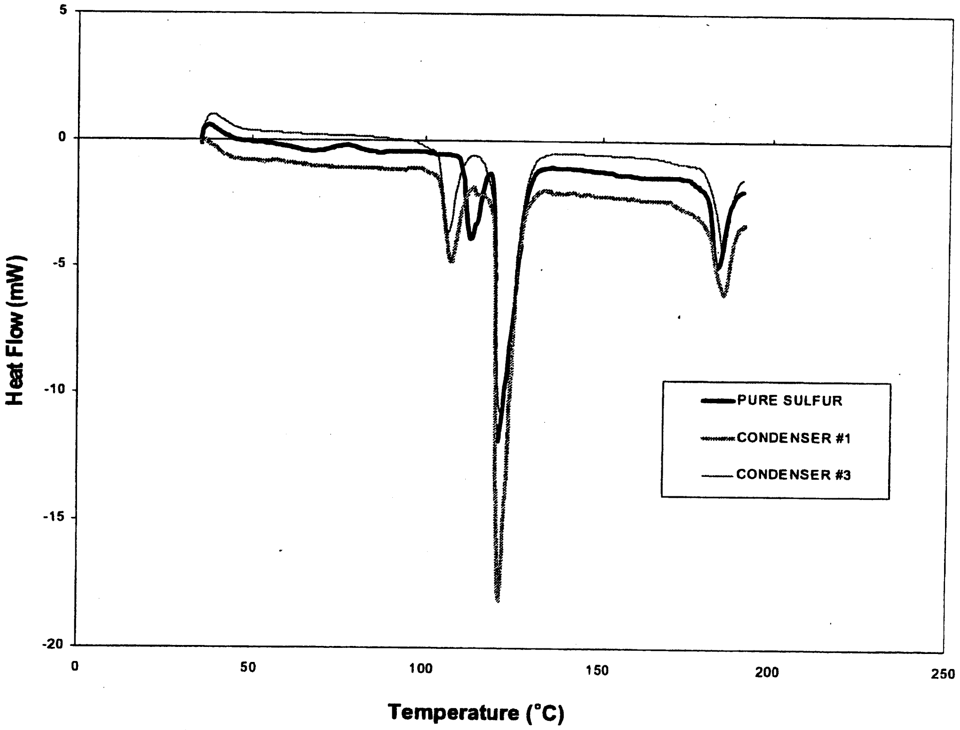

Figure 13. DSC test of pure sulfur and sulfur from DSRP.

2.4 DESIGN/CONSTRUCTION FOR 1995 FIELD TEST

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

- A 160-h test of single-stage DSRP with actual coal gas and simulated regeneration
- A 100-h test of 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

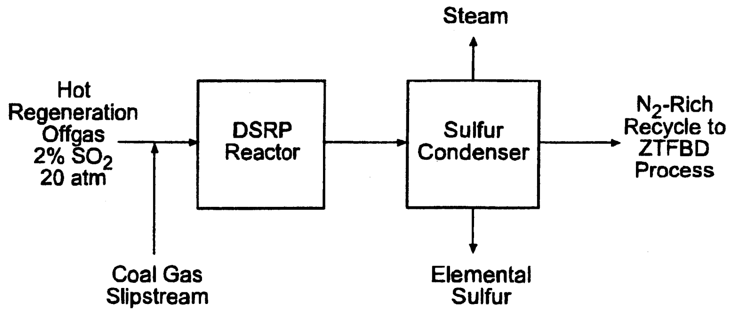

Figure 14. New single-stage DSRP.

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 Nm^3/h (70 std L/min) of synthetic regeneration offgas with 1.4 to 4.9 percent SO_2
  - 0.45 Nm^3/h to 0.96 Nm^3/h (7.5 to 16 std L/min) of actual coal gas
  - Space velocity of 5,100 std $cm^3/cm^3 \cdot h$.

- ZTFBD unit operated at
  - 1.1 MPa (150 psig)
  - 780 °C
  - 4.1 Nm^3/h (68 std L/min) of actual coal gas
  - Space velocity of 5,000 std $cm^3/cm^3 \cdot h$.

- DSRP catalyst exposed to coal gas for 160 h.

- DSRP took coal gas 91 percent of the time it was available from FETC-Morgantown.

- DSRP operated with simulated regeneration offgas (LSO_2 flowing; producing molten sulfur) for nine periods during run, totaling 44 h.

- NH_3 decomposition catalyst exposed to coal gas for 102 h.

2.5.2 Summary of Results

- Single-stage DSRP design resulted in high conversion of sulfur compounds to elemental sulfur—98+ percent during steady-state operation.

- No effect on DSRP of the trace contaminants in actual coal gas over duration of run; conversion at end was as high as at beginning.

- Measured NH_3 decomposition ranged from 85 to 95 percent (depending on analytical technique).

- No effect of exposure time on NH_3 decomposition.

2.5.3 Chronology of July 1995 Run

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

The initial operating strategy was to operate the DSRP for 160 h continuously with coal gas feed and simulated regeneration offgas (using vaporized LSO_2). In parallel, the ZTFBD unit was to operate for 100 h. Startup of both units was smooth, and after about 3 h of operation, steady-state performance of the DSRP was achieved. Unfortunately, after the DSRP had been operating with coal gas for only 4 h, the FETC gasifier shut down. This initial period of operation was designated as **Run #1.**

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

For **Run #3**, which was contiguous with Run #2 and started about noon on July 18, the DSRP reactor furnace setpoint was raised 20 °C. This caused the reaction temperature (the bottom catalyst bed temperature) to increase from 612 to 622 °C. The sulfur plugging in the low-temperature DSRP outlet piping was first noticed during this run. The flow of LSO_2 was stopped briefly several times during this run in order to allow time for clearing plugs.

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

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

The morning of July 19 was spent clearing sulfur plugs from the outlet piping and devising a temporary piping arrangement that would permit back-pulsing of the coal gas (Mott) filter. At this point in the test program it became apparent that with continuous operation of the DSRP with LSO_2 feed, the production rate of sulfur by the reactor system was overwhelming the capacity of the offgas system (including the knock-out pot) to handle it. It was surmised that not all of the condensed sulfur was being removed from the gas stream by the separator pot. The presumed "mist" was then being vaporized in the reheater, passing through the back-pressure control valve as a vapor, and finally condensing elsewhere in the cool offgas system either as a crystalline form or as a sublimed "flowers of sulfur" form. A decision was made to modify the operating strategy for the remainder of the test program.

The new operating plan was to run coal gas through the DSRP at all times in order to expose the catalyst for 160 h. The nitrogen portion of the simulated regeneration offgas would also be flowing through the DSRP reactor. The LSO_2 would only be run at selected times to observe how the catalyst was continuing to perform. The coal gas flow was restarted the afternoon of July 19 with the revised operating plan.

The coal gas filter back-pulsing procedure was followed for the first time, and it successfully reduced the pressure drop across the Mott filter from 517 to 69 KPa (75 to <10 psi). At this time the small Balston filters were removed from trace contaminant sampling points TCT-1 and TCT-2 (on the ZT unit). It was decided that gas from those sample points would not have large amounts of particulate that would clog the sampling apparatus and so would need to be filtered out in order to get reliability. Furthermore, any small amount of particulate should preferably be collected as part of the sample in order to get a valid reading of the trace contaminants present.

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

Coal gas flow was restarted the evening of July 19 and continued to flow through the night. The flow was interrupted in the late morning in order to install the cooling coil inside the knock-out pot. LSO_2 was not used again until the afternoon of July 20, the start of Run #6. There were a number of control problems encountered during this run. The pressure had to be continually decreased due to rising pressure drop across the coal gas filter. The output of the Western SO_2 analyzer appeared to be at odds with the reading on the LSO_2 rotameter. A brief experiment in which the automatic valve on the LSO_2 supply was closed showed an immediate effect on the rotameter but no effect on the Western reading. Only a very brief period of steady-state operation was achieved during this run. The LSO_2 flow was stopped in the late afternoon of July 20, and coal gas continued to flow.

A modification was made to the DSRP equipment to add heat tracing to the LSO_2 feed line where it intersected the nitrogen line upstream of the preheater. This modification was expected to prevaporize the liquid and ensure more complete mixing of the stream before the sample point for the Western SO_2 analyzer. The results were apparent during Run #7 on the afternoon of July 21. The analyzer output was steady and consistent with the rotameter reading. Steady-state operation was achieved easily.

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

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

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

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

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

With the coal gas flow restored on the evening of July 26, **Run #8** was started. A higher SO_2 concentration (3.6 percent compared to 2.5 percent typically for the previous runs) was used, with the same DSRP furnace set points, so that the reaction temperature was slightly higher. Some experimentation with controllability of the process was attempted, as described below.

Following several hours of operation of Run #8 with LSO_2 flowing, the flow of coal gas into the DSRP unit was stopped briefly, in order to clear sulfur plugs. Even with the additional cooling inside the knock-out pot, sulfur (vapor or aerosol) apparently passed through and into the outlet piping. Plugging continued to be observed at tees and elbows in the 19-mm (3/4-in.) outlet piping. Plugging in the 1-in. line outside the trailer was also suspected. Coal gas flow through the DSRP unit was restored to continue exposing DSRP catalyst to coal gas.

Later in the morning of July 27 a problem was noted with coal gas flow through the ZT unit. A plug in the condensate receiver was cleared. But then later that afternoon a plug developed in the ZT outlet piping so that coal gas would no longer flow. The hypothesis was that with a reduced temperature in the ZT reactor (but not a cold reactor) the nickel-based ammonia decomposition catalyst was causing a dissociation of the CO in the coal gas to carbon and CO_2. The soot particles could then plug up the outlet piping. The outlet lines were not disassembled, though, to test this hypothesis.

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

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

The final DSRP runs were started during the late evening of July 28. For **Run #9A** the goal was to achieve the best operation possible, with operating conditions the same as earlier in the run. This was achieved with an operating temperature of 620 °C, 1.8 MPa (250 psig), and 3.5 percent SO_2 in the simulated regeneration offgas. For **Run #9B** the system pressure was raised to 1.9 MPa (265 psig)—the maximum that could be achieved given the pressure of the coal gas, and the observed pressure drop through the Mott coal gas filter. Steady-state operation was easily achieved.

For the final experiment of the 160-h DSRP test run, **Run #9C**, the nitrogen flow making up the simulated regeneration offgas, was reduced, thereby increasing the SO_2 concentration. A distinct increase in reactor temperature was noted. There was some difficulty getting the proper coal gas flow to line out the unit. During this time the LSO_2 in the supply tank was exhausted, so the DSRP runs were ended.

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

DSRP Engineering/Design Success Stories

- Automatic/stoichiometric computer control of coal gas resulted in smooth operation of DSRP for extended periods.
- Automatic control of DSRP system pressure using HTHP control valve improved the stability of the system pressure.
- LSO_2 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 SO_2 inlet concentration.
- The SO_2 response time from sample point A6 probably needs to be improved. An apparent lag time was suspected, perhaps caused by the Drierite trap. An alternative sample preparation approach could probably be devised.
- More alarms are needed to alert operators who are monitoring a continuous process for long hours. A relay board with annunciator could be interfaced with existing process monitoring and control software.
- The MFC used as a meter for the ZTFBD unit was ruined when water inadvertently was drawn backwards through it from the vent header. A similar problem occurred in the 1994 test program. A more rugged flow metering scheme (e.g., orifice flow meter) would be required to make the process immune from this type of problem.
- The mechanical BPRs used on the ZTFBD unit experienced a small amount of plugging (for no apparent reasons). This may be corrosion-induced; the concept of using BPRs in a flow stream that is potentially moist needs to be reevaluated.
- The "Mott" porous metal filter was very effective at eliminating plugging in the coal gas control valve. However, since the filter itself plugged up, a proper back-pulsing system needs to be designed into the piping layout.

2.5.4 Details of Results/Parametric Studies

2.5.4.1 Data Reduction

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

The flow rate of nitrogen making up the synthetic regeneration offgas was known from the electronic MFC. The concentration of SO_2 in the mixture of nitrogen and vaporized LSO_2 was measured by a continuous SO_2 analyzer, so that the molar flow rate of SO_2 into the reactor could be calculated. The coal gas flow into the reactor was measured on a wet basis by the orifice flow meter used as part of the flow control instrumentation. The composition of the coal gas (H_2S, H_2, and CO) on a dry sample basis was measured by an online GC/MS operated by FETC and located near the gasifier. The water content of the coal gas was determined gravimetrically from timed condensate samples, by FETC (with confirming information from RTI condensate sampling). The wet basis coal gas composition was then calculated, and the molar flow rates of H_2S, H_2, CO and H_2O were determined.

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

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

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

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

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

2.5.4.2 Summary of Results

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

2.5.4.3 Parametric Studies

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

Table 16. Summary of July 1995 DSRP Test Runs

										Run #9		
		Run #1	Run #2	Run #3	Run #4	Run #5	Run #6	Run #7	Run #8	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)

[a] System pressure when steady-state.

[b] Probably false high value from SO_2 analyzer. Based on LSO_2 rotameter, the concentration was probably actually about 1.4%.

[c] Additional heat tape added to LSO_2 line for this and subsequent runs. SO_2 analyzer values should be more reliable.

[d] Calculated percent reduction of sulfur compounds in 96% based on inlet SO_2 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.

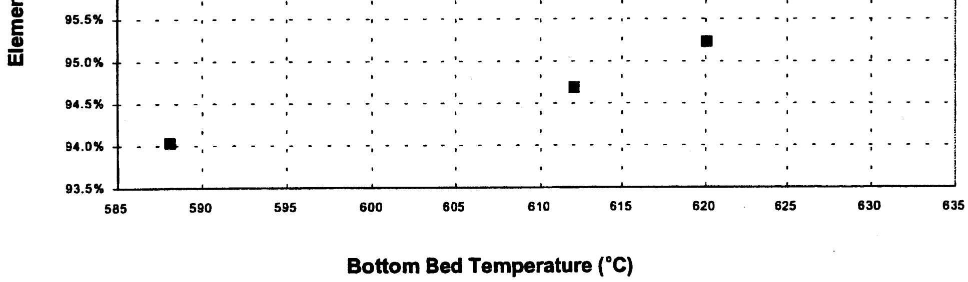

Figure 15. Effect of catalyst bed temperature on yield of elemental sulfur.

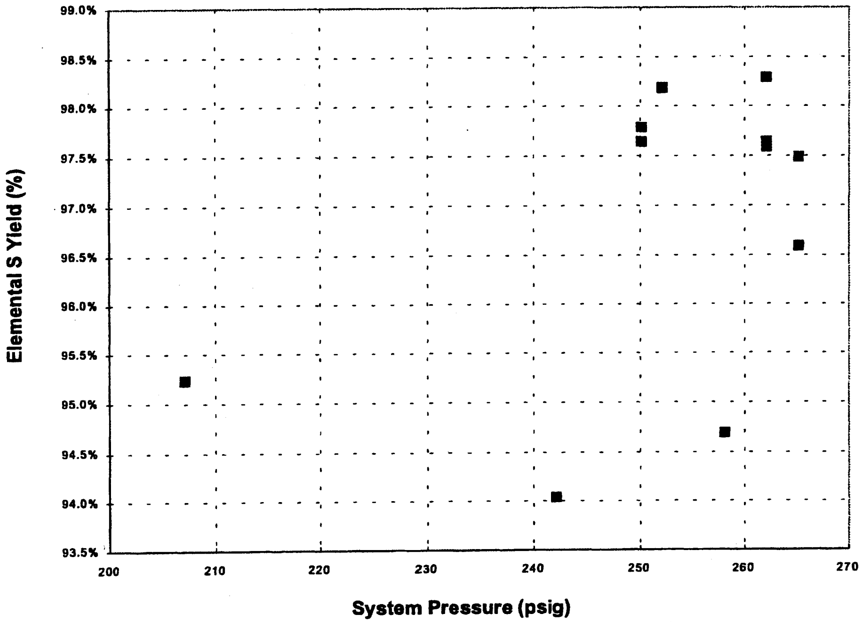

Figure 16. Effect of system pressure on yield of elemental sulfur.

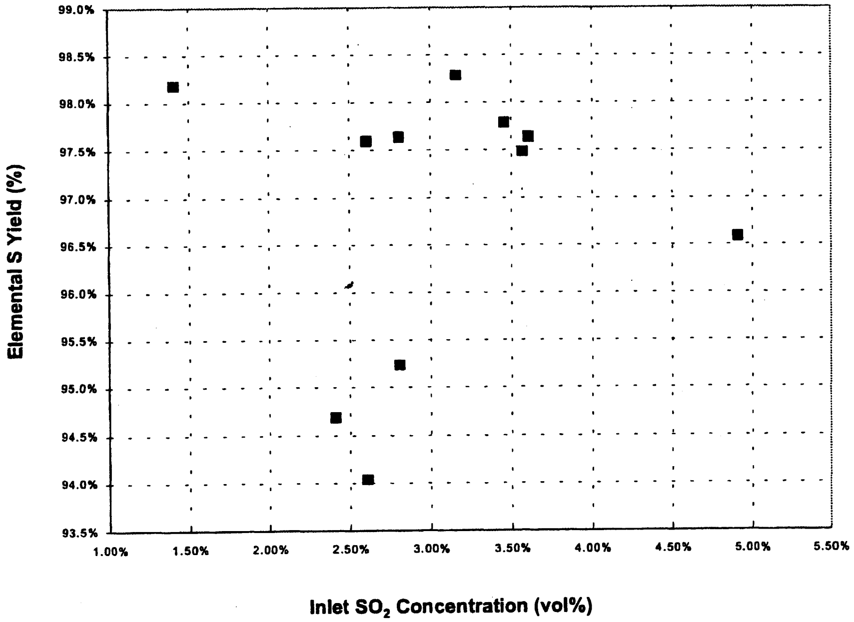

Figure 17. Effect of inlet SO_2 concentration on yield of elemental sulfur.

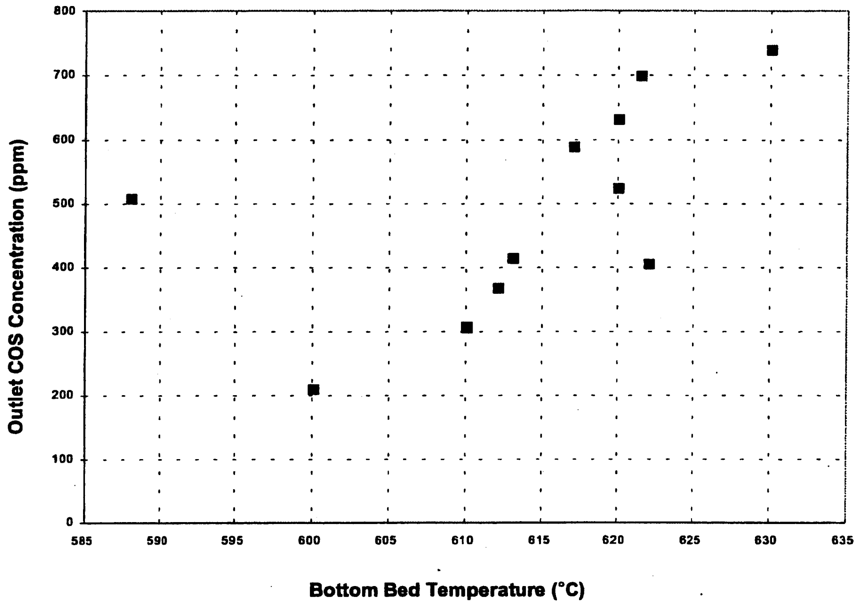

Figure 18. Effect of catalyst bed temperature on outlet COS concentration.

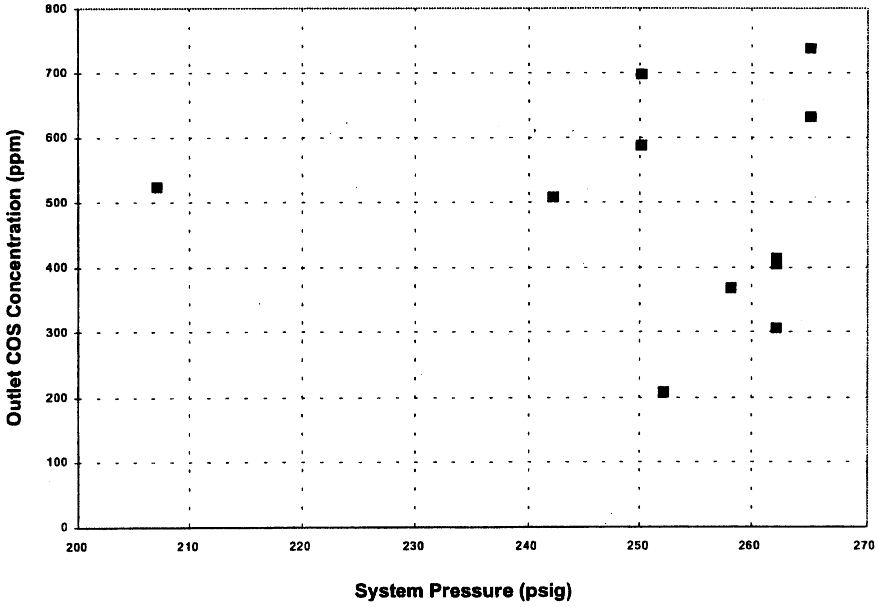

Figure 19. Effect of system pressure on outlet COS concentration.

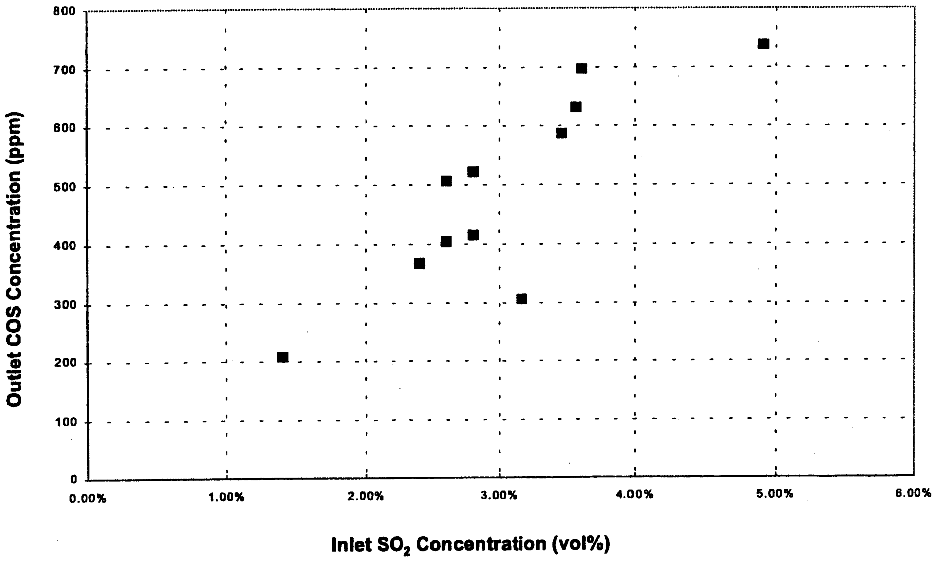

Figure 20. Effect of inlet SO_2 concentration on COS concentration.

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

Figure 17 reports the effect of inlet SO_2 concentration on conversion. The data cover a good range of concentrations: from 1 to 5 percent. Most of the conversions to sulfur range from 97.5 to 98.3 percent. The three data points around 2.5 percent SO_2 that lie below this value were taken at lower pressures. Conversion at 5 percent inlet SO_2 concentration was also slightly lower, at 96.6 percent. This was the last run and during this run it was not clear if the conditions had been fully optimized.

Figure 18 reports the effect of catalyst bed temperature on COS concentration in the offgas. An apparent increase in COS formation with higher temperature is observed. However, it should be noted that reactor temperature is not entirely an isolated, independent variable. Figure 21 shows the relationship of reactor temperature to inlet SO_2 concentration, a variable suspected of influencing COS formation. It can be seen that the higher reactor temperatures are associated with higher SO_2 concentrations.

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

Finally, Figure 20 reports the effect of inlet SO_2 concentration on COS concentration in the offgas. This is the clearest trend observed in this series of parametric studies, with COS increasing with increasing SO_2. This trend is consistent with the understanding of the chemistry

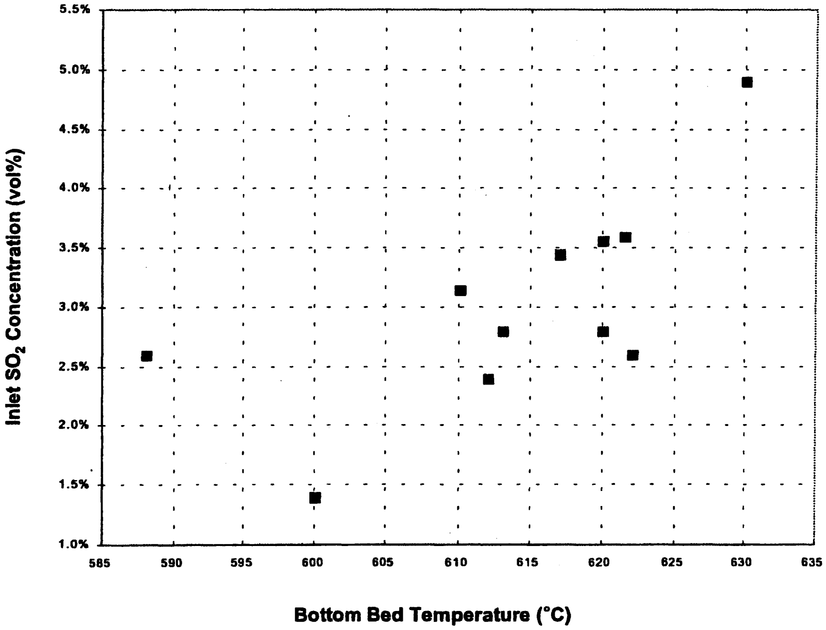

Figure 21. Relationship of inlet SO_2 concentration to catalyst bed temperature.

of the DSRP where COS is produced from the reaction of SO_2 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.

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

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 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

	Concentration on catalyst (μg/g)			
Trace metal	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

[a] As and Se analyses are unreliable. See text.

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

2.6 CANISTER EXPOSURE TESTING IN 1996

2.6.1 Concept and Experimental Plan

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

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

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

Table 19. GE Exposure Test Conditions

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

The most effective way to demonstrate the continued activity of the DSRP catalyst is to install it in an HTHP reactor and actually conduct the SO_2 reduction reaction using a reducing gas mixture. Thus, to determine if additional coal gas exposure of the catalyst had any deleterious effects, the doubly exposed catalyst was tested in a bench-scale DSRP unit set up in a laboratory in RTI's main campus in Research Triangle Park, North Carolina. The reactor design was essentially identical to that of the trailer-mounted unit; the sulfur condenser design was identical. The coal gas was simulated by using a purchased custom gas mixture, and the simulated regeneration offgas was generated similar to the method used in the slipstream testing at FETC: vaporization of LSO_2 under pressure. The continuous H_2S/SO_2 tail gas analyzer used in the mobile laboratory was moved to RTI for the duration of the bench-scale testing.

2.6.2 Results of Bench Unit Testing

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

Table 21 summarizes the results from operating the DSRP bench unit with the "canister" catalyst. Several test runs were made, with a total operating time (with SO_2 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 $cm^3/cm^3 \cdot h$)	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

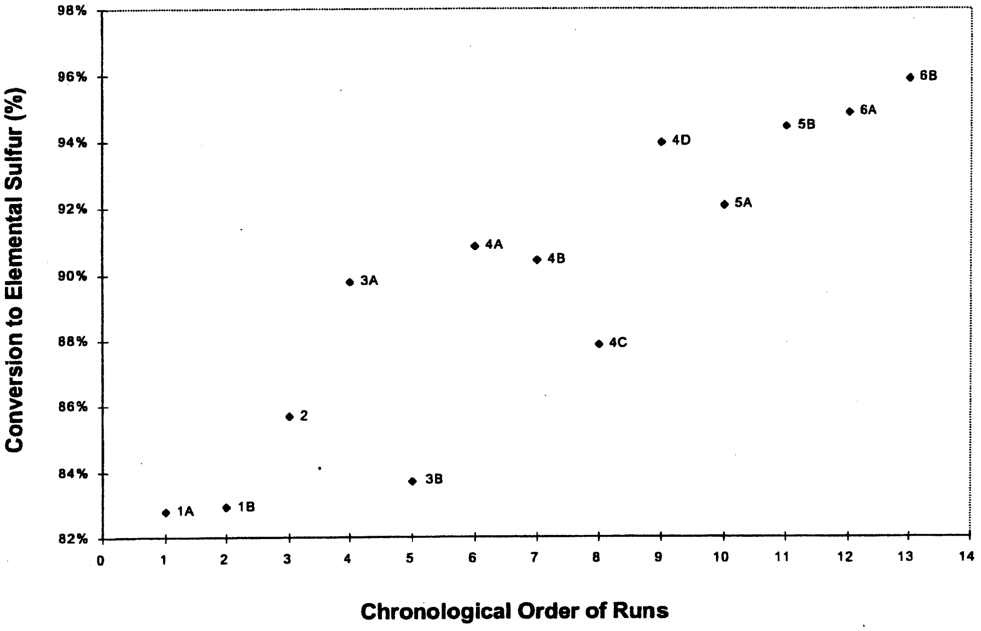

Figure 22. Conversion improvement with operating time.

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

					Outlet gas composition (dry)			
Run no.	Bed temp. (°C)	Press. (atm. abs.)	Inlet space velocity (h^{-1})	Inlet SO_2 Conc'n (vol%)	H_2S (ppmv)	SO_2 (ppmv)	SO_2 (ppmv)	Conv. to sulfur (%)
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.

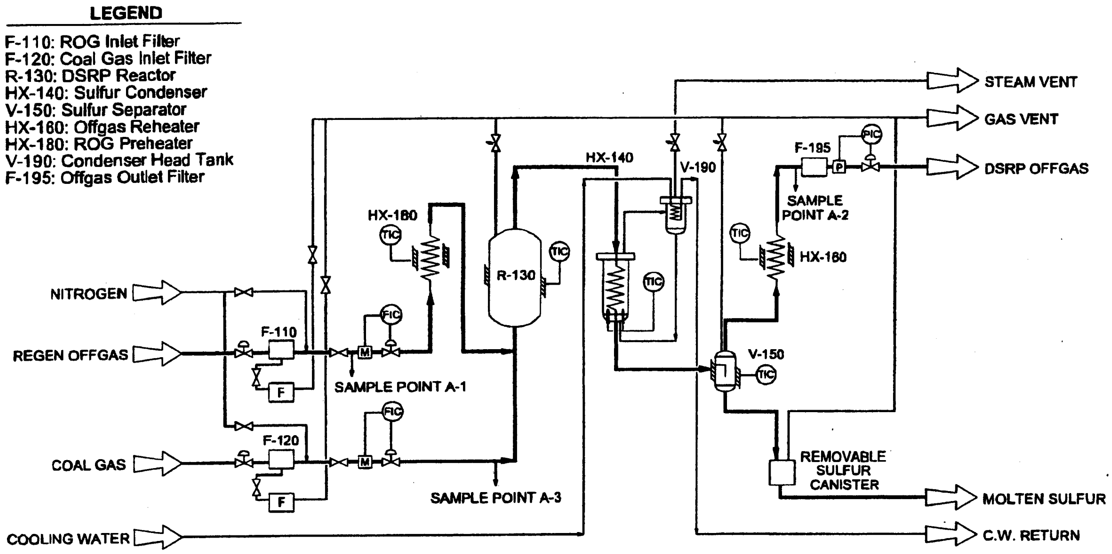

Figure 23. Process flow diagram for 6X DSRP unit.

- 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.

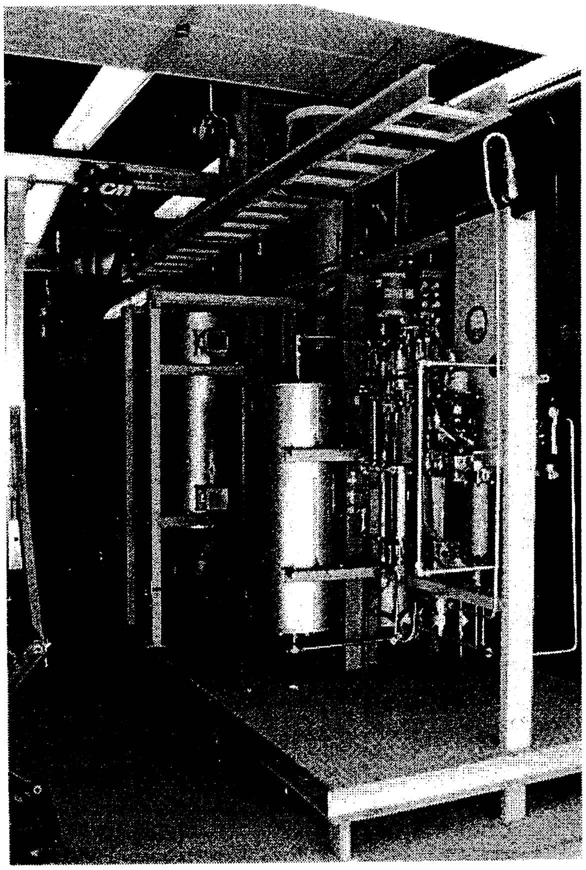

Figure 24. Skid-mounted 6X DSRP unit in fabrication shop at RTI (gas inlet end).

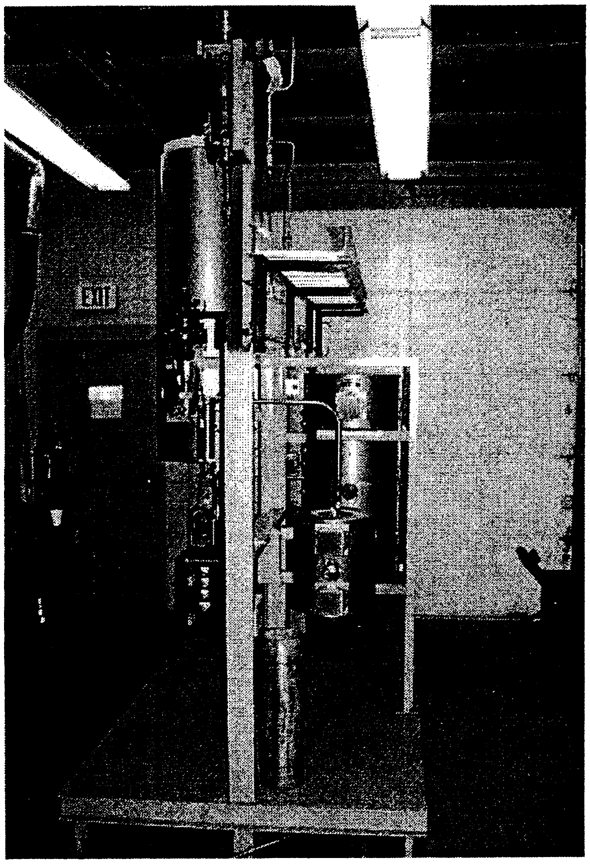

Figure 25. Gas outlet end of 6X unit.

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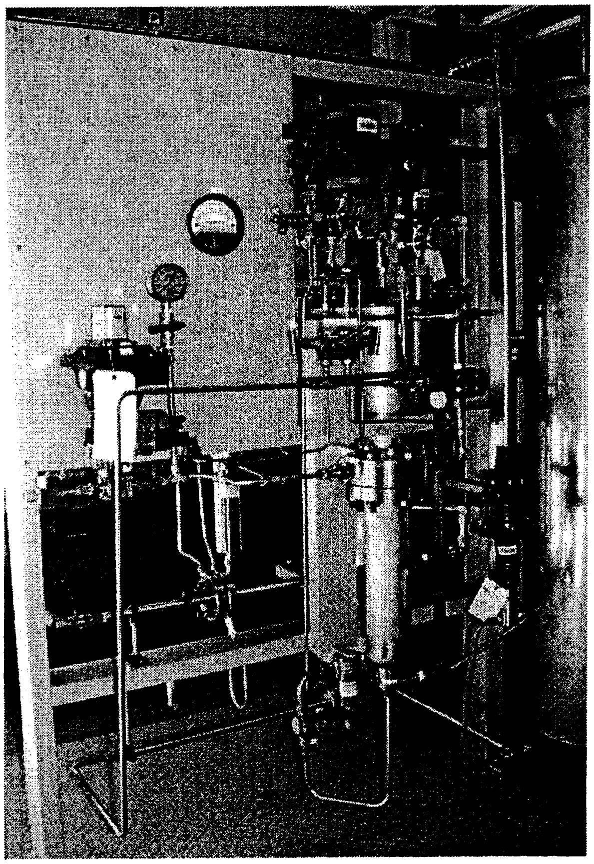

Figure 26. Coal gas inlet flow control and filter.

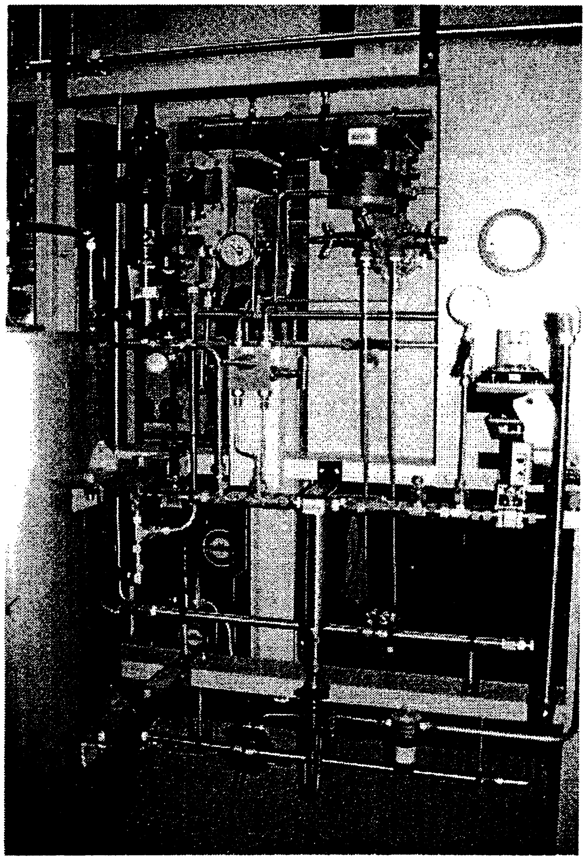

Figure 27. Regeneration offgas inlet flow control and preheater furnace (left).

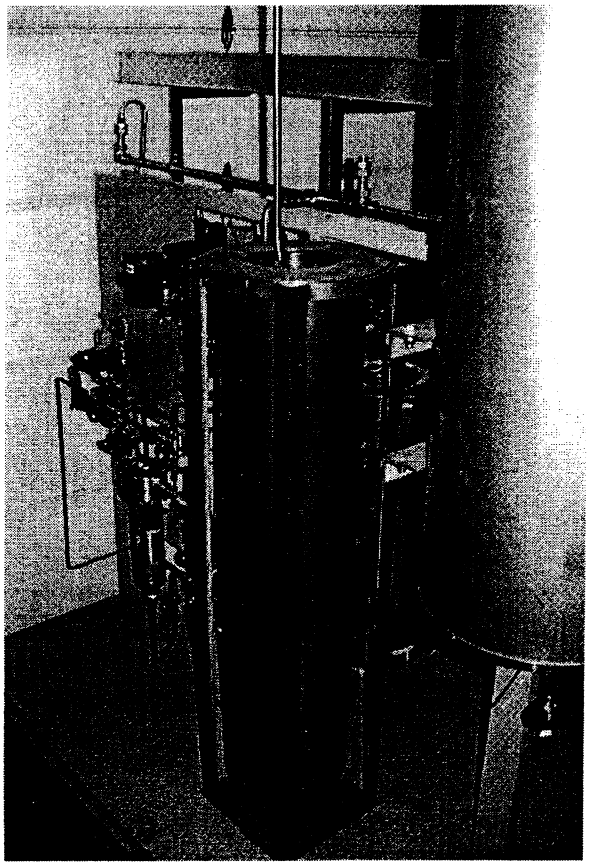

Figure 28. Single-stage reactor in furnace (sulfur condenser in right foreground; ROG preheater coil in rear).

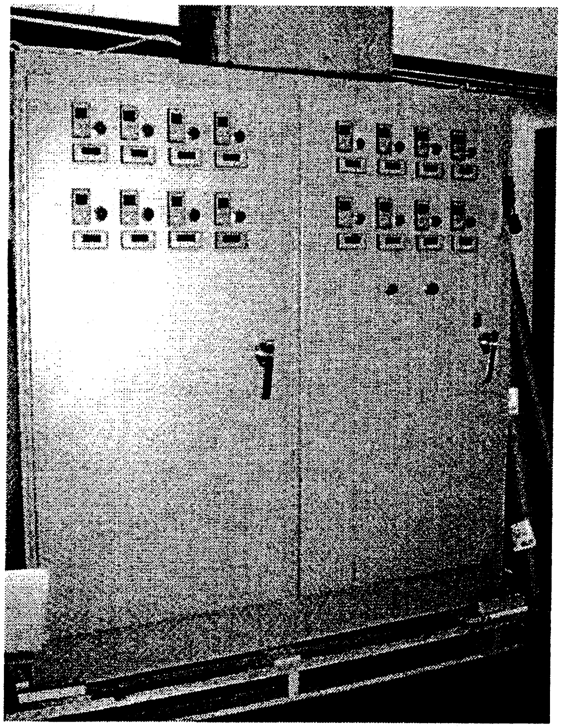

Figure 29. Heater control panel.

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.

SECTION 4
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Appendix B

Bench-Scale Demonstration of Hot-Gas Desulfurization Technology, presented at the Advanced Coal-Based Power and Environmental Systems '98 Conference (July 1998)

Bench-Scale Demonstration of Hot-Gas Desulfurization Technology

Jeffrey W. Portzer (jwp@rti.org; 919-541-8025)
Santosh K. Gangwal (skg@rti.org; 919-541-8033)
Research Triangle Institute
3040 Cornwallis Road
P.O. Box 12194
Research Triangle Park, NC 27709-2194

Introduction

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 off-gas at HTHP conditions. Over the past 10 years, the U.S. Department of Energy/Federal Energy Technology Center (DOE/FETC) has sponsored a number of approaches for ultimate disposal of this off-gas. The patented Direct Sulfur Recovery Process (DSRP) being developed by Research Triangle Institute (RTI) is a highly attractive option for recovery of sulfur from this regeneration off-gas. 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.

In the DSRP (Dorchak et al., 1991), the SO_2 tail gas is reacted with a slipstream of coal gas over a fixed bed of a selective catalyst to directly produce elemental sulfur at the HTHP conditions of the tail gas and coal gas. Overall reactions involved are shown below:

$$2\,H_2 + SO_2 \rightarrow (1/n)\,S_n + 2\,H_2O$$

$$2\,CO + SO_2 \rightarrow (1/n)\,S_n + 2\,CO_2$$

$$CO + H_2O \rightarrow H_2 + CO_2$$

$$H_2 + (1/n)\,S_n \rightarrow H_2S$$

$$2\,H_2S + SO_2 \rightarrow (3/n)\,S_n + 2\,H_2O\,.$$

Slipstream tests with actual coal gas (Portzer and Gangwal, 1995; Portzer et al., 1996) demonstrated that, with careful control of the stoichiometric ratio of the gas input, sulfur recovery of 96 to 98 percent can be consistently achieved in a single DSRP stage. The single-stage process, integrated with a metal oxide sorbent regenerator, is shown in Figure 1. Since the tail gas from the DSRP can be recycled as shown in this figure, there are no sulfur emissions from the DSRP.

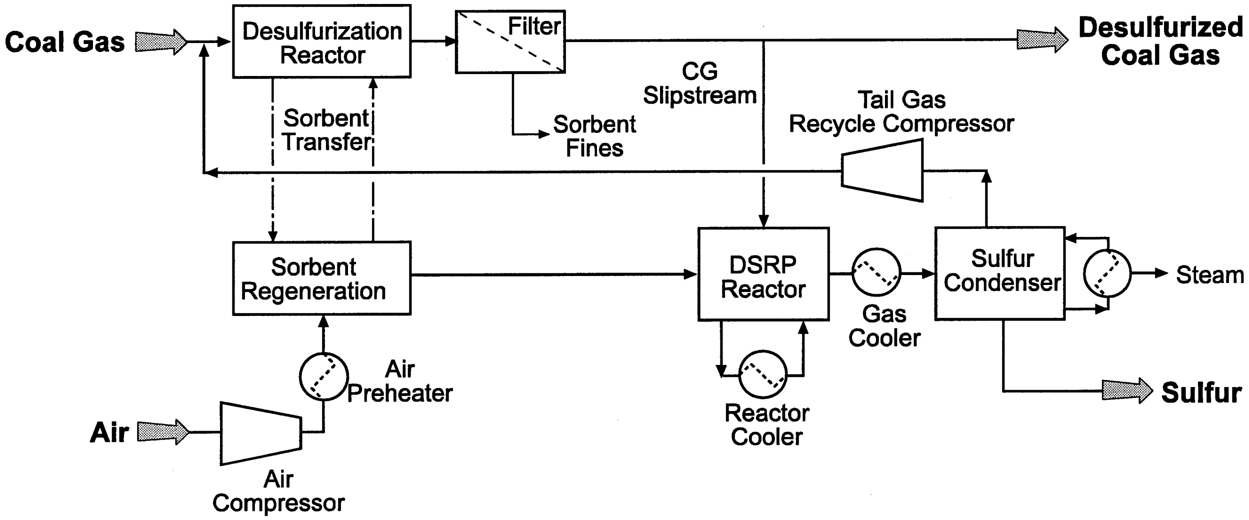

Figure 1. Hot-gas desulfurization with DSRP.

Objectives

Prior to the current project, development of the DSRP was only done in a laboratory setting, using synthetic gas mixtures to simulate the regeneration off-gas and the coal gas feed. The aim of the current work is to further the development of zinc titanate fluidized-bed desulfurization (ZTFBD) and the DSRP for hot-gas cleanup by testing with actual coal gas. The objectives of this project are to:

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

- Test the bench-scale DSRP over an extended period with a slipstream of actual coal gas to quantify the degradation in performance, if any, caused by the trace contaminants present in coal gas (including heavy metals, chlorides, fluorides, and ammonia)

- Expose the DSRP catalyst to actual coal gas for extended periods and then test its activity in a laboratory reactor to quantify the degradation in performance, if any, caused by static exposure to the trace contaminants in coal gas

- Design and fabricate a six-fold larger-scale DSRP reactor system for future slipstream testing

- Further develop the fluidized-bed DSRP to handle high concentrations (up to 14 percent) of SO_2 that are likely to be encountered when pure air is used for regeneration of desulfurization sorbents

- Conduct extended field testing of the 6X DSRP reactor with actual coal gas and high concentrations of SO_2.

The accomplishment of the first four objectives—testing the DSRP with actual coal gas, integration with hot-gas desulfurization, catalyst exposure testing, and fabrication of the 6X DSRP—was described previously (Portzer and Gangwal, 1994, 1995; Portzer et al., 1996; Portzer and Gangwal, 1997).

This paper reports the results of further development of the fluidized-bed DSRP, describes the current activities, and presents plans to accomplish the remaining objective–the extended field testing of the 6X DSRP unit.

Fluidized-Bed DSRP Background

The early development work and scaleup of the DSRP focused on treating a regeneration off-gas stream that would have a relatively low concentration of sulfur dioxide, say 1 to 3 vol%. With the desulfurization sorbents and regenerator reactor designs being considered at the time, dilute air regeneration was required and resulted in low SO_2 concentrations. Subsequently, improvements in the sorbents, and the introduction of other regenerator reactor designs (notably the Kellogg transport reactor as implemented in the Sierra Pacific Power Company's Piñon Pine plant) have suggested that "neat air" is a preferred commercial embodiment for hot gas desulfurization. Thus, there is a need for the DSRP to be able to treat high-SO_2 concentration regeneration off-gas.

The DSRP reactions are highly exothermic, and for optimum conversion need to be conducted at a fairly high temperature (550 to 600 °C). Although a fixed-bed reactor design is possible, alternative designs, such as a bubbling fluidized-bed or transport reactor, are likely to be more feasible for dealing with the high exothermicity of the high SO_2 concentration feed streams. The idea of using a fluidized-bed reactor for DSRP had been explored in previous work, but because the catalyst that was used then was simply a crushed material, and had not been optimized for fluidized-bed operation, the single-stage conversion (94 percent) was relatively low and the catalyst was prone to attrition. These preliminary findings suggested the need for the additional catalyst development and testing that was conducted in this task.

Task Objectives

The specific objectives of this task were defined as follows:

- Obtaining and characterizing a suitable fluidizable catalyst for fluid-bed DSRP
- Preparing the catalyst for use in the fluidized-bed reactor
- Conducting shake-down runs with typical SO_2 concentrations to establish operating conditions.

- Conducting an experiment design set looking at the effects of SO_2 concentration, fluidization velocity (space time), oxygen contamination of the regeneration off-gas, reactor pressure, and catalyst bed temperature on SO_2 conversion efficiency.

Approach /Project Description

The approach taken was to use a multipurpose bench-scale test apparatus at the RTI laboratory with a nominal 4-in. diameter HTHP reactor. The regeneration off-gas feed was simulated by evaporating liquid SO_2 into a preheated nitrogen stream. The reducing coal gas was simulated using a synthetic gas mixture. A 3-in. diameter stainless steel cage with an alumina frit was fitted inside the reactor to hold the fluidized bed of catalyst.

Two different alumina-based fluidized-bed catalysts—a proprietary catalyst, and a nonalumina catalyst—were tested. Because the exact formulations contain proprietary information, the candidate catalysts are identified by letters in this report. Table 1 shows the key physical characteristics of the fresh materials.

In Table 1, Catalysts A and B, with moderate attrition resistance, were selected as candidates for a bubbling fluidized-bed reactor. Catalyst C was identified as a candidate for a transport or riser-type fluidized-bed reactor. Catalyst D was selected as an intentional choice of a poor DSRP catalyst to be a "blank" run.

The tests were conducted with a synthetic gas mixture simulating the composition of a coal gas from an air-blown gasifier. The coal gas produced by the 10-in. pilot gasifier at FETC-Morgantown was used as the basis, as shown in Table 2. It should be noted that a simplification in the experiment protocol introduces a complication in data analysis and interpretation. Because the coal gas feed to the DSRP reactor and the simulated regeneration off-gas (ROG) contain nitrogen, a single nitrogen feed line was used for both, and the synthetic coal gas mixture that was actually fed to the reactor did not contain any nitrogen. The SO_2 was mixed with this nitrogen stream that represents both the ROG nitrogen and the coal gas nitrogen so that the

Table 1. Catalyst Physical Characteristics

	Catalyst A	Catalyst B	Catalyst C	Catalyst D
Base material	Alumina	Alumina	Proprietary	Nonalumina
BET surface area (m^2/g)	227	212	103	10
Attrition loss per RTI 20-h test (%)	7.2	7.2 (est'd)	1.0 (est'd)	
Hg porosimetry pore volume (mL/g)	0.62	0.41	0.32	
Particle size, weighted average diameter (µm)	168	168 (est'd)	100 (approx.)	
Bulk Density (g/mL)	0.81	0.94	0.90	0.85

experimentally measured concentration is not the same as the nominal SO_2 concentration that is being simulated with the experiment. Table 3, based on material balance calculations, relates the two values, and for interest shows the approximate rotameter setting for the supply of liquid SO_2 to the preheater.

A typical test run was conducted in one day, with the reactor heated with a low-pressure nitrogen purge overnight. Following calibration of the analyzers, the unit was pressurized with nitrogen, and a stable flow was established. The coal gas flow and the liquid SO_2 (LSO_2) flows were started essentially simultaneously at given flow rates that were established from material balance calculations. The LSO_2 flow was controlled with a needle valve and a rotameter to get the desired SO_2 concentration in the reactor feed to simulate the ROG composition. The coal gas flow rate, controlled by a mass flow controller (MFC), was fine-tuned from observation of the tail gas analyzer output. A shortage of coal gas results in a high outlet SO_2 concentration; conversely, an excess of coal gas results in high outlet H_2S concentration.

Table 2. Coal Gas Composition

Component	Volume %
CO	14.4%
CO_2	13.0%
H_2O	10.0%
H_2	17.5%
H_2S	1,400 ppm
N_2	45.0%

Table 3. Simulated ROG Concentrations

SO_2 content of simulated ROG (%)	SO_2 content of actual feed to bench-scale reactor (%)	Calculated LSO_2 flow rate (cc/min)
7.2	6	3.2
14	10	5.8
18	12	6.9

Once stable outlet concentrations had been achieved, the unit was allowed to run for 20 min or more so that several gas chromatograph (GC) data points could be collected. The reactor temperatures, pressure, flow rates, and analyzer outputs were logged using a personal computer-based data logger. Two or three different operating conditions could be set and lined-out conditions obtained in a good day's run.

For two of the runs, air was introduced into the DSRP reactor along with the simulated ROG and the coal gas. This was done to represent the situation in commercial practice when oxygen "slip" occurs in the regenerator. That is, if the air-blown regenerator is not in perfect control, it would be possible for excess air to be fed to that unit, so that some unconsumed oxygen would be discharged along with the SO_2/N_2 stream. The experiments were run to see what the effect would be of having oxygen in the SO_2 stream that goes to the DSRP reactor.

At the end of each day's run, molten sulfur was withdrawn from the pot downstream of the steam-heated sulfur condenser. Due to the variety of operating conditions that was used, no attempt was made to verify a sulfur material balance.

Results

A single number is used to report the results of each run: the "percent reduction of sulfur compounds," by gas analysis. By material balance, all gaseous sulfur compounds that disappear must have been converted to elemental sulfur, so therefore this number represents the percent conversion. The laboratory bench-scale DSRP unit is equipped with a continuous gas analyzer to measure H_2S and SO_2 in the tail gas. By a simple calculation, the output of this analyzer gives an instantaneous measure of the degree of conversion. However, the analyzer does not correctly account for the presence of COS in the tail gas. A GC equipped with a thermal conductivity detector (TCD) samples the outlet gas approximately every 8 min, and the results of that analysis, which include COS concentration, are used in this report to calculate the percent reduction value. Furthermore, the calculation takes into account the fact that H_2S is introduced in the coal gas (in addition to the SO_2 of the regeneration off-gas) as a sulfur compound that must be converted to elemental sulfur.

Figure 2 summarizes the results of all the test runs, reporting conversion as a function of catalyst type. Catalyst D clearly has unacceptably low conversion, as expected, and Catalyst B showed the best performance, although it was only slightly better than Catalyst A.

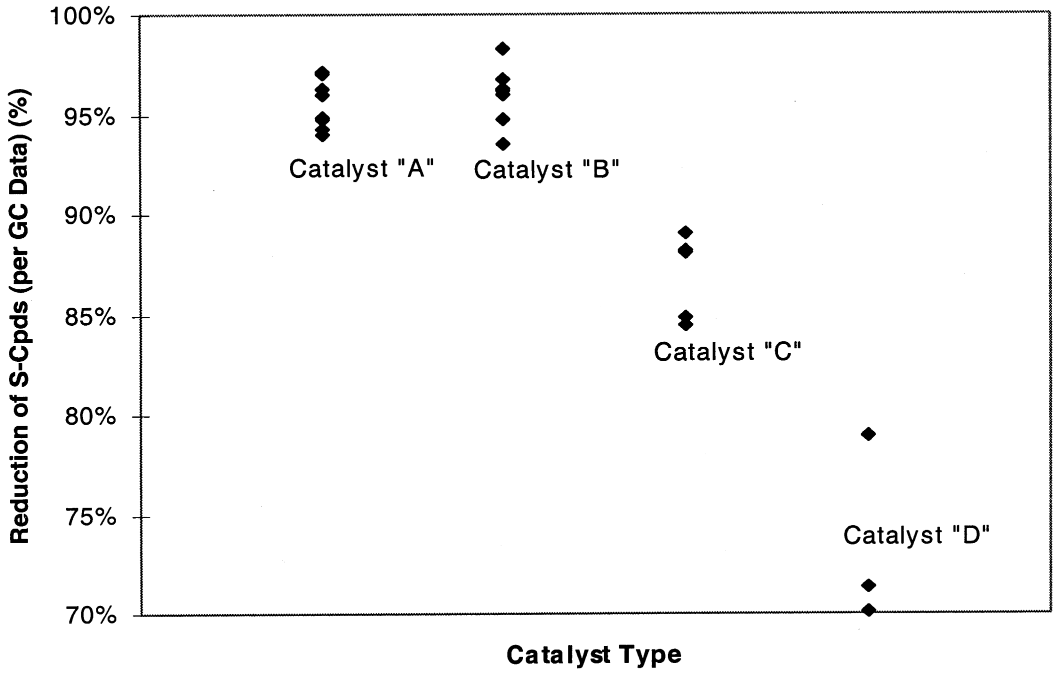

Figure 2. Effect of catalyst type.

Most of the runs were conducted at either of two pressure levels. The higher pressure—250 psig—represents a typical operating pressure that would expect to be encountered in a commercial embodiment of the DSRP. The lower pressure—150 psig—was chosen because that may be the coal gas pressure at the Power Systems Development Facility (PSDF) at Wilsonville, Alabama, during the slipstream testing under certain operating scenarios. Figure 3 shows a slightly favorable trend with increased pressure, as has also been shown in previous work.

The operating conditions selected for the test series intentionally span only a narrow range of temperature. The test protocol called for adjustment of the furnace temperature to attempt to maintain the same catalyst bed temperature for all runs. Nonetheless, there was some variation in actual bed temperature. As Figure 4 shows, a higher catalyst temperature results in greater conversion to elemental sulfur. This result is consistent with previous experience.

Figure 5 shows the effect of inlet concentration of SO_2 on the conversion; the runs made with the higher SO_2 concentrations have higher conversions. This particular response is well known in Claus technology and Selectox technology. Figure 6 plots the actual measured concentration of sulfur compounds in the outlet as a function of inlet concentration. From those data it appears that outlet concentration is independent of inlet concentration. Thus, by material balance considerations, higher apparent reduction efficiencies are achieved when the inlet concentration is higher, as Figure 5 shows.

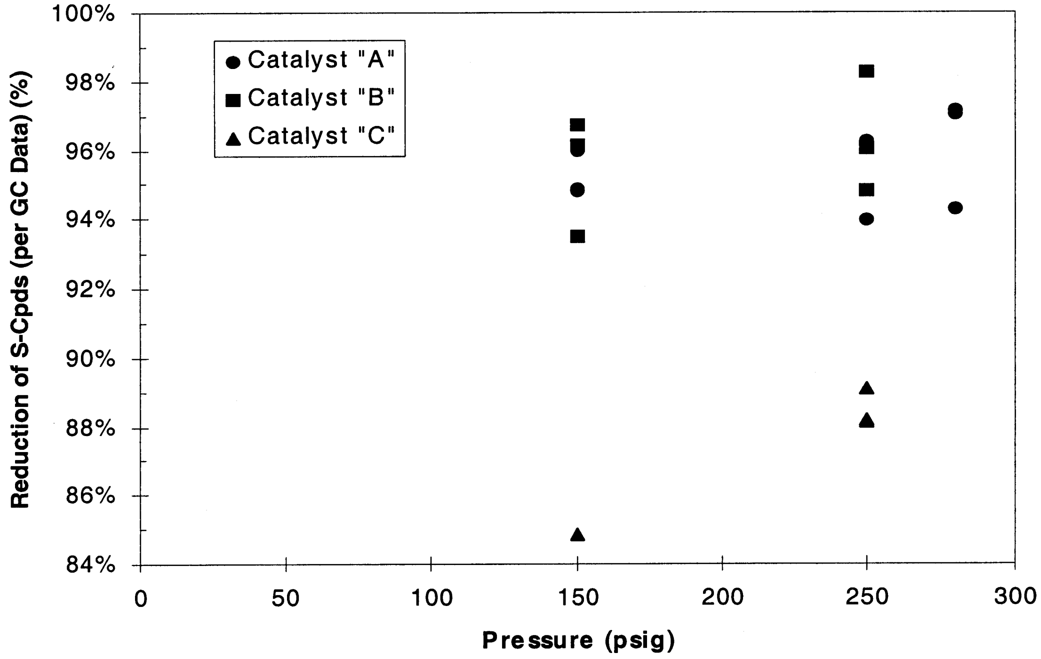

Figure 3. Effect of pressure.

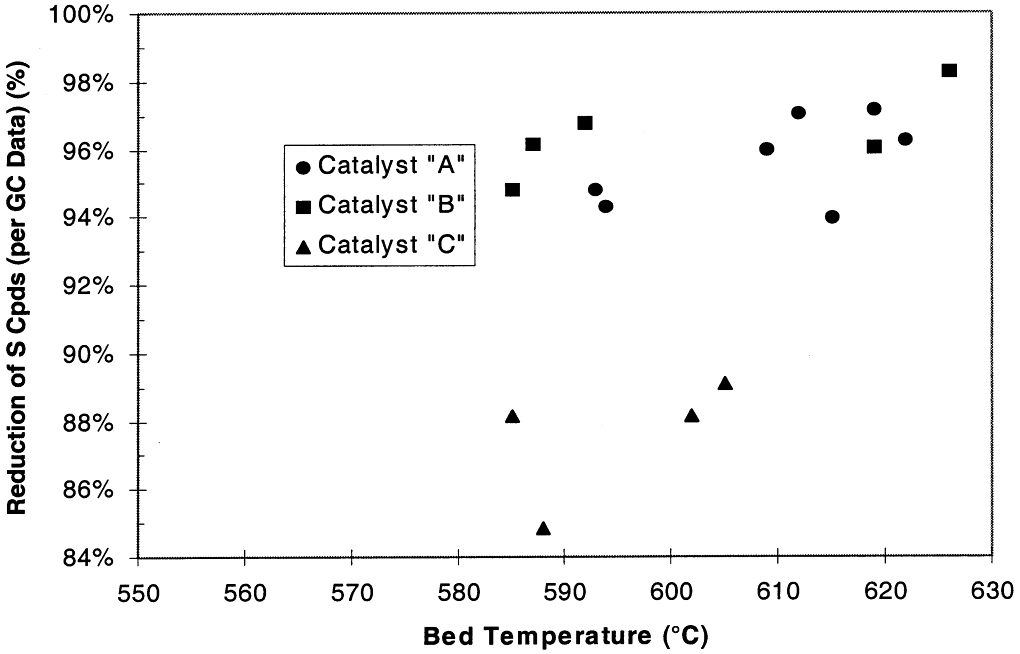

Figure 4. Effect of bed temperature.

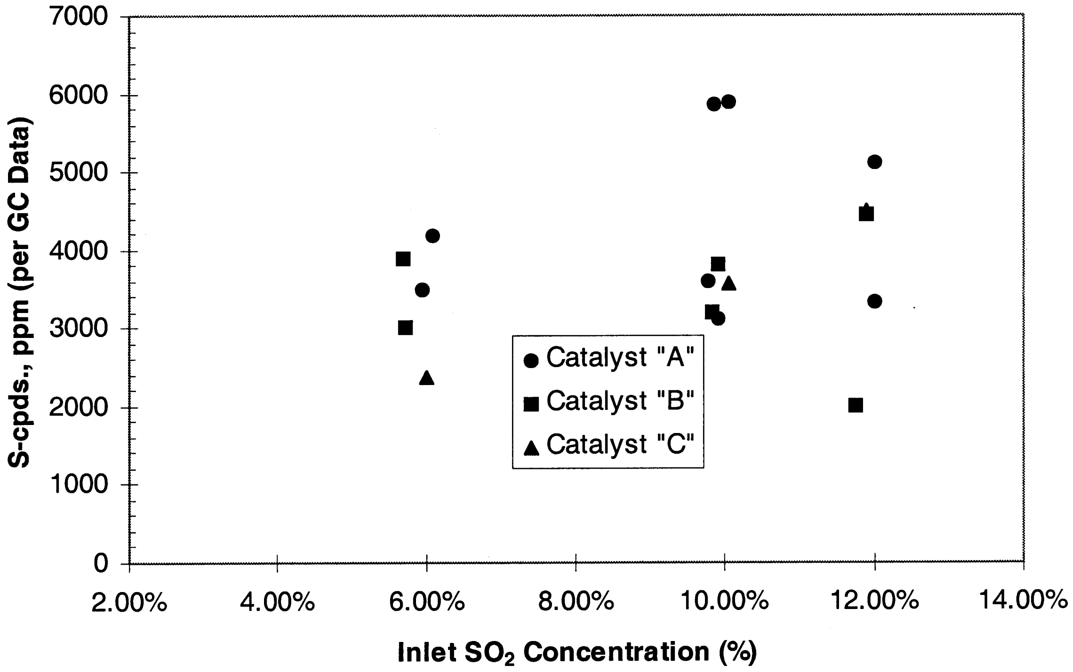

Figure 6. Outlet concentration of sulfur compounds.

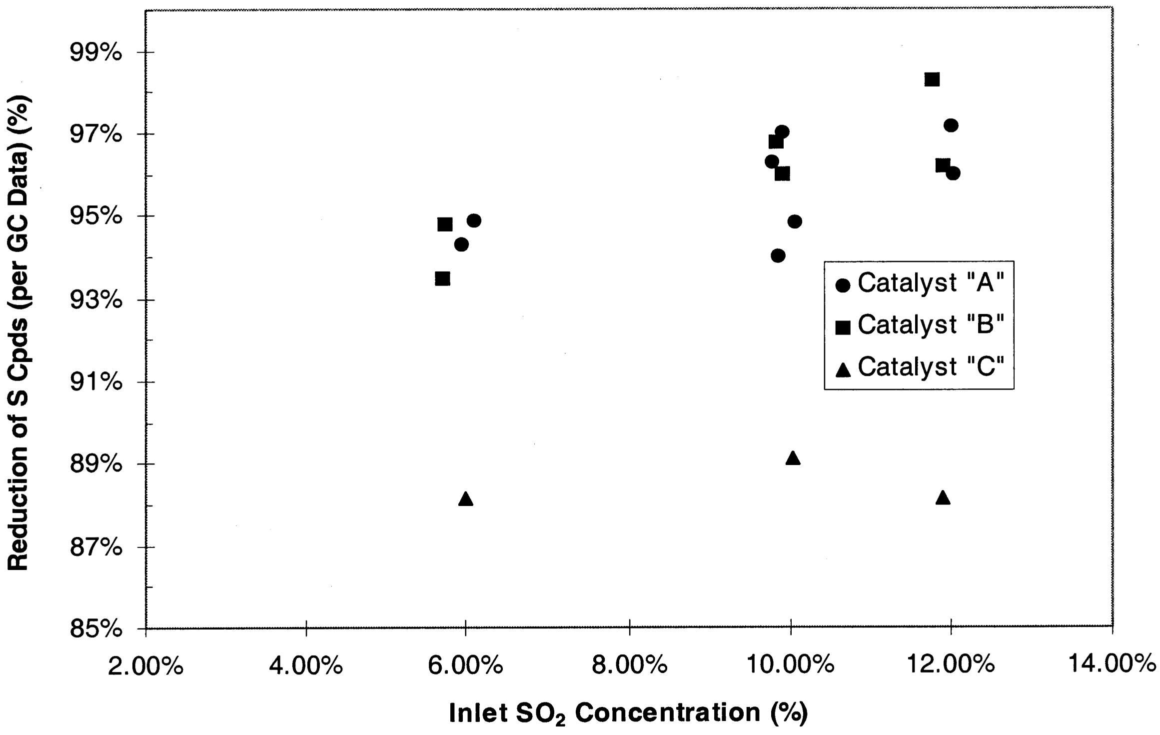

Figure 5. Effect of inlet concentration.

The introduction of approximately 1 percent oxygen along with the ROG into the DSRP reactor did not seem to have any deleterious effects. Without any adjustment of the coal gas flow, the outlet concentrations of sulfur compounds increased dramatically, as was expected. Increasing the coal gas flow rate to correct for consumption by oxygen returned the outlet sulfur compound concentrations to their previous values. Similarly, with shutdown of the oxygen flow (after 3 h of operation in one case), and subsequent reduction in coal gas flow, the outlet sulfur concentrations returned to original values, indicating no change in the performance of the catalyst.

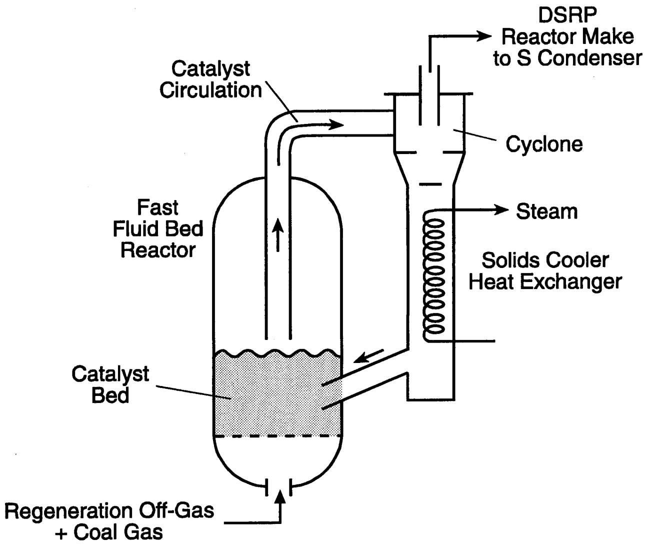

Figure 7. Conceptualized fast fluidized-bed reactor.

Applications/Benefits

To address the need for the DSRP to process sorbent regeneration off-gases containing high concentrations of SO_2 (up to 14 vol%), the commercial embodiment of the process is likely to be based on some type of fluidized-bed reactor that incorporates a heat exchanger to remove the high heat of reaction. A bubbling bed reactor, a fast fluidized-bed reactor, and a transport (entrained bed) reactor have all been considered. Figure 7 is a schematic representation of a fast fluidized-bed reactor incorporating a solids cooler that has been conceptualized for DSRP.

From the experimental work described in this paper, a good bubbling bed catalyst—designated "B"—has been developed, using a commercially available alumina. Conversions were 98 percent in a single stage, based on GC data. Attrition is low with this material, but probably not low enough for this catalyst to be affordable for commercial-scale transport reactor use, especially considering that the alumina material is fairly expensive. To address the need for a lower cost, highly attrition-resistant material for transport reactor use, catalyst C was developed and tested. Although the activity was disappointing—single-stage conversion was 90 to 92 percent—it has low enough attrition for use in a transport reactor, and it is much less costly than Catalyst B or A.

Even as the technology for the sorbent-based gas desulfurization develops, and the characteristics of the resulting regeneration off-gas change, the DSRP continues to look favorable as a feasible commercial process for the production of elemental sulfur.

Future Activities

The planning is nearly complete, and construction/fabrication activities are underway for the future field test of the DSRP with actual coal gas at FETC's PSDF field test using the skid-mounted six-fold larger (6X) DSRP with a slipstream of actual coal gas at PSDF. Modification of the 6X unit will be completed, consistent with specific site requirements. The mobile laboratory will be refitted at RTI as a control room for the 6X unit and will be moved along with the skid-mounted 6X unit to Wilsonville, Alabama, for the testing to be conducted in FY 1999-2000. Figure 8 shows an artist's conception of how the mobile laboratory will be used in conjunction with the 6X unit at that field test site. The proposed route of the coal gas slipstream line is overlaid on the photograph.

Acknowledgments

The research is sponsored by the U.S. Department of Energy's Federal Energy Technology Center, under contract DE-AC21-93MC30010 with Research Triangle Institute (telefax: 919-541-8000). RTI gratefully acknowledges the assistance and guidance of the FETC Contracting Officer's Representative (COR) on this project, Thomas P. Dorchak. Southern Company Services has been an active participant in the planning for the PSDF test program. The period of performance is July 1993 to June 1999.

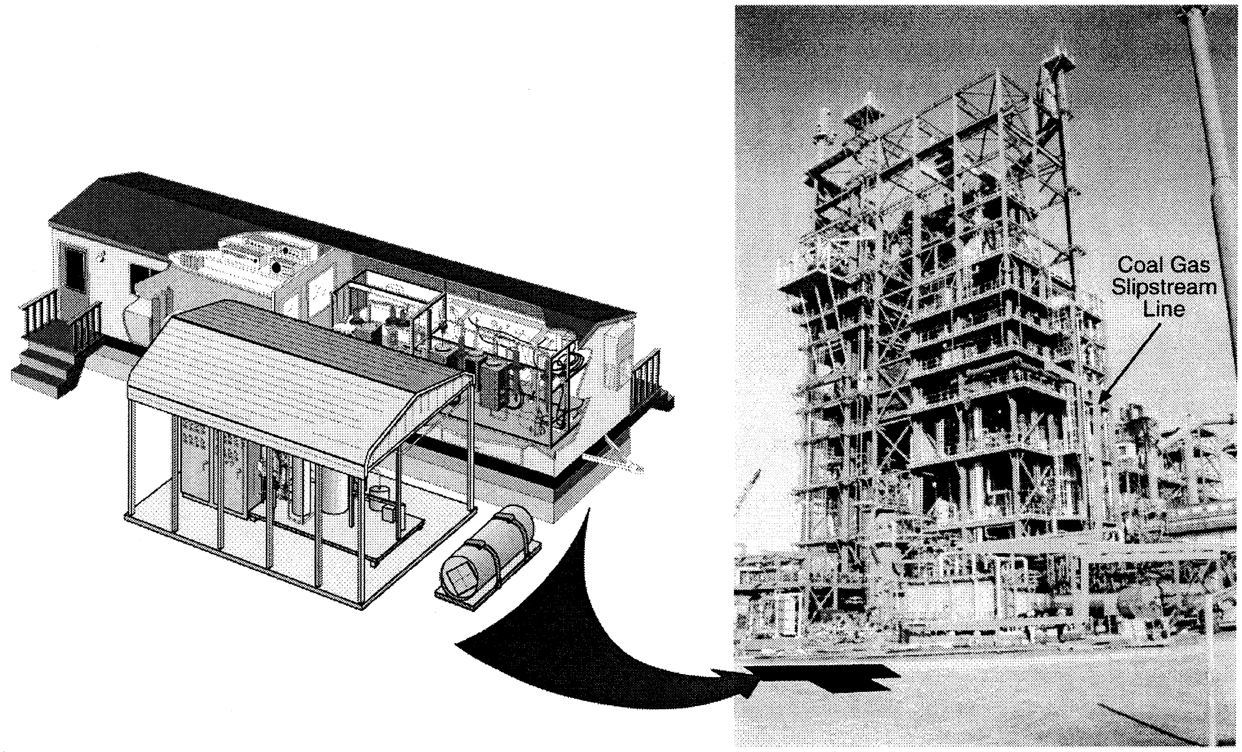

Figure 8. Artist's conception of equipment arrangement for PSDF field test.

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Appendix C

Design Hazard Review: DSRP Bench Unit

Design Hazard Review

SLIPSTREAM PILOT TEST UNITS FOR DIRECT SULFUR RECOVERY PROCESS AND ADVANCED HOT GAS PROCESS

Design:

Research Triangle Institute
Center for Engineering and Environmental Technology
Process Research Program
3040 Cornwallis Road
Research Triangle Park, NC 27709

Sponsor:

U.S. Department of Energy
National Energy Technology Laboratory
3610 Collins Ferry Road
Morgantown, WV 26505

August 2000

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TABLES AND ATTACHMENTS

APPENDICES

Summary:

A design hazard review (DHR) was conducted at the Research Triangle Institute (RTI), Research Triangle Park, North Carolina, from July 31, 2000 through August 8, 2000.

The review was conducted using piping and instrumentation drawings (P&ID) for two process test units at various stages of modifications. The slipstream test units designed by RTI consist of a direct sulfur recovery process (DSRP) pilot test unit and an advanced hot gas process (AHGP) bench test unit. The process test units were redesigned for field slipstream testing to be integrated with the operation of the Kellogg Brown & Root (KBR) gasification test unit located at the Southern Company Services (SCS) power system development facility (PSDF) in Wilsonville, Alabama.

For reference, an overview of the two hot-gas desulfurization processes is described in Appendix A. The development of these processes are being directed and sponsored by the U.S. Department of Energy (DOE), National Energy Technology Laboratory, Morgantown, West Virginia.

This report summarizes the results of DHR and includes the following reference documents:

DHR Work Sheets	-	Appendix I
Reference P&IDs	-	Appendix II
Process Description	-	Appendix A

Meeting Objectives and Review Documents:

The objectives, assumptions, and constraints for the review sessions are identified in Table I. The P&IDs developed by RTI for the DSRP Pilot test unit and AHGP bench units were the primary review documents. Table II lists the P&IDs subjected to the review. Other reference documents were required in support of review and these are listed in Table III.

TABLE I - MEETING OUTLINE

Meeting Objectives:

- Identify safety and operability hazards during the review of P&IDs and team discussions and develop recommendations for project implementation.
- Develop recommendations for any identified deviations that could significantly affect operability.

Assumptions:

- Design is finalized and necessary design reviews have been completed.

Constraints:

- Review team will refrain from redesign efforts at the meeting and will limit discussions to meet the review meeting objectives.

TABLE II – REVIEW DRAWINGS

Drawing No.	Title	Revision
	DSRP Field Test Pilot Unit	
PID-0010	SIM ROG System	F
PID-0011	Filters and Reactor	H
PID-0012	Sulfur Collection	H
PID-0013	Analytical	H
	AHGP Field Test Bench Unit	
PID-0014	Feed Gases and Preheaters	E
PID-0015	Reactor and Product Recovery	D
PID-0016	Analytical	C
	PSDF Field Test	
PID-0017	SCS-RTI Interface	F
PID-0018	LSO_2 Delivery System	D
PID-0020	Instrument Air	

TABLE III – REFERENCE DRAWINGS

Drawing No.	Title	Revision
Sketch BER 02/11/00	SCS Piping for RTI's DSRP/AHGP Process	02/08/00
E-M-D0002	PSDF General Arrangement Plant Site	O
DSRP RTR 1	Design & Assembly R-101, R-201, and R-211	A
V-188	V-188 Sulfur Canister	A
V-150	Sulfur Separator Pot	G
HX-140	Sulfur Condenser	E
R-130	DSRP Reactor	G
HTR-131	HTR-131 DSRP Reactor Furnace	A
R-130 FLG	R-130 Flange and Cage Detail	-
1	Sorbent Cage	B
HX-090	SIM ROG PHTR Coil	-
V-190	Condenser Head Tank	D
HX-160	Design and Assembly Reheater	B

Methodology:

The procedure selected for this review used an abbreviated guideword approach that incorporated guidewords used in classical HAZOP studies. Using selected guidewords (Table IV), the facilitator directed the discussions to identify operating deviation that was the most likely scenarios for each guideword. The discussions reviewed the failure modes to identify potential hazards or operability problems. Based on the developed scenarios, probability of occurrence and risk consequences were discussed and assessed for the identified hazards or operational problems. Only events and/or issues that resulted in recommendations were recorded on the worksheets. The suggested recommendations are included in Column 7 of the DHR worksheets in Appendix I. The guidelines for the each of the worksheet columns are defined in Table V. The DSRP P&IDs listed in Table II were the subject of the review first. The P&IDs were divided into nodes. The modes generally were separated in two categories, feed streams to the reactors and reactor/product streams. In some cases, the reactors were individually evaluated and product streams divided into functional subsystems. Table VI outlines the review modes used for this study. Two exceptions were the review of PSDF/RTI interfacing and test protocol (study reference E) and analytical P&ID (study reference F).

Study reference number E-1 through E-6 was developed from the plot plan of site shown on drawing E-M-D0002. This review was other than an operating deviation and was reviewed to the following potential interfacing issues.

- Safety and Restriction Zones
- Personnel Access and Egress Routes
- Event Alarms and Personnel Assembly Areas
- Construction/Equipment Access and Egress Routes.

Study reference numbers F-1 through F-3 was conducted on the planned analytical sampling system and required the expertise from RTI's engineer who participated in similar sampling of test units.

TABLE IV – GUIDEWORD CHECKLIST

Guideword	Operating Deviation
Flow	-No -High -Low -Reverse -Misdirected -Plugged
Level	-High -Low -No
Leak	-Oxidation -Corrosion -Seal -Connector
Pressure	-High -Low
Temperature	-High -Low
Contaminants	-Process -Disposal -Handling
Concentrations	-High -Low
Power	-Loss
Instrument Air	-Loss
Operation	-Startup -Shutdown -Emergency/Evacuation Plan -Integrated Test -Sampling
Maintenance	-On-line -Off-line
Exposure	-Fire -Toxic Release -Heat -Explosion

TABLE V – DESIGN HAZARD REVIEW GUIDELINES FOR WORK SHEET COLUMNS

Column 1: Study Reference Number

Identifier that will be located on each of the review P&IDs for easy recall and reference during corrective action and implementation phases.

Column 2: Line Number or Equipment Number or other Identifier

Item identified with subject of deviation and guideword.

Column 3: Guideword and Operating Deviation

Refer to checklist guidewords (Table IV).

Column 4: Possible Causes of Deviation or Problem

Identified failure mode or process upset condition or operability event in reference to Column 3.

Column 5: Consequences and Reasons for Action

Categorize the potential effect of Column 4. "S" for safety, "O" for an operability problem, and include the potential consequences of the event if necessary for added clarification.

Column 6: Existing Precaution

Identify instrumentation and control devices and/or operator action and/or equipment items and/or procedures that prevents or minimize the effect of the event.

Column 7: Recommended Action or Notes/Queries

Review teams recommendations or inquiries with reference to Columns 4, 5, and 6. The recommendations from the team are only suggestions for subsequent evaluation by projects in developing the final corrective action plan. The team's recommendations may be subject to change based on follow-up engineering reviews and/or studies.

Column 8: Action By

To be assigned by project following the review.

Column 9: Further Implications or Follow-up Reviews or Comments

Optional. If applicable, identify other related study reference numbers having similar event conditions or identify specific follow-up review requirements or specific information comments for further clarification.

TABLE VI – PROCESS REVIEW MODES

DSRP Pilot Test Units

Drawing	Node Identifier	Process Nodes
PID-0011	A1	Coal Gas Feed to Reactor
PID-0011	A2	F-120 Blow Back
PID-0011	A3	Nitrogen Feed
PID-0011	A4	F-110 Blow Back
PID-0011	A5	R-130 Reactor
PID-0012	A6	Sulfur Removal System
PID-0012	A7	Reheated Off-gas System

AHGP Bench Test Units

PID-0014	B1	Coal Gas Feed to Reactor
PID-0014	B2	H_2S/Nitrogen Feed
PID-0014	B3	REGEN SO_2/Nitrogen Feed
PID-0014	B4	REGEN Air/Nitrogen Feed
PID-0015	B5	Reactor/Sulfidation Off-gas
PID-0015	B6	Reactor/ SO_2 REGEN Off-gas
PID-0015	B7	Reactor/Air REGEN Off-gas
PID-0017	C1	Instrument Air
PID-0018	D1	LSO_2 Delivery System
E-M-D0002	E	PSDF/RTI Test Protocol
PID-0013/PID-0016	F1	Analytical Sampling

Review Team:

The review team consisted of several representatives from the Research Triangle Institute at the Center for Engineering and Environmental Technology, Process Research Program, Research Triangle Park, North Carolina and one safety engineer from Southern Company Services at the Power System Development Facility, Wilsonville, Alabama. A hired consultant familiar with conducting hazard review for pilot scale operations facilitated the meeting and directed the team discussions.

Members of the review team are identified in Table VII. Other participants attended part-time and are also listed as attendees on the worksheets.

TABLE VII – DESIGN HAZARD REVIEW TEAM

Jeffrey Portzer	RTI	Process Engineer
Daryl Smith	RTI	Operation/Construction
Brandon Russell*	SCS	Safety/Engineering
Gary Howe	RTI	Analytical Sampling (part-time only)
Peter Cherish**	Consultant	Facilitator

*Scribe for meeting.

**Developed document worksheets based on scribes recorded information and follow-up discussion.

Results:

The results of the Design Hazard Review are documented in Appendix I and Appendix II. Appendix I documents the results of the meeting discussions and tabulates the event scenario, consequence, and existing precautions on the worksheets. Appendix II further identifies a study reference number for the event scenario on each corresponding P&ID. Also included in Appendix I is a column with suggested recommendations for each of the study reference numbers. These suggested recommendations are to be reviewed by the SCS/RTI project team subsequent resolution and implementation.

Follow-up Requirements:

A follow-up action plan for implementation is required to close out the items identified in the review. The following is offered for consideration.

- RTI/SCS project team reviews the event scenarios for each of the study reference numbers and address the validity of each recommendation on a "to-do" or "no-to-do" basis.

- From the results of the above review, develop a corrective action/status list finalizing the recommendations. For reference, a sample of a DHR action item/status form is shown in Attachment I.

  NOTE: Study reference items requiring no follow-up implementation or that are deemed not applicable should be so identified in the status column of the listing.

- It is recommended that prior to startup, the status of each item of the DHR action item list be reviewed by SCS/RTI project/operations team to assess status of completion and operational readiness.

ATTACHMENT I
DHR Action Items

Study Ref. #	Action By	Recommended Action	Status	Estimated Completion Date

APPENDIX I

DHR WORKSHEETS

P&ID: PID-0011
DSRP Filters & Reactor
DATE: July 31, 2000
ATTENDEES: Daryl Smith, RTI Brandon Russell, SCS
Jeff Portzer, RTI Pete Cherish, Facilitator

STUDY REF	• LINE NO • EQUIPMENT NO • OTHER	• OPERATING DEVIATION • POSSIBLE CONDITION • GUIDE WORD	• POSSIBLE CAUSES OF DEVIATION • PROBLEM	CONSEQUENCES & REASONS FOR ACTION O-OPERABILITY S-SAFETY HAZARD	EXISTING PRECAUTION	• RECOMMENDED ACTION REQUIRED • NOTES/QUERIES	ACTION BY	• FURTHER IMPLICATIONS • FOLLOW-UP REVIEW • COMMENTS
A1-1	PID-0011	High flow to DSRP via YV-017	Syngas flow valves YV-016 and YV-017 on cascade control. YV-017 opens and YV-016 closes on demand signal from operator.	• O-Potential damage to F-120 filter elements • Potential high reactor carryover and catalyst elutriation.	Valve CV and line flow restriction may limit flow.	• Confirm maximum allowable pressure drop for pall filter. • If required, consider adding impedance in series with YV017 to limit maximum flow on switchover.	RTI	
A1-2	PID-0011 F-120	Low flow to R-130	F-120 filter element plugging from coal gas tars and/or particulates.	• O-Suboptimum reaction in DSRP. • Pilot unit shutdown	• PDI-112 filter pressure drop increases. • FCV-116 valve opens and FIC output signal increases. • Reactor temperature drops. • Operator intervention.	Provide process upset action plan in operating procedure.	RTI	
A1-3	PID-0011 CKV-173	Reverse flow via CKV-173	KBR transport reactor depressurizes rapidly without notification to DSRP operators.	O-Potential damage to CKV-173 resulting in emergency S/D with forced venting and possible line blowout.	None	Provide computer pressure signal from transport reactor pressure to RTI/DSRP PC for monitoring and trending.	SCS	
A1-4	PID-0011 PDI-0010	Misdirected flow from coal gas line to low pressure nitrogen line via HV-108.	Operator inadvertently leaves or adjusts HV-108 in open position following F-120 filter blowback cycle.	• O-Potential for contaminating low-pressure nitrogen line. • Contaminating SIMROG rotameter FE-097 during purge cycle.	Procedure	Confirm procedure provides precautionary action plan to prevent event occurrence.	RTI	
A1-5	PID-0011 Line 103	Misdirected flow from coal gas line into SIMROG system via HX-180 outlet line.	SCS/RTI operator inadvertently closes isolation valve on LP nitrogen supply to RTI and CKV-171 fails to open.	O-Potential for contaminating SIMROG supply system to R-130.	• Procedure • CKV-171	Consider carseal open manual valve at SCS tie-in connection and provide tagout procedure with RTI	SCS	
A1-6	PID-0011 Drawing pressure/temperature notation for equipment	High pressure From SCS.	• SCS nitrogen supply PCV fails. • KBR transport reactor operation increased to 285 psig test conditions without notification.	S-Potential to over pressure R-130 DSRP reactor.	• Equipment design parameters exceeds operating condition. • PCV-612 • PI measurements • Operator intervention	• Provide proper-drawing notations to clarify noted parameters. • Confirm tubing, piping, and vessel design meets or exceeds API B31.3 petroleum piping requirements.	RTI	

P&ID: PID-0011
DSRP Filters & Reactor

DATE: August 1, 2000

ATTENDEES: Daryl Smith, RTI Brandon Russell, SCS
Jeff Portzer, RTI Pete Cherish, Facilitator
Suresh Jain, DOE

STUDY REF	• LINE NO • EQUIPMENT NO • OTHER	• OPERATING DEVIATION • POSSIBLE CONDITION • GUIDE WORD	• POSSIBLE CAUSES OF DEVIATION • PROBLEM	CONSEQUENCES & REASONS FOR ACTION O-OPERABILITY S-SAFETY HAZARD	EXISTING PRECAUTION	• RECOMMENDED ACTION REQUIRED • NOTES/QUERIES	ACTION BY	• FURTHER IMPLICATIONS • FOLLOW-UP REVIEW • COMMENTS
A1-7	PID-0011 TIC Heater Controllers	High temperature tracing on heaters.	Tracing fails and shorts to ground during operation.	S-Potential for overheating tubing and vessels.	TSHH high/high temperature power shutoff protection.	Confirm temperature controller failure mode is fail safe and over current protection is adequate in the configured installation.	RTI	
A1-8	PID-0011 Coal gas feed system	Leaks similar to those experienced from RTI lab test.	• Fusible plug failure on SO_2 tank. • Flange leaks. • Connector leaks. • Valve packing leaks. • Condenser tube failure.	• S-Toxic gas release under pressure. • Personnel exposure hazard	Pressure leak test during assembly and prior to shipment to SCS.	• Develop leak check procedure and leakage rate criteria for acceptability. • Conduct pressure leak test after arrival at PSDF.	RTI	
A1-9	PID-0011 SO_2 feed line to DSRP.	Leaks same as A1-8.	• Connector leaks. • Instrument leaks. • Valve packing leaks.	• S-Potential for high SO_2 gas release. • Operator exposure hazard.	• Pressure leak test prior to operation. • Operator leak check monitoring.	Install SO_2 sensor behind heater control panel and integrating in RTI alarm/monitoring system with audible alarm capabilities.	RTI	
A1-10	PID-0011 Line DSRP-OG-1/2	Leaks same as A1-8.	• Flange leaks. • Connector leaks. • Valve packing leaks.	• S-Potential for high toxic gas (>2000ppm H_2S) release. • Personnel/operator exposure hazard.	• Pressure leak test prior to operation. • Operator leak check monitoring.	Install H_2S sensor located above V-150 sulfur separator pot.	RTI	(refer to B2-2)
A1-11	PID-0011 Vessel and line heaters.	Power loss local failure.	Circuit trips and auto resets.	S-Potential for high temperature equipment damage by overheating.	Design configured for heaters to latch in "off" mode on power failure.	Review and confirm heater latching "off" on power loss meets operating requirements.	RTI	
A1-12	PID-0011 F-110 CKV-171 YV-101	High pressure. Equipment pressure/temperature ratings.	Existing procured equipment incompatible with the new process operating conditions.	S-Potential for equipment overpressure damage and personnel injury.		Review existing equipment for MAWP/temperature ratings and verify compatibility with process operating conditions.	RTI	

P&ID: PID-0011
DSRP Filters & Reactor

DATE: August 1, 2000

ATTENDEES: Daryl Smith, RTI Brandon Russell, SCS
Jeff Portzer, RTI Pete Cherish, Facilitator
Suresh Jain, DOE

STUDY REF	• LINE NO • EQUIPMENT NO • OTHER	• OPERATING DEVIATION • POSSIBLE CONDITION • GUIDE WORD	• POSSIBLE CAUSES OF DEVIATION • PROBLEM	CONSEQUENCES & REASONS FOR ACTION O-OPERABILITY S-SAFETY HAZARD	EXISTING PRECAUTION	• RECOMMENDED ACTION REQUIRED • NOTES/QUERIES	ACTION BY	• FURTHER IMPLICATIONS • FOLLOW-UP REVIEW • COMMENTS
A2-1	PID-0011 Filter F-120	Maintenance online cleaning.	Filter plugs.	O-Potential damage to filter element.	PDI-112 filter differential measurements.	• Review filter data and confirm maximum allowable pressure drop across filter element with forward and reverse flow. • Based on data, develop operator procedure and criteria for operation.	RTI	
A2-2	PID-0011 Filter F-120	Maintenance off-line	Filter plugs, unable to be cleaned on-line and unable to vent pressure.	S-Potential for personnel injury due to sudden release of pressure on disassembly.	None.	Develop off-line maintenance procedure for back flushing and cleaning F-120 and F-121.	RTI	
A2-3	PID-0011 F-120 Filter PCV-612	High pressure in F-120 from SCS nitrogen supplies.	PCV-612 and PCV-165 fail.	• O-Potential for filter element damage. • Potential for overpressure equipment vessels.	Low probability of failure for two regulators in series.	• Review and determine pressure conditions in event of PCV-612 and PCV-165 failure. • Determine MAWP for equipment and develop PSV-139 set pressure based on limiting equipment.	RTI	
A2-4	PID-0011 Line 118 nitrogen startup line to coal gas Line 104.	Startup.	Backflow of coal gas into nitrogen purge line up to HV-613.	O-Potential for acid condensation in cold dead leg.	None.	In developing startup procedure, consider opening coal gas supply valve into higher-pressure nitrogen flow before closing HV-163.	RTI	
A2-5	PID-0011 PCV-612 nitrogen supply line.	Low flow during nitrogen startup flow demand.	PCV-612 undersized to flow required capacity.	O-Potential to limit startup pressure and flow requirements.	N/A	• Verify PCV-612 sized to meet requirements for startup demand. • Consider adding upstream pressure indicator for • PCV-612 nitrogen regulator.	RTI	
A2-6	PID-0011 Nitrogen startup and backpulse lines.	Low temperature contaminants.	Uninsulated lines between heated lines and nitrogen block valves.	O-Potential for purge lines to plug with tar and corrode from formed acid condensibles.	None.	Consider adding check valve similar to CKV-173 at branch connection if problem occurs.	RTI	

P&ID: PID-0011
SIMROG System

DATE: August 1, 2000

ATTENDEES: Daryl Smith, RTI Brandon Russell, SCS
Jeff Portzer, RTI Pete Cherish, Facilitator
Suresh Jain, DOE

STUDY REF	• LINE NO • EQUIPMENT NO • OTHER	• OPERATING DEVIATION • POSSIBLE CONDITION • GUIDE WORD	• POSSIBLE CAUSES OF DEVIATION • PROBLEM	CONSEQUENCES & REASONS FOR ACTION O-OPERABILITY S-SAFETY HAZARD	EXISTING PRECAUTION	• RECOMMENDED ACTION REQUIRED • NOTES/QUERIES	ACTION BY	• FURTHER IMPLICATIONS • FOLLOW-UP REVIEW • COMMENTS
A3-1	PID-0010 FIC-318-4	High flow of nitrogen in SIMROG.	FIC mass flow controller fails to close due to mechanical damage.	O-Potential for low % SO_2 in SIMROG causing process upset.	• FCV-115 downstream flow control. • Operator action monitoring analysis of SIMROG sampling gas.	None.		
A3-2	PID-0010 F-092	Low flow of nitrogen in SIMROG.	F-092 inline filter plugs.	O-Potential for high % SO_2 in SIMROG causing process upset and high temperature catalyst exposure.	• FIC-318-4 and FIC-115 flow measurements. • SIMROG gas analysis. • Operator action.	For operator procedure, calculate worse case scenario and limits for SO_2 concentration and temperature.	RTI	
A3-3	PID-0018 T-500 PCV-506	Reverse flow of nitrogen to T-500 LSO_2 cylinder.	Low nitrogen pad pressure on T-500.	O-Loss of SIMROG flow (refer to A3-2)	• Operator procedure and monitoring. • Rotameter float may close restricting backflow. • Nitrogen pressure via • PCV-612 available.	Confirm procedure and data logging monitors T-500 tank pad pressure at acceptable frequency.	RTI	
A3-4	PID-0010 HX-090	High temperature from loss of nitrogen flow.	HTR-091 heater fails in shorted condition with TIC-094 selected to control outlet line temperature.	• S-Potential for tube failure and release of toxic gas. • Personnel exposure hazard.	• Operator monitoring and intervention. • TSH-094. • Dual temperature control mode configured.	Review and confirm high temperature shutdown can be accommodated in either control modes to prevent equipment damage.	RTI	
A3-5	PID-0010 FE-097	Reverse flow during online clean out of FE-097 with low pressure N_2.	H-086 3-way valve fails.	O-LSO_2 back flow into low-pressure nitrogen purge line 140.	None.	Consider adding check valve in low-pressure nitrogen line to HV-086.	RTI	

P&ID: PID-0011
DSRP Filters & Reactor

DATE: August 1, 2000

ATTENDEES: Daryl Smith, RTI Brandon Russell, SCS
Jeff Portzer, RTI Pete Cherish, Facilitator
Suresh Jain, DOE

STUDY REF	• LINE NO • EQUIPMENT NO • OTHER	• OPERATING DEVIATION • POSSIBLE CONDITION • GUIDE WORD	• POSSIBLE CAUSES OF DEVIATION • PROBLEM	CONSEQUENCES & REASONS FOR ACTION O-OPERABILITY S-SAFETY HAZARD	EXISTING PRECAUTION	• RECOMMENDED ACTION REQUIRED • NOTES/QUERIES	ACTION BY	• FURTHER IMPLICATIONS • FOLLOW-UP REVIEW • COMMENTS
A4-1	PID-0011 Line 103 R-130	High flow SIMROG to R-130.	FIC-115 fails control valve open causing high flow to reactor.	• O-Potential catalyst carryover from R-130. • Major maintenance clean out problem.	• Control valve trim size. • Operator monitoring and intervention.	• Review trim size for valve and determine maximum flow and velocity in R-130 reactor. • Develops limits as required.	RTI	
A4-2	PID-0011 F-110	Reverse flow.	Valve misalignment during filter cleaning.	S-Personnel exposure hazard. Leaks from corrosion in SIMROG line.	Operator procedure for low pressure filter cleaning.	Confirm procedure in place prior to operation.	RTI	
A4-3	PID-0011 F-110 F-111 F-121	Maintenance offline cleaning of filter.	F-110 plugs and requires offline cleaning.	S-Personnel exposure hazard. Sudden pressure release when opening fills to replace filter element.	Operator procedure.	• Consider adding vent, PI, at F-111 and F-121 filters to confirm depressurized condition acceptable for filter element removal. • Consider changing P&IDs to depressurize filters to a low-pressure vent header (see V-188 study reference notes).	RTI	
A4-4	Same as A4-3	Same as A4-3	Same as A4-3	S-Potential handling and disposal hazard.	Unknown.	Confirm storage/disposal requirements of filter media at PSDF.	SCS	
A4-5	PID-0011 F-110 F-120	High temperature shutdown.	Heater element hot spot and/or failures.	S-Equipment overpressure damage at operating temperatures.	High temperature cutout switch TSHH-117.	Confirm temperature S/D conditions and maximum allowable operating temperature of F-110 and F-120 is consistent.	RTI	

P&ID: PID-0011
DSRP Filters & Reactor

DATE: August 2, 2000

ATTENDEES: Daryl Smith, RTI Brandon Russell, SCS
Jeff Portzer, RTI Pete Cherish, Facilitator

STUDY REF	• LINE NO • EQUIPMENT NO • OTHER	• OPERATING DEVIATION • POSSIBLE CONDITION • GUIDE WORD	• POSSIBLE CAUSES OF DEVIATION • PROBLEM	CONSEQUENCES & REASONS FOR ACTION O-OPERABILITY S-SAFETY HAZARD	EXISTING PRECAUTION	• RECOMMENDED ACTION REQUIRED • NOTES/QUERIES	ACTION BY	• FURTHER IMPLICATIONS • FOLLOW-UP REVIEW • COMMENTS
A5-1	PID-0011 R-130	High temperature. Over heating reactor vessel.	• Indirect temperature control of vessel by TIC-314 and TIC-135 through radiation heating. • Local overheating due to hot spots. • Reaction exothermal heating along with external vessel heating could exceed allowable design temperature	• S-Potential equipment damage. • Personnel exposure hazard. • Personnel injury potential.	• R-130 design pressure 350 psig at 675°C. • TSHH 134 and TSHH 135 set at 675°C.	• Consider moving TSHH 134 and TSHH 135 temperature sensor to measure wall temperature directly. • Consider alarm for TI-129 (R-130 freeboard). • Estimate the effect of reaction heating in conjunction with control scheme. • Develop procedure to mitigate reaction exotherm by flow adjustment or addition of inerts. • Calculate maximum possible outlet temperature of bed given configured CV for FC-115 and FC-116. • Based on results of calculation develop operating control philosophy and procedures. • Determine TI failure mode-high or low signal output to controllers.	RTI	
A5-2	PID-0011 R-130	Low temperature in feed and off-gas lines.	• Loss of heating. • High heat loss.	• O-Unable to initiate reaction (below 500°C). • O-Potential to condense sulfur (approximately 200°C). Sulfur solidifies at 130°C. • O-Potential for S/D corrosion products to condense.	• Heaters capable to preheat mixed feed and off-gas line to 999°F (537°C). • Reactor vessel and process lines insulated. • Feed and off-gas lines alonized.	Review requirements and status for alonizing feed and off-gas lines for R-130.	RTI	
A5-3	PID-0011 R-130	High-pressure. R-130 vessel overpressure.	• Relief line plugs and PSV-139 fails to open. • Relief line hot insulated.	• S-Potential equipment damage. • Potential for personnel injury.	PSV-139 set at 392 psig (MAWP of vessel 350 psig).	• Confirm release pressure of PSV-139 and readjust as required. • Consider moving overpressure protection to upstream location. Move PSV-139 or install new PSV downstream of PCV-612 in nitrogen supply to process.	RTI	

P&ID: PID-0011
DSRP Filters & Reactor

DATE: August 2, 2000

ATTENDEES: Daryl Smith, RTI Brandon Russell, SCS
Jeff Portzer, RTI Pete Cherish, Facilitator

STUDY REF	• LINE NO • EQUIPMENT NO • OTHER	• OPERATING DEVIATION • POSSIBLE CONDITION • GUIDE WORD	• POSSIBLE CAUSES OF DEVIATION • PROBLEM	CONSEQUENCES & REASONS FOR ACTION O-OPERABILITY S-SAFETY HAZARD	EXISTING PRECAUTION	• RECOMMENDED ACTION REQUIRED • NOTES/QUERIES	ACTION BY	• FURTHER IMPLICATIONS • FOLLOW-UP REVIEW • COMMENTS
A5-4	PID-0011 R-130	Leaks in feed and off-gas line connectors to vessel.	• Thermal cycling. • Misaligned ferrules. • Compression fittings close coupled to bottom of vessel.	• S-Potential toxic gas release. • Personnel exposure hazard.	Monitoring and leak checking.	• Consider moving compression fittings for ¾ inch inlet line and for TI-125 outside of insulation. • Review best position for locating H_2S sensor (refer to A1-10). • Consider installing Conax fittings on R-130 TI's 126-129.	RTI	
A5-5	PID-0011 R-130	Low pressure. Startup, process upset, or off-design pressure operation.	• Low pressure process operation. • Shutdown sequence. • Startup	• O-Potential for high-pressure velocity and catalyst carryover. • Potential for catalyst to plug downstream orifice in V-150.		Develop operating velocity and pressure limit to prevent catalyst carryover.	RTI	

P&ID: PID-0012
Sulfur Collection

DATE: August 2, 2000

ATTENDEES: Daryl Smith, RTI Brandon Russell, SCS
Jeff Portzer, RTI Pete Cherish, Facilitator

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A6-1	PID-0012 HX-140 V150 V-190	High flow. PCV-164 backpressure control valve fails to open.	• Loss of instrument air. • Loss of local power.	O-Potential for R-130 catalyst to elutriate over into HX-140 and plugs orifice in V-150 feed line.	None.	• Consider adding filter in R-130 outlet. • Review fail position of PCV-164.	RTI	
A6-2	PID-0012 V-150	Low flow.	Orifice in V-150 partially plugged.	O-Shutdown and maintenance required for orifice clean out.	Procedure not developed at this time.	Confirm shutdown and clean out procedure in place.	RTI	
A6-3	PID-0012 PSV-143	High pressure in HX-140.	HX-140 sulfur condenser tube failure.	• O-Potential to overpressure HX-140 pressure vessel. • S-Toxic gas release. • Hot liquid spray burn hazard.	• PSV-143 relief valve on vessel. • Steam/gas vent discharge to pad.	Consider venting PSV-143/PSV-191 into a KO pot to knockout hot water and vent gas to a safe location.	RTI	
A6-4	PID-0012 HX-140 Condenser coil	Maintenance hazard.	Removal of coil following failure.	S-Personnel hazard. Operator must climb skid for access to HX-140/V-190.	None.	Develop fall protection plan.	RTI	
A6-5	PID-0012 DSRP	Maintenance hazard DSRP under vent header pressure.	RTI operator opens DSRP process containment equipment while KBR is running.	S-Personnel hazard and potential for operator injury.		• Consider providing double block and bleeds for syngas, nitrogen, and tail gas at RTI skid for maintenance. • Consider providing additional bleed off to relieve system pressure to L.P. vent header/K.O. POT (refer to A6-3).	RTI	

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Sulfur Collection

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A6-6	PID-0012 V-150 (refer to A6-1)	Low pressure. PCV-164 fails to open.	• Loss of instrument air. • Loss of power. • Rapid depressurization.	• O-Potential for choke flow across V-150 orifice resulting in high velocity jet penetration. • Jet impacts vessel sidewall and erodes.		Estimate jet velocity and penetration length and confirm acceptability.	RTI	
A6-7	PID-0012 V-188	Maintenance under pressure.	• On-line removal of sulfur from V-188. • V-188 depressured to vent header pressure.	• S-Personnel exposure hazard. • V-188 not depressured when flange bolts are loosened. • (PI-196 plugs).	PI-196 indicates pressure in V-188.	Develop procedure to inspect PI-196 tap and clean as needed when opened for sulfur removal.	RTI	
A6-8	PID-0012 V-188	Maintenance under pressure.	On-line removal of sulfur from V-188.	S-Personnel exposure hazard to toxic gas vented from V-188. V-188 depressured to vent header.		• Provide high point atmospheric vent for V-188 to safe location. • Develop a design for on-line venting and discharge.	RTI RTI/SCS	Review design when complete.
A6-9	PID-0012 V-188	Maintenance under pressure.	On-line removal of sulfur V-188.	S-Personnel exposure to residual gas remaining in V-188.		• Review requirement and provide procedure for wearing respirator during V-188 disassembly and disconnect for sulfur removal. • Consider personnel monitor.	RTI/SCS	
A6-10	PID-0012 HX-140 V-190	No flow. Loss of cooling water.	Supply valve inadvertently closed.	S-Potential for steam generated overpressure in V-190/HX-140.	PSV-143/PSV-191 relief valves.	Verify criteria sizing PSVs and flow rates and discharge capacities.	RTI	

P&ID: PID-0012
Sulfur Collection

DATE: August 4, 2000

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A7-1	PID-0012 HX-160	Leak from damaged reheater tube.	• Local corrosion hole in HX-160 tube wall. • Heater overheating reheater tube wall.	S-Personnel exposure hazard. Toxic release of high temperature tailgas under system pressure (>2000ppm H_2S).	Tube material of construction.	Provide local toxic gas sensor over skid (refer to A1 leaks.) (refer to A1-10).	RTI	Investigate vendor sources for better corrosion resistant material at operating conditions.
A7-2	PID-0012 PCV-164	Low pressure. Plugged PT-164 pressure tap resulting in false control pressure to PC-164.	Sulfur carryover from V-150 and condensing in unheated pressure sensing line.	O-Operability upset. Loss of reactor pressure at normal flow rates resulting in high velocity carryover of catalyst.	Off-gas filter F-195.	• Consider alternate location for relocating PI-164. • If tap plugging becomes an unmanageable operability problem relocate tap.	RTI	
A7-3	PID-0012 Line 136/137 DSRP OG	High pressure. Plugged line/filter.	Local heater failure and/or cold spot.	• O-Operability upset. • Unable to control back pressure. • Potential for overpressuring equipment. • Unable to depressure.	System/equipment PSVs.	• Identify required bleed points for final depressuring prior to breaking into pressure containment equipment (refer to A6-5). • Review need to vent tailgas at thermal oxidizer for plugged line.	RTI SCS	

P&ID: PID-0014
Feed Gases & Preheaters

DATE: August 4, 2000

ATTENDEES: Daryl Smith, RTI Brandon Russell, SCS
Jeff Portzer, RTI Pete Cherish, Facilitator

STUDY REF	• LINE NO • EQUIPMENT NO • OTHER	• OPERATING DEVIATION • POSSIBLE CONDITION • GUIDE WORD	• POSSIBLE CAUSES OF DEVIATION • PROBLEM	CONSEQUENCES & REASONS FOR ACTION O-OPERABILITY S-SAFETY HAZARD	EXISTING PRECAUTION	• RECOMMENDED ACTION REQUIRED • NOTES/QUERIES	ACTION BY	• FURTHER IMPLICATIONS • FOLLOW-UP REVIEW • COMMENTS
B1-1	PID-0014 R-330	High pressure. PSV-334 relief line plugged from off-gas condensibles.	PCV-602 fails. Potential for AHGP to pressurize to nitrogen supply pressure (425-450 psig).	• S-Equipment damage. • Potential to overpressure R-330 reactor.	PSV-334	• Consider overpresssure protection on upstream feed system. • Consider setting PSV-602 at MAWP of R-330.	RTI	
B1-2	PID-0014 YV-05 YV-016	Reverse flow. Nitrogen backflows into DSRP coal gas feed.	Startup switchover from nitrogen startup mode to coal gas processing with YV-05 and YV-016 are first opened.	O-Startup upset.	Procedure calls for AHGP operating pressure less coal gas supply pressure.	Flag startup upset potential in procedure.	RTI	
B1-3	PID-0014 PCV-303 PCV-306	High pressure. 1800 psig H_2S and air cylinders feed AHGP.	PCV-303 or PCV-306 fails.	• S-System overpressure. • Potential equipment damage. • Potential personnel hazard.	PCV regulators show built-in overpressure relief valves.	• Confirm that a relief valve is integrated into regulator and can protect downstream equipment. • Review (TBD) vent design to safe location (refer to A6-3).	RTI	

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Feed Gases & Preheaters
DATE: August 4, 2000
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B2-1	PID-0014 CYL-302	Leaks. Location unknown (TBD).	Hookup connectors, valve, or regulator leak H_2S into trailer.	S-Toxic gas release.	Gas monitoring alarms.	Suggest outside location in safe location and off loading convenience.	RTI/SCS	
B2-2	PID-0014 (Same as B2-1)	Leaks. Outside location (refer to B2-1).	(Same as B2-1)	S-Toxic gas release.	Not defined.	Locate H_2S sensor head for outside cylinder rack (refer to A1-10).	RTI/SCS	

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Feed Gases & Preheaters
DATE: August 4, 2000
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B3-1	PID-0014 HX-325 SO_2 REGEN PHTR coil	Leaks.	Over temperature tube rupture.	S-Personnel exposure hazard. Toxic gas release in trailer under pressure.	• SO_2 toxic gas alarm. • Close YV-9 SO_2 isolation valve. • Close manual HV-513 outside trailer.	Develop failure mode action plan for operating procedure.	RTI	
B3-2	PID-0014 FCV-309 Line 1007- SO_2 REGEN gas	Reverse flow.	Blocked flow in Line 1007 and LSO_2 pressure greater than nitrogen pressure in 1005.	S-Equipment failure. Potential to backflow LSO_2 into nitrogen supply.	Procedure PCV pressure settings.	• Confirm procedure. • Consider check valve in line 1005.	RTI	

P&ID: PID-0014 **DATE:** August 7, 2000 **ATTENDEES:** Daryl Smith, RTI Brandon Russell, SCS
AHGP Feed Gases & Preheaters Jeff Portzer, RTI Pete Cherish, Facilitator

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B4-1	PID-0014 Air REGEN feed CYL-301	High pressure. Process air from high-pressure cylinder (1800 psi).	• PCV-306 failure with system blocked. • MAWP of V-320 and F-335 unknown.	S-Potential for equipment overpressure V-320 air REGEN PHTR and R-330 designed for lower pressure service.	• MFC/FCV-309 pressure rating 3000 psig at ambient temperature. • R-330 MAWP 365 psig @ 1250°F.	• Confirm MAWP/temp for V-320 and F-335 and other equipment upstream of PCV-366 in air REGEN path. • Consider overpressure of process air feed with downstream PSV set at limiting MAWP of equipment.	RTI	
B4-2	PID-0014 Air REGEN feed R-330	Leak. Air leak into process during sulfidation mode of operation.	HV-311 cylinder isolation valve open and YV-1 isolation valve unable to close completely.	• S-Equipment and personnel hazard. • Potential to introduce air into fuel gas at elevated pressure and temperature.	• Procedure • HV-311 and air cylinder valve closed by procedure and checklist.	• Consider adding bleed valve inside trailer to vent line between cylinder valve and HV-311 and confirm procedural checklist in place. • Determine flammability range of fuel gas inside reactor and potential combustion rate and pressure rise.	RTI	Review the existing precautions in light of results of the flammability analysis.
B4-3	PID-0014 Air REGEN feed MFC/FCV-309 MFC/FCV-313	Reverse flow. LSO_2 backflows into process nitrogen line tie in at HX-325 SO_2 REGEN PHTR coil.	Product line at/or downstream of R-330 plugs.	O-MFC fails and leaks.	MAWP/temp of MFC.	• Consider adding check valve process N2 line 1005. • Consider adding check valve in process air line 1004.	RTI	
B4-4	PID-0014 YV-03 Emergency nitrogen purge flow.	High flow. High velocity through R-330.	Emergency S/D valve sequence.	O-Potential for sorbent carryover and distributor damage.		• Determine maximum velocity and nitrogen flow rate. • Consider installing RO downstream of YV-03 to limit emergency nitrogen purge flow.	RTI	
B4-5	PID-0014 R-330	Process air feed continues after sorbent regeneration is complete.	Operator error.	O-Potential intrusion into thermal oxidizer syngas inlet.	• Procedure. • TE-338 reactor temperature. • Off-gas analyzer monitoring.	Determine maximum flow through FCV-313 required for sorbent regeneration.	RTI	

P&ID: PID-0015
AHGP Reactor & Product Recovery
DATE: August 7, 2000
ATTENDEES: Daryl Smith, RTI Brandon Russell, SCS
Jeff Portzer, RTI Pete Cherish, Facilitator

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B5-1	PID-0015 R-330 Fluid bed reactor	High pressure.	Plugged reactor outlet and plugged relief line to PSV-334.	S-Vessel overpressure.	PSV-334 relief valve for R-330.	• (Refer to B1, B2, B3, and B4) • Consider overpressure of system via feed stream PSVs.	RTI	
B5-2	PID-0015 V-375 Condensate pot	Leaks.	HV-376 liquid discharge valve leaks under system pressure.	S-Potential toxic gas release inside trailer.		Consider adding second valve downstream at end of gooseneck discharge line.	RTI	
B5-3	PID-0015 Line 1002 H_2S feed to reactor.	High concentration.	• Loss of instrument air. Isolation valve fail position. • No isolation of H_2S supply.	• S-Potential high H_2S concentration in tail gas with nitrogen by-pass flow via YV-3. • Possible high velocity in R-330 causing carryover of bed material.	None.	Identify closing H_2S cylinder valve in the procedure failure action plan for loss of instrument air and if emergency shutdown is initiated.	RTI	
B5-4	PID-0015 Cooling water FE-352A Rotameter	High pressure. FE-352A installed for lower pressure service.	CW supply to RTI from KBR closed loop cooling at 140 psig.	S-FE-352A fails due to over pressure.		Provide rotameter for the higher-pressure service.	RTI	
B5-5	PID-0015 Cooling water	Leak. Process leak into cooling water.	Corrosion failure of HX-370 condenser tube.	S-Potential for over pressure failure of rotameters in CW supply line.		Consider adding check valve in CW supply lines.	RTI	
B5-6	PID-0015 R-330	Contaminants. Oxygen in coal gas.	KBR upset, startup, or S/D.	O-Potential for high reactor outlet temperature.		• Provide typical oxygen concentrations in KBR syngas. • Review concentrations and assess process effects and define action plan, if required.	SCS RTI	

P&ID: PID-0014
AHGP Reactor & Product Recovery
DATE: August 8, 2000
ATTENDEES: Daryl Smith, RTI; Brandon Russell, SCS; Jeff Portzer, RTI; Pete Cherish, Facilitator

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B6-1	PID-0017 PCV-602	High pressure. Supply nitrogen pressure delivered to process.	PCV-602 failure.	O-Potential for equipment over pressure.	• PSV setting for high-pressure protection of nitrogen supply to line 1005. • MAWP/temp of equipment.	Confirm PSV setting and MAWP/temp.		
B6-2	PID-0015 HX-340/V-350	High pressure.	Tube rupture failure in HX-340.	S-Potential for equipment over pressure.	PSV-345 set at 50 psig for over pressure protection.	• Verify sizing flow capacity for PSV-345 based on steam generation with a ruptured tube. • Confirm MAWP/temp of equipment.		
B6-3	PID-0015 R-330	High flow/high velocity through R-330.	Rapid process depressurization.	O-Potential for sorbent carryover and distributor damage.	Filter F-335 provided as barrier and collector.	None.		
B6-4	PID-0015 V-350	Material of construction.	Tube coil may be fabricated from copper.	O-Material selection not per design requirement.		• Confirm MOC for tube coil. • If coil is copper, replace with stainless steel.		

P&ID: PID-0015
AHGP Reactor & Product Recovery

DATE: August 8, 2000

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Jeff Portzer, RTI Pete Cherish, Facilitator

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B7-1	PID-0015 Line 1012	Reverse flow. Integrated operation startup.	AHGP online and operating with DSRP off-line for maintenance and YV-010 leaks through.	S-Potential for toxic gas from AHGP off-gas line 1012 to by-pass leakage to DSRP with concentrated SO_2 in off-gas.	YV-010 positive tight shutoff.	• Review operating modes for line 1012 AHGP REGEN off-gas to DSRP. • Consider adding positive isolation of line 1012 when not in use.	RTI	
B7-2	PID-0015 AHGP Process Unit.	Shutdown containment pressure.	System riding on 15-17 psig vent header pressure.	O-Potential of venting process gas to trailer and discharging toxic gas.	Procedure (TBD).	Provide vent lines to vent AHGP process gas to vent blower.	RTI	
B7-3	PID-0015	Shutdown sorbent damage.	• Normal shutdown sequence in stopping feed flows. • Operator error.	O-Potential for catalyst damage by SO_2 flow.	Procedure for S/D.	Verify procedure identifies that SO_2 flow is shutdown first.	RTI	

P&ID: PID-0020
Instrument Air

DATE: August 3, 2000

ATTENDEES: Daryl Smith, RTI Brandon Russell, SCS
Jeff Portzer, RTI Pete Cherish, Facilitator

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C1-1	PID-0017 DSRP instrument air skid. Line 1027-IA	Low pressure supply to DSRP.	Valve upstream of instrument air supply filter F-630 inadvertently closed to isolate air supply to trailer.	• Loss of air supply to DSRP. • DSRP instrument air failure.		Consider adding isolation valve on 1027-IA HDR-1/2" T-SS.	RTI	

P&ID: PID-0018
LSO$_2$ Delivery System

DATE: August 3, 2000

ATTENDEES: Daryl Smith, RTI Brandon Russell, SCS
Jeff Portzer, RTI Pete Cherish, Facilitator

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D1-1	PID-0018 Line 1052-LSO$_2$	Leak.	• Routing path of 1/8" LSO$_2$-tubed. • LSO$_2$ line accidentally breaks.	S-Toxic gas release under pad pressure.	• Unknown • Design TBD	• Provide safe routing path to mitigate tubing damage. • Consider providing tube shielding for damage protection.	RTI	
D1-2	PID-0018 Line 1052-LSO$_2$	High-pressure. Thermal liquid expansion.	Liquid SO$_2$ trapped between closed valves (HV-51, HV-512, and HV-513) at pad gas pressure.	S-Potential for high pressure tube rupture and toxic gas vented.	None.	• Develop procedure for long down periods to allow LSO$_2$ boil off prior to closing line block valves. • Consider adding expansion pot and venting under ambient vapor pressure to safe location.	RTI	
D1-3	PID-0018 T-500	High-pressure.	PCV-506 nitrogen pad regulator fails and PSV-508 undersized.	• S-Potential for fuse plug blowout. • High volume toxic gas release.	• PSV-508 (sizing unknown) • T-500 fuse plug.	• Confirm sizing capacity of PSV-508. • Get written guidance from air products for overpressure relief venting on T-500 padded cylinder.	RTI	
D1-4	PID-0018	Low flow. High-pressure drop through tubing.	1/8" LSO$_2$ supply tubing undersized for length of run.	O-SO$_2$ feed limited to DSRP.	Unknown.	Review routing requirements (refer to D1-1) and check pressure drop at maximum feed rate.	RTI	

P&ID: E-M-D0002
PSDF/RTI Test Protocol

DATE: August 4, 2000

ATTENDEES: Daryl Smith, RTI Brandon Russell, SCS
Jeff Portzer, RTI Pete Cherish, Facilitator

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E-1	E-M-D0002 SCS Structure	Leaks detected.	Shaft seal or valve packing leak.	• S-Emergency response. • Gas monitor alarms activated in SCS structure.	TBD	• Develop SCS/RTI emergency response plan. • Provide a wall placard in the RTI trailer identifying alarms and emergency action sequence.	SCS/RTI	Review gas monitor alarms, trailer personnel assembly plan, control room notification plan, shutdown, and evacuation plan.
E-2	E-M-D0002 Propane vaporizer/tanks.	Leaks identified.	Venting or equipment wear/damage.	S-Potential fire/explosion hazard.	TBD	Develop RTI shutdown and evacuation plan.	RTI/SCS	Suggest SCS on-site safety review with RTI, et al.
E-3	E-M-D0002 Assembly building.	Operation emergency. Severe weather.	• Thunder storms. • Tornadoes. • Hurricanes.	S-Potential operator/personnel injury.	• Radio/TV weather warning alerts. • Evacuate to safe shelter.	Finalize RTI shutdown and evacuation plan.	RTI/SCS	Suggest SCS on-site safety review with RTI, et al.
E-4	E-M-D0002 Proposed pilot units and SO_2 cylinder.	Leaks. SO_2 cylinder/skid.	• Thermal cycling mechanical tube connectors. • RTI equipment damage. • SO_2 cylinder/valve/line damage.	• S-Toxic gas release. • Personnel hazard.	TBD. Gas detector alarms.	• Develop RTI/SCS operation and emergency response plan. • Provide orange strobe light at skid for SO_2 sensor alarm to alert RTI for closing supply valve and need to evacuate.	RTI/SCS SCS	Suggest SCS on-site safety review with RTI, et al.
E-5	E-M-D0002 DSRP, AHGP, trailer.	Leaks. Hot and cold pressure leaks.	Equipment, tubing pressure/temperature cycling.	• S-Toxic/flammable gas leaks. • Personnel and fire hazard.	Gas detector alarms.	• SCS to specify and install LEL and oxygen sensors inside trailer and at skid. • RTI to provide contact closure to SCS for gas monitor high/high alarm. • RTI to evaluate feasibility of locating all gas cylinders outside, as required to insure adequate atmosphere inside trailer.	SCS/RTI RTI/SCS RTI/SCS	
E-6	E-M-D0002 SO_2 cylinder	Storage inventory.	Excess inventory supplied by vendor (greater 1000 pounds).	S-PSDF/site reportable inventory storage violation.	TBD	Develop inventory control procedure for receiving, delivery, and installation of cylinders.	SCS/RTI	

P&ID: PID-0013/PID-0016
Analytical

DATE: August 4, 2000

ATTENDEES:
Daryl Smith, RTI
Jeff Portzer, RTI
Gary Howe, RTI
Brandon Russell, SCS
Pete Cherish, Facilitator

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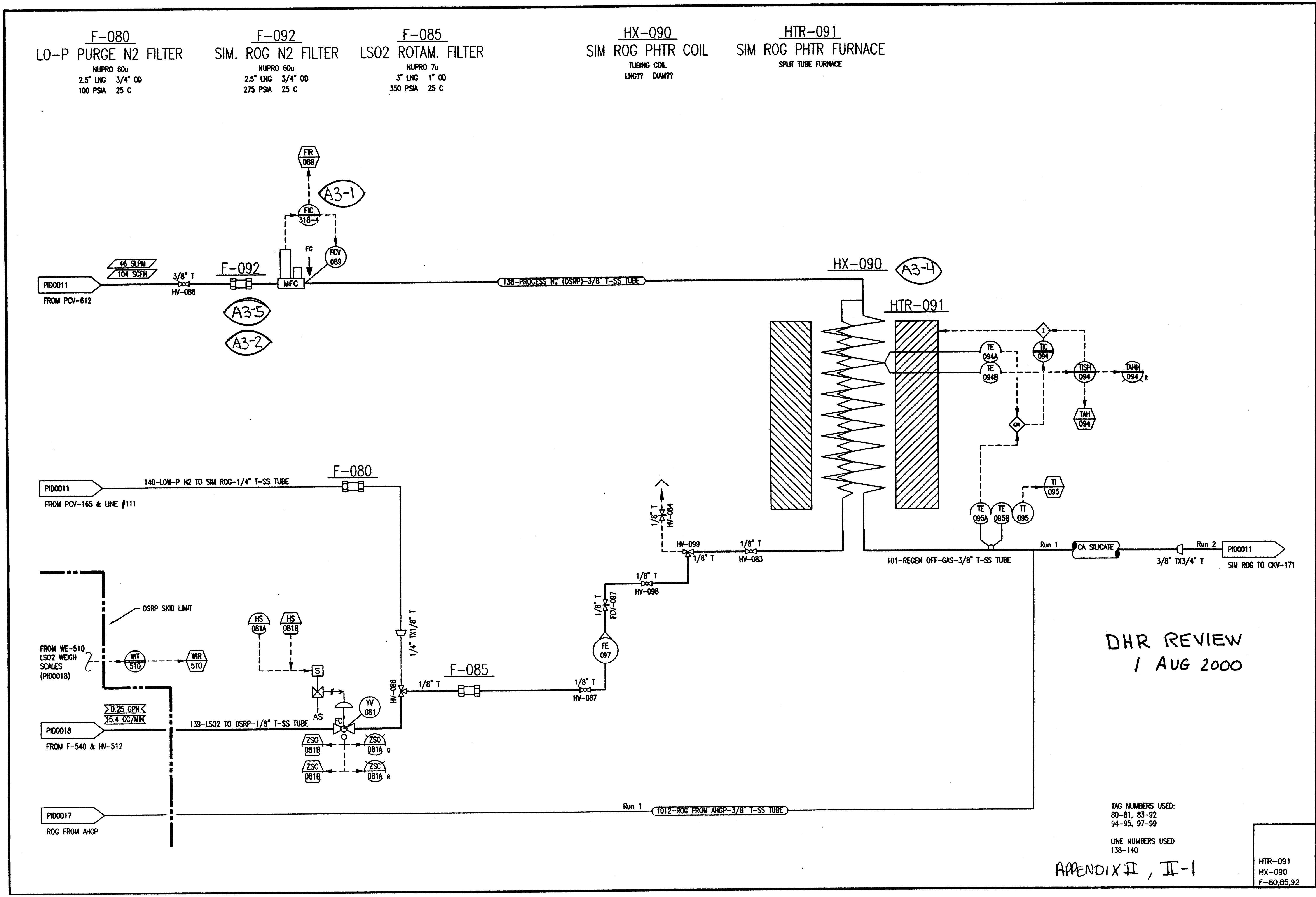
F1-1	PID-0013 HX-210 A-1 Sample Coil. Line 117-ROG sample.	Leak/tube rupture.	Corrosion.	O-S/D DSRP to replace coil and perform maintenance.		Consider installing high temperature valve at tail gas sample line tie-in to perform replacement/maintenance of coil.	RTI	
F1-2	PID-0013 HX-225 Sample Cooler.	High pressure.	PCV-223 regulator failure while blocked in.	O-Potential for over pressure and damage to HX-225.		• Determine MAWP/temp of HX-225. • Consider PSV for over pressure protection.	RTI	
F1-3	PID-0013/PID-0016 Support gas cylinders.	Leak. H_2/N_2 cylinders.	Fusible plug failure from service age/pressure creep.	S-Potential for flammable mixture or low oxygen trailer atmosphere.	HVAC system designed for 4-6-volume change per hour.	• Confirm/test volume change rates. • Leave HVAC on when trailer not occupied and cylinders are in trailer. Include in procedure checklist.	RTI	

APPENDIX II

DHR REVIEW P&IDs



DHR REVIEW
1 AUG 2000

TAG NUMBERS USED:
80-81, 83-92
94-95, 97-99

LINE NUMBERS USED
138-140

APPENDIX II , II-1

HTR-091
HX-090
F-80,85,92

NO.	DATE	BY	REVISIONS	APP.
A	5/20/98	JWP	INCORPORATES CHECKER'S COMMENTS	
B	02/11/99	JWP	ADDED YY-081	
C	5/20/99	JWP	REVISED CNTRLS; CHANGED TO 1-Z FURNACE	
D	02/02/00	JWP	REVISED LINE ID'S AND LABELS	
E	04/05/00	JWP	ADDED TE-095; REVISED LOOP #094	
F	07/25/00	JWP	ADDED SKID LIMIT "FENCE"	

REFERENCE DRAWINGS

DWG. NO.	

ENGINEERING RECORD	DATE
DRN:JWP	4/6/98
CHK:BST	5/8/98
APP:	
W.O.: 5666	
SCALE: NONE	

DSRP FIELD TEST PILOT UNIT
P&ID – SIM ROG SYSTEM
Direct Sulfur Recovery Process
Wilsonville, AL

DOE-FETC

DWG. NO. PID0010
REV F

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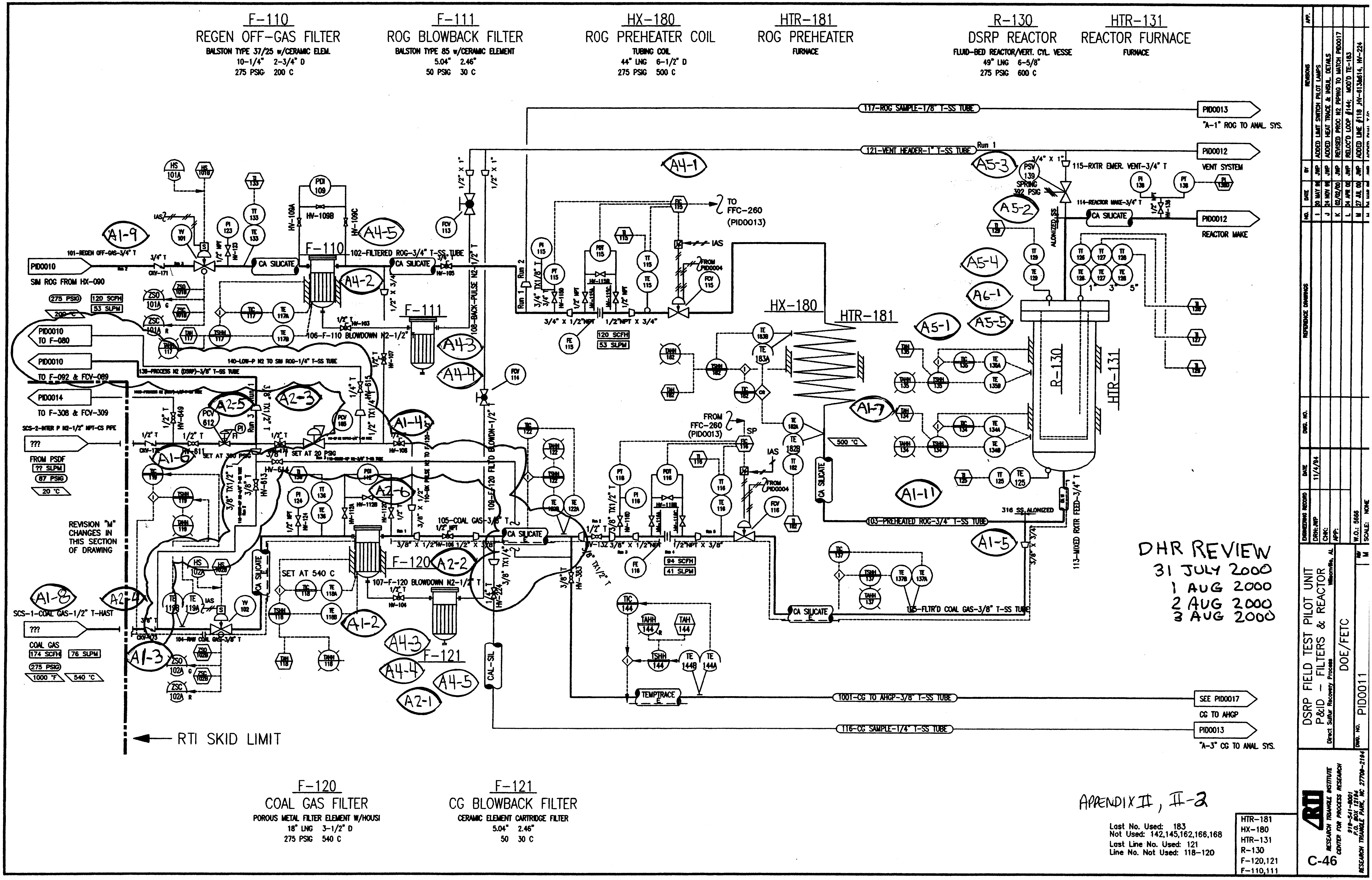
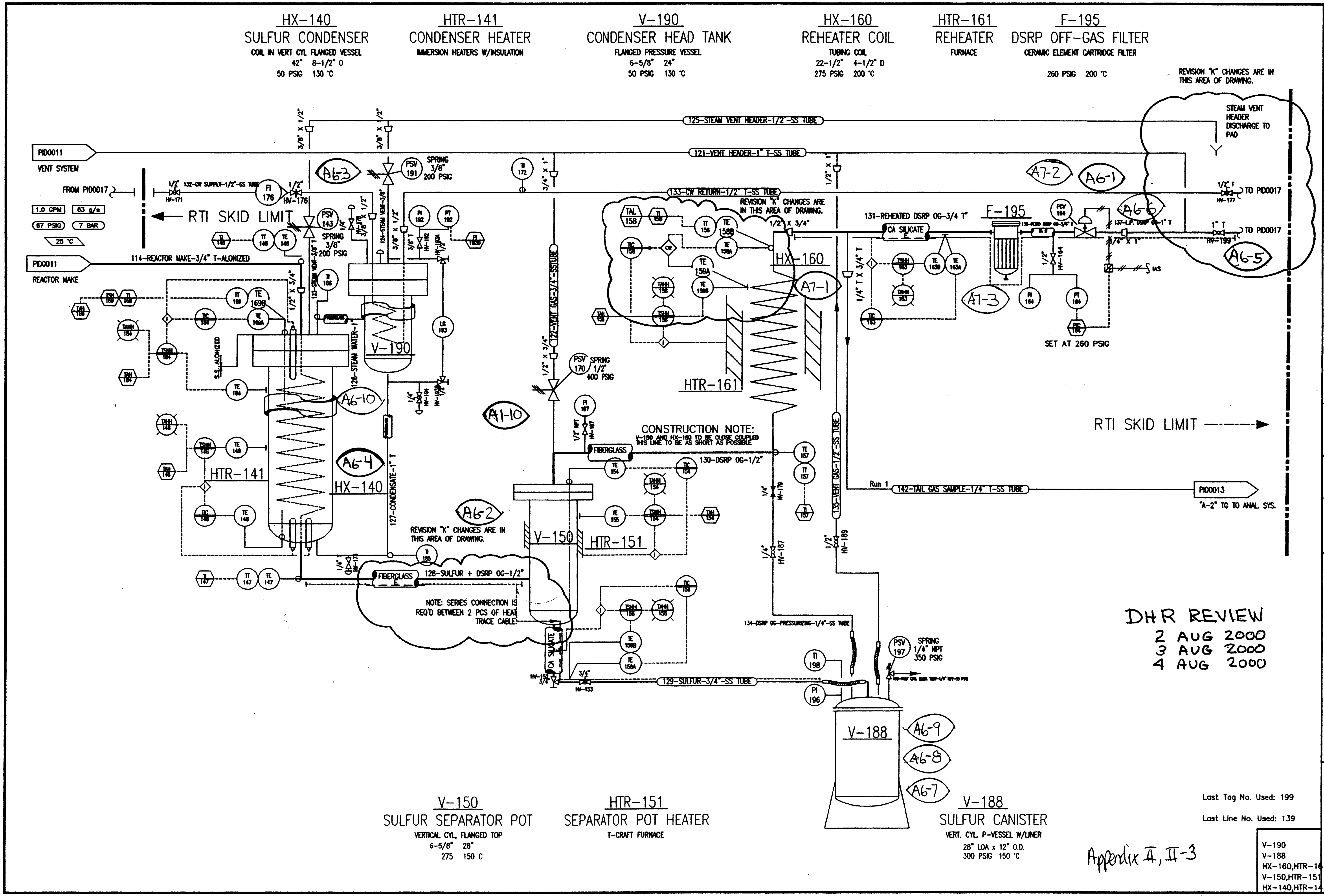


DHR REVIEW
31 JULY 2000
1 AUG 2000
2 AUG 2000
3 AUG 2000

APPENDIX II, II-2



DHR REVIEW
2 AUG 2000
3 AUG 2000
4 AUG 2000

Appendix II, II-3

NO.	DATE	BY	REVISIONS	APP.
I	20MAY99	JWP		
J	24NOV98	JWP	ADDED HEAT TRACING & INSUL. DETAIL	
K	04APR00	JWP	MOVE LOOP #144,CHG LOOP#158,ADD HV-199	
F	11MAR98	JWP	ISSUED FOR SKID ASSEMBLY	
G	30JUL98	JWP	CONVERTED DWG TO AUTOCAD REL 14	
H	04MAR99	JWP	ADDED V-188, DUAL T/C'S	

REFERENCE DRAWINGS

DWG. NO.	DATE
	12/12/94

ENGINEERING RECORD
DRN: JWP
CHK:
APP:
W.O.: 5666
SCALE: NONE

DSRP FIELD TEST PILOT UNIT
P&ID - SULFUR COLLECTION
Direct Sulfur Recovery Process
Wilsonville, AL

DOE/FETC

DWG. NO. PID0012
REV K

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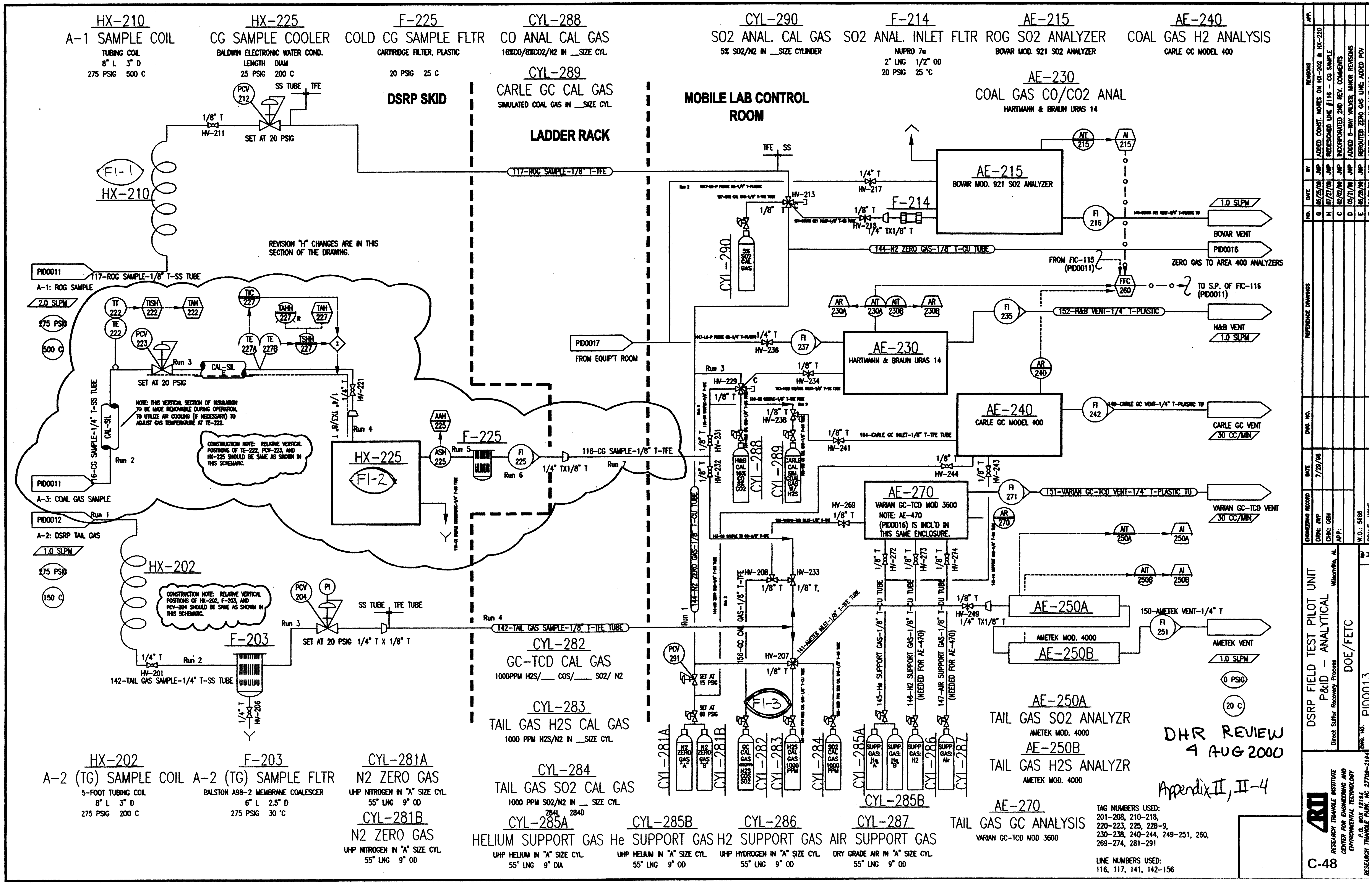
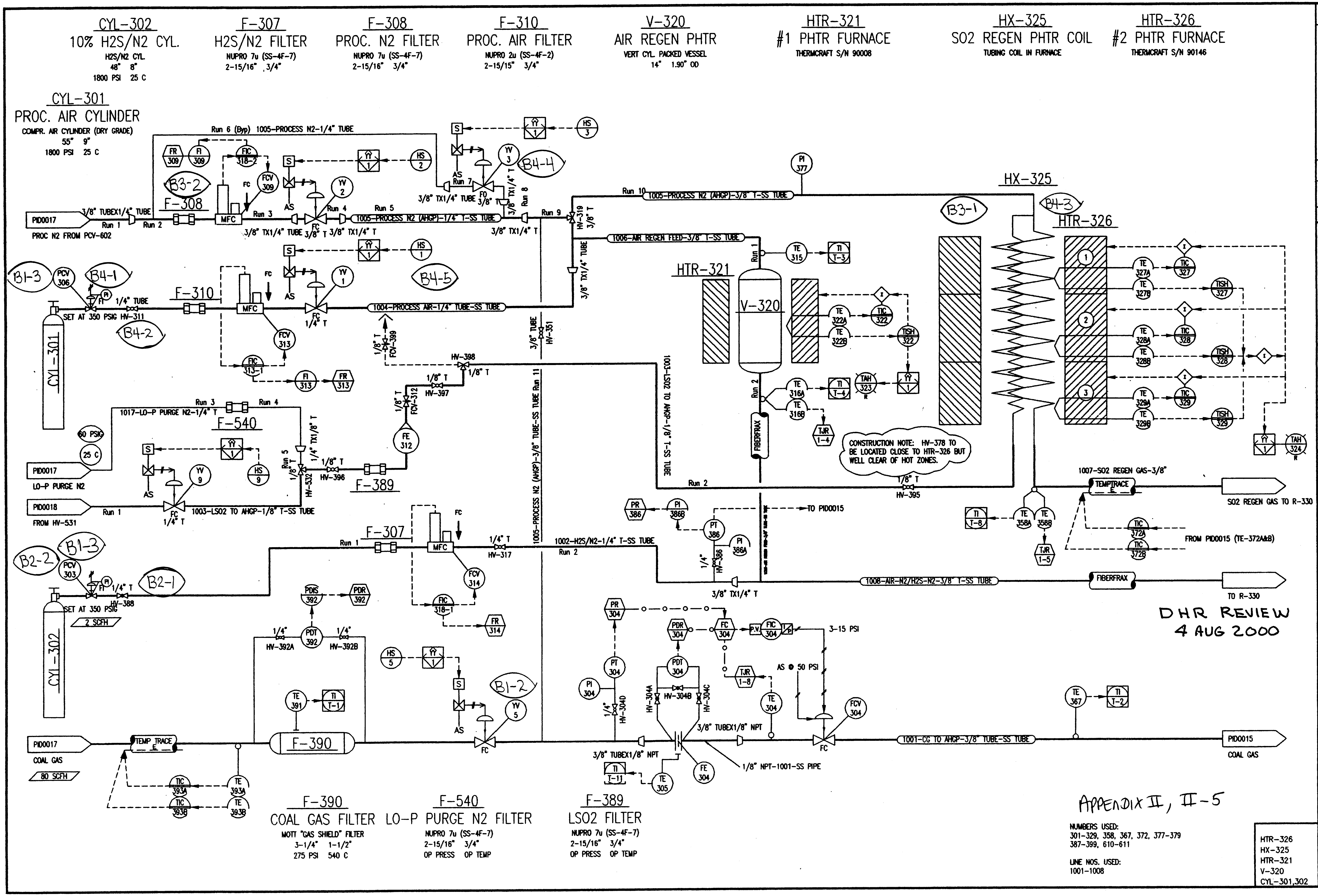


DHR REVIEW
4 AUG 2000

Appendix II, II-4



DHR REVIEW
4 AUG 2000

APPENDIX II, II-5

NUMBERS USED:
301-329, 358, 367, 372, 377-379
387-399, 610-611

LINE NOS. USED:
1001-1008

HTR-326
HX-325
HTR-321
V-320
CYL-301,302

C-49

NO.	DATE	BY	REVISIONS	APP.
A	5/21/98	JWP	INCORPORATED CHECKER'S COMMENTS	
B	09/14/98	JWP	ADDED T/C READOUTS	
C	10/6/98	JWP	GENERAL REVISIONS	
D	02/05/99	JWP	ADDED YV-9	
E	01/11/00	JWP	CLEANED UP PIPE RUN DOCUMENTATION	

REFERENCE DRAWINGS

DWG. NO.	

ENGINEERING RECORD	DATE
DRN: JWP	2/10/98
CHK: BST	5/8/98
APP:	
W.O.: 5869	

AHGP FIELD TEST BENCH UNIT
P&ID - FEED GASES + PREHEATERS
Advanced Hot Gas Desulfurization
Wilsonville, AL

DOE-FETC

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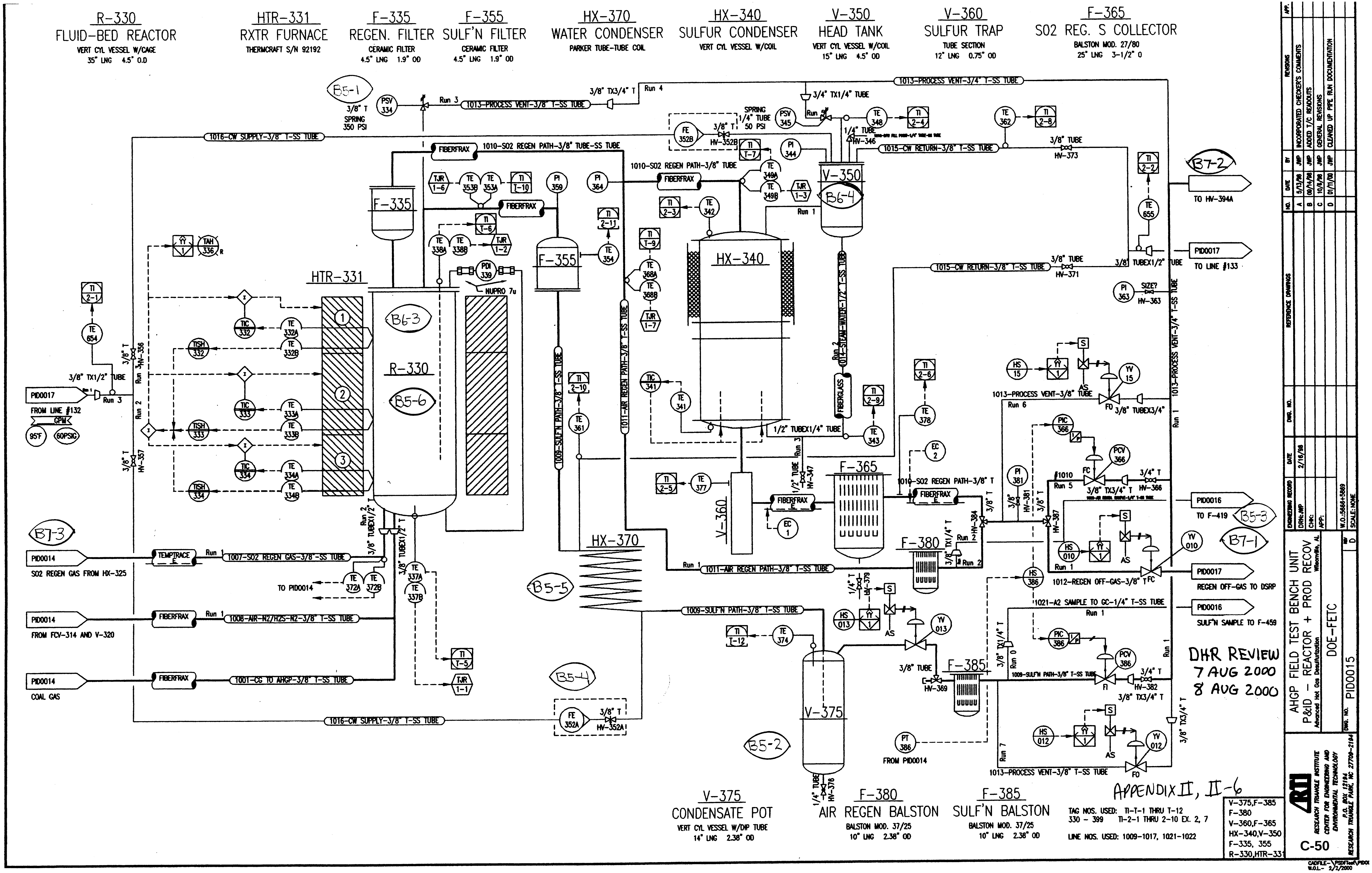
DWG. NO. PID0014

REV



DHR REVIEW
7 AUG 2000
8 AUG 2000

APPENDIX II, II-6

F-419
AIR REG. SAMP. FILT.
NUPRO 7u INLINE FILTER
2" 1/2"

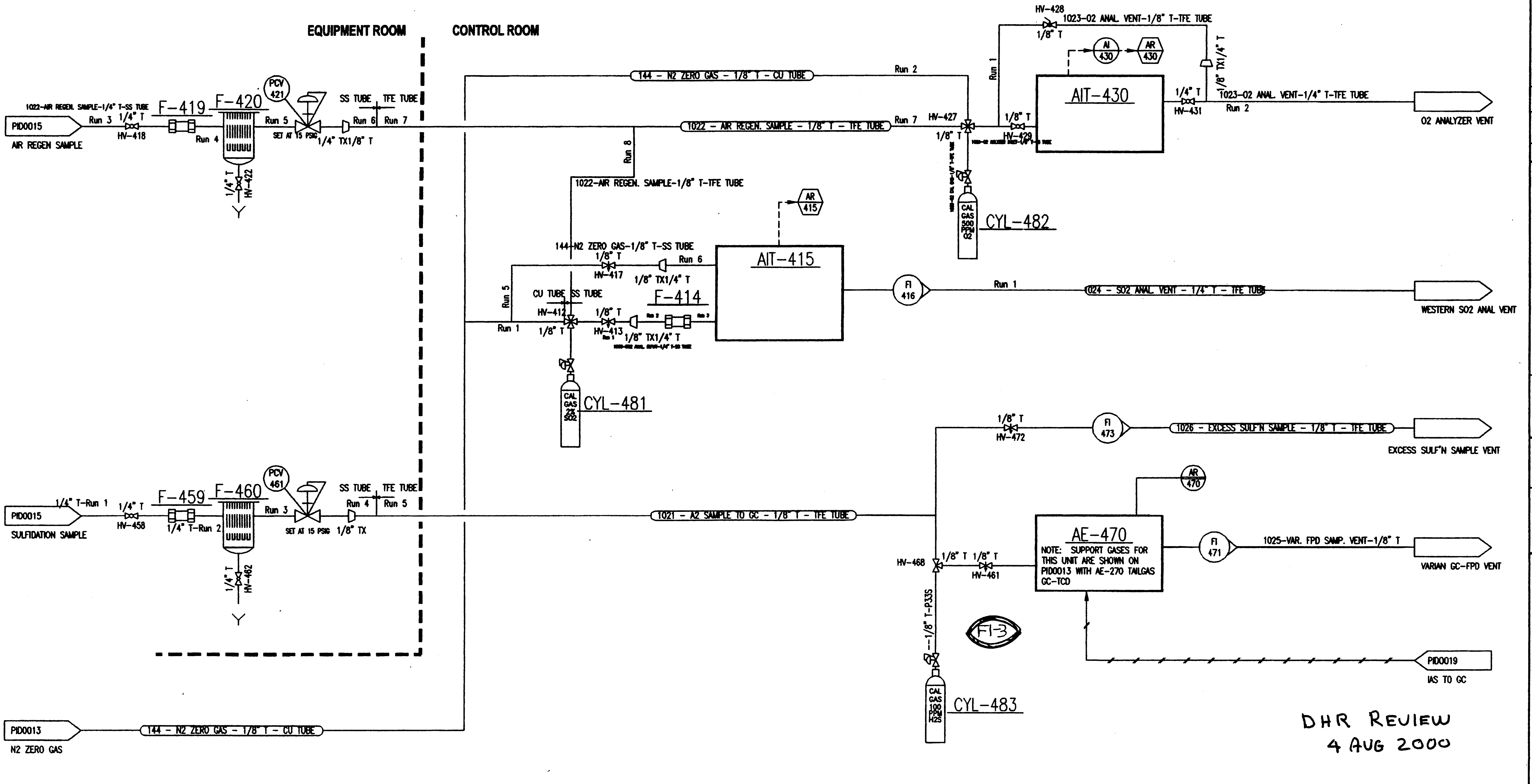
F-420
AIR REG. SAMP. COND.
BALSTON MOD. 95S6
3-3/4" 1-5/8"

F-414
SO2 ANAL INLET FLTR.
NUPRO 7u INLINE FILTER

AIT-415
AIR REGEN SO2 ANAL.
WESTERN RESEARCH MOD.721-AT

AIT-430
AIR REGEN O2 ANAL.
TELEDYNE TRACE O2 ANALYZER

AE-470
SULFIDATION GC-FPD
VARIAN MOD. 3600 GC w/FPD



DHR REVIEW
4 AUG 2000

F-459
SULF. SAMPLE FILTER
NUPRO 7u INLINE FILTER
2" 1/2"

F-460
SULF'N SAMPLE COND.
BALSTON MODEL 95S6 CARTRIDGE FILTER
3-3/4" 1-5/8"

CYL-481
SO2 ANAL CAL GAS
2% SO2/N2 IN __ SIZE CYL.

CYL-482
O2 ANALYZER CAL GAS
500 PPM O2/N2 IN __SIZE CYLINDER

CYL-483
SULF. GC-FPD CAL GAS
500 PPM H2S/N2 IN __ SIZE CYLINDER

APPENDIX II, II-7

TAG NUMBERS USED:
412-422; 427-431
458-462; 468-473; 481-3

LINE NUMBERS USED:
1023-1026

AE-470
AIT-430
AIT-415

NO.	DATE	BY	REVISIONS	APP.
A	09/18/98	JMP	DRAFT-- FOR REVIEW	
B	02/02/99	JMP	INCORPORATED REVIEW COMMENTS	
C	01/11/00	JMP	CLEANED UP PIPE RUN DOCUMENTATION	

REFERENCE DRAWINGS | DWG. NO.

ENGINEERING RECORD	DATE
DRN: JMP	9/8/98
CHK:	
APP:	
W.O.: 5869	
SCALE: NONE	

AHGP FIELD TEST BENCH UNIT
P&ID - ANALYTICAL
Advanced Hot Gas Desulfurization Wilsonville, AL
DOE-FETC
DWG. NO. PID0016
REV C

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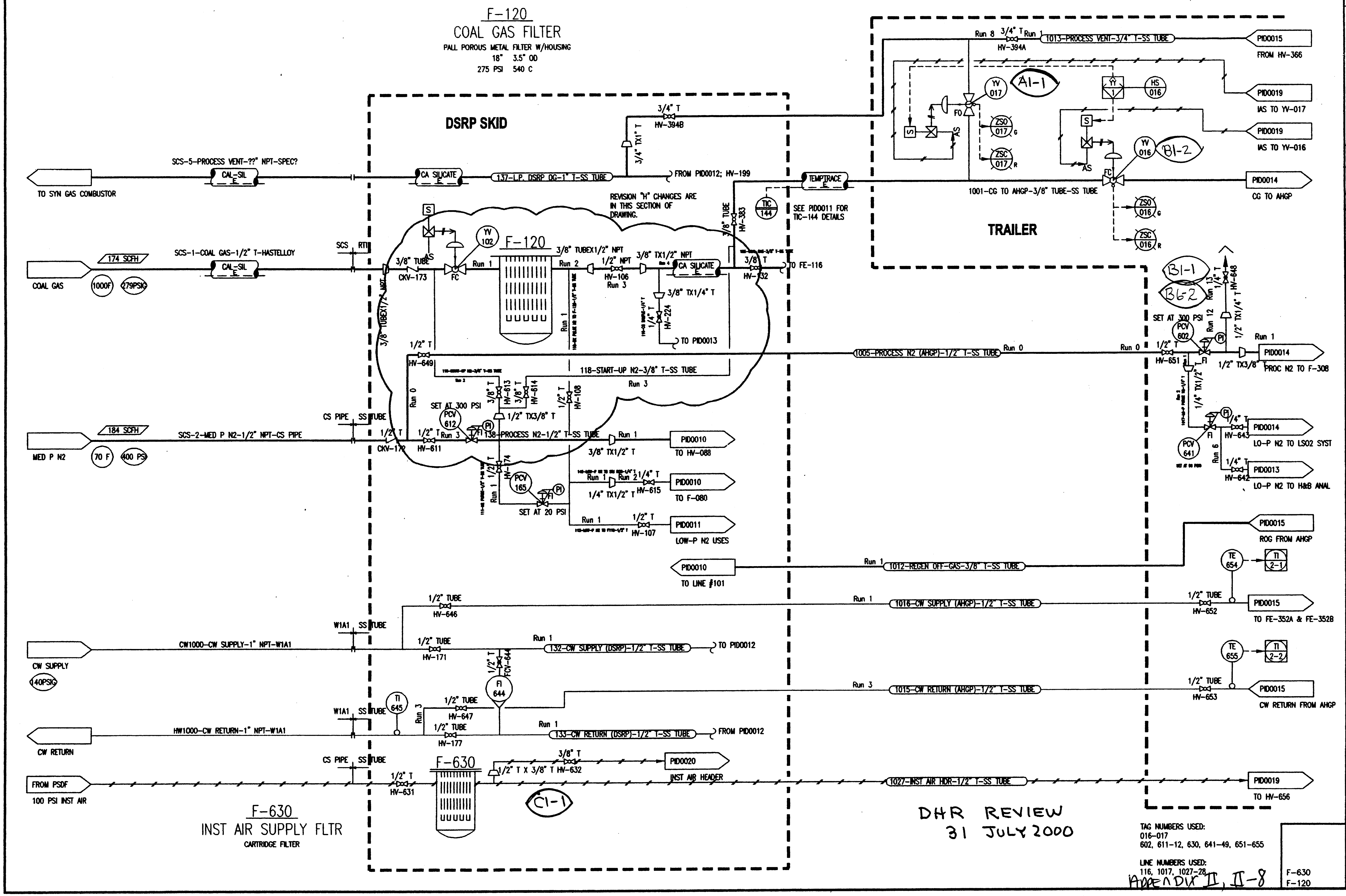

DHR REVIEW
31 JULY 2000

TAG NUMBERS USED:
016-017
602, 611-12, 630, 641-49, 651-655

LINE NUMBERS USED:
116, 1017, 1027-28

Appendix II, II-8

F-630
F-120

NO.	DATE	BY	REVISIONS	APP
G	3/31/00	JWP	REV'D VENT LINE, OTHER SCS INTERFACES	
H	07/28/00	JWP	ADDED LINE #118; HV-613,614; HV-224	
C	3/6/99	JWP	REVISED TAG NOS.	
D	08/17/98	JWP	ADDED INST AIR SUPPLY HEADER, F-630	
E	12/14/99	JWP	CHANGED TAG NOS. OF HV-646, 647	
F	01/11/00	JWP	CLEANED UP PIPE RUN DOCUMENTATION	

REFERENCE DRAWINGS

DWG. NO.	ENGINEERING RECORD	DATE
	DRN: JWP	2/27/98
	CHK: BST	7/10/98
	APP:	
	W.O.: 5666 & 5869	
	SCALE: NONE	

PSDF FIELD TEST
P&ID SCS-RTI INTERFACE
DSRP + AHGP
Wilsonville, AL

DOE-FETC

DWG. NO. PID0017
REV H

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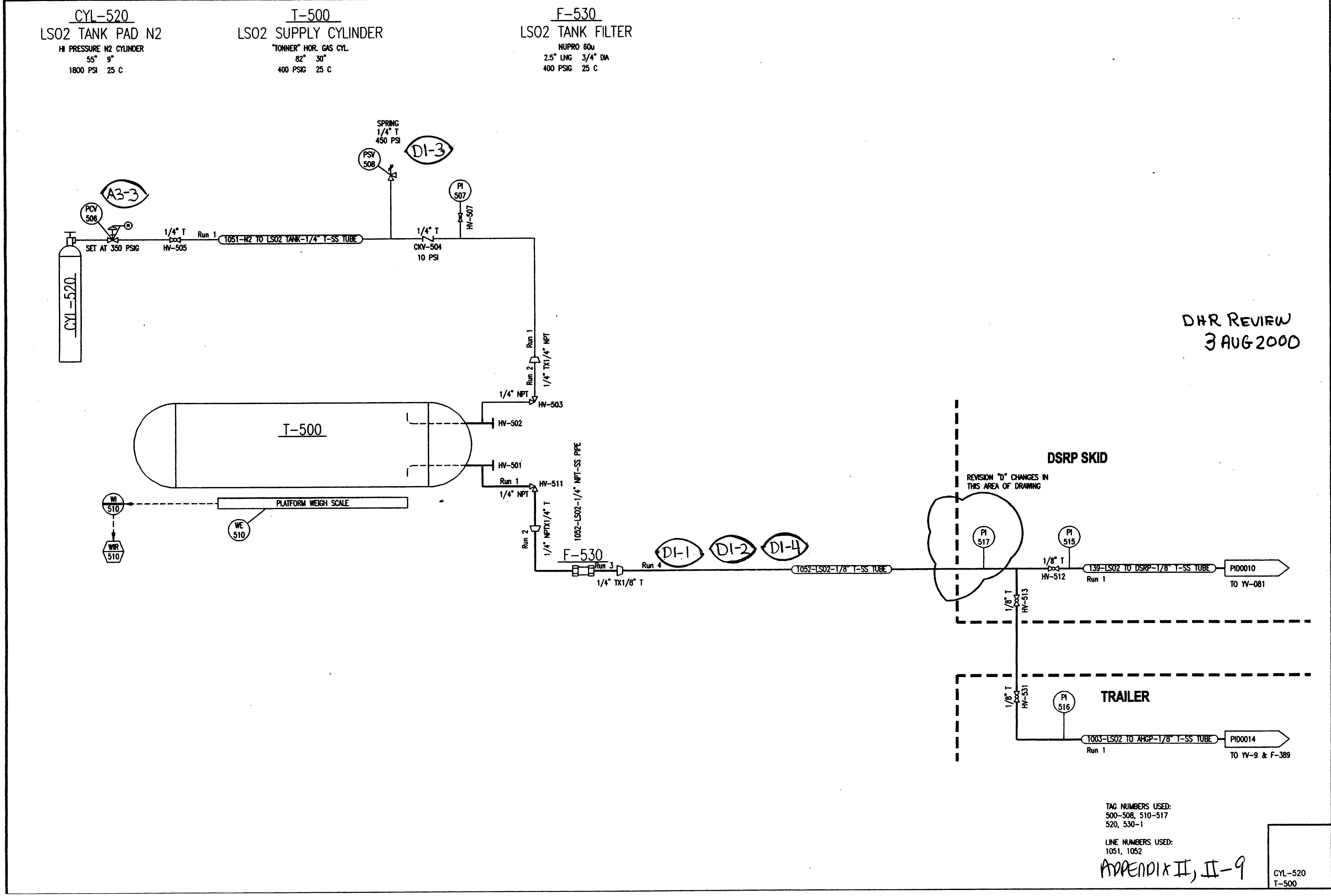
C-52

CADFILE-\PSDF&AHGP\
W.O.L.- 7/28/2000



DHR REVIEW
3 AUG 2000

TAG NUMBERS USED:
500-508, 510-517
520, 530-1

LINE NUMBERS USED:
1051, 1052

APPENDIX II, II-9

NO.	DATE	BY	REVISIONS	APP.
A	05/20/98	JWP	INCORPORATES CHECKER'S REVISIONS	
B	01/11/00	JWP	CLEANED UP PIPE RUN DOCUMENTATION	
C	04/05/00	JWP	ADDED PSV-508	
D	07/14/00	JWP	ADDED PI-517	

REFERENCE DRAWINGS

DWG. NO.

ENGINEERING RECORD	DATE
DRN: JWP	4/2/98
CHK: BST	5/8/98
APP:	
W.O.: 5666 + 5869	

PSDF FIELD TEST
P&ID - LSO2 DELIVERY SYSTEM
DSRP & AHGP
Wilsonville, AL

DOE-FETC

DWG. NO. PID0018

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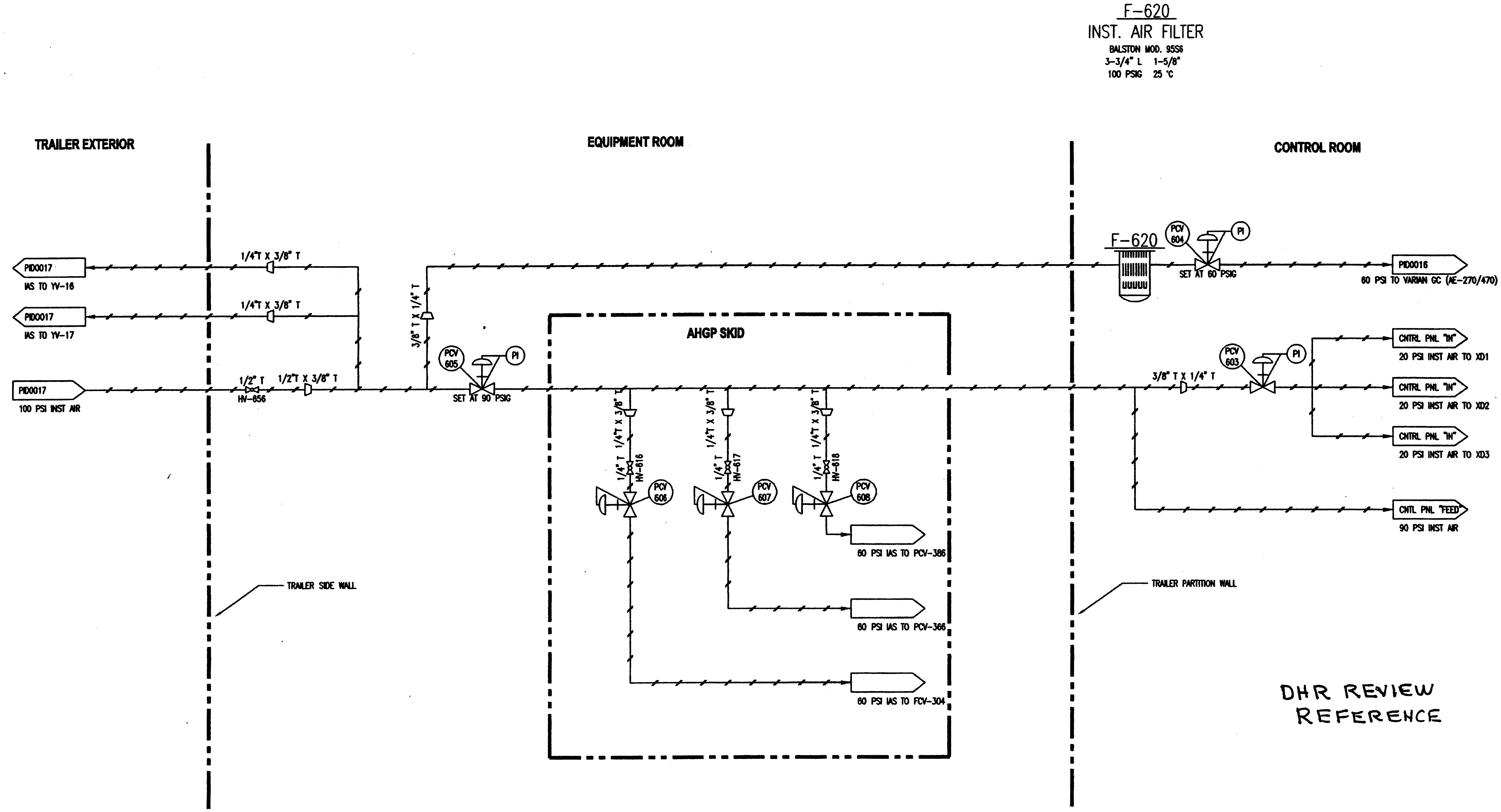

DHR REVIEW
REFERENCE

TAG NUMBERS USED:
603-608
616-618, 620
656

APPENDIX II, II-10

NO.	DATE	BY	REVISIONS	APP.
A				

REFERENCE DRAWINGS

ENGINEERING RECORD	DATE	DWG. NO.
DRN: JMP	2/4/98	
CHK: DDS		
APP:		
W.O.: 5869		
SCALE: NONE		

AHGP FIELD TEST UNIT
AREA 600 - UTILITIES/INST AIR
Advanced Hot Gas Desulfurization Wilsonville, AL
DOE-FETC
DWG. NO. PID0019
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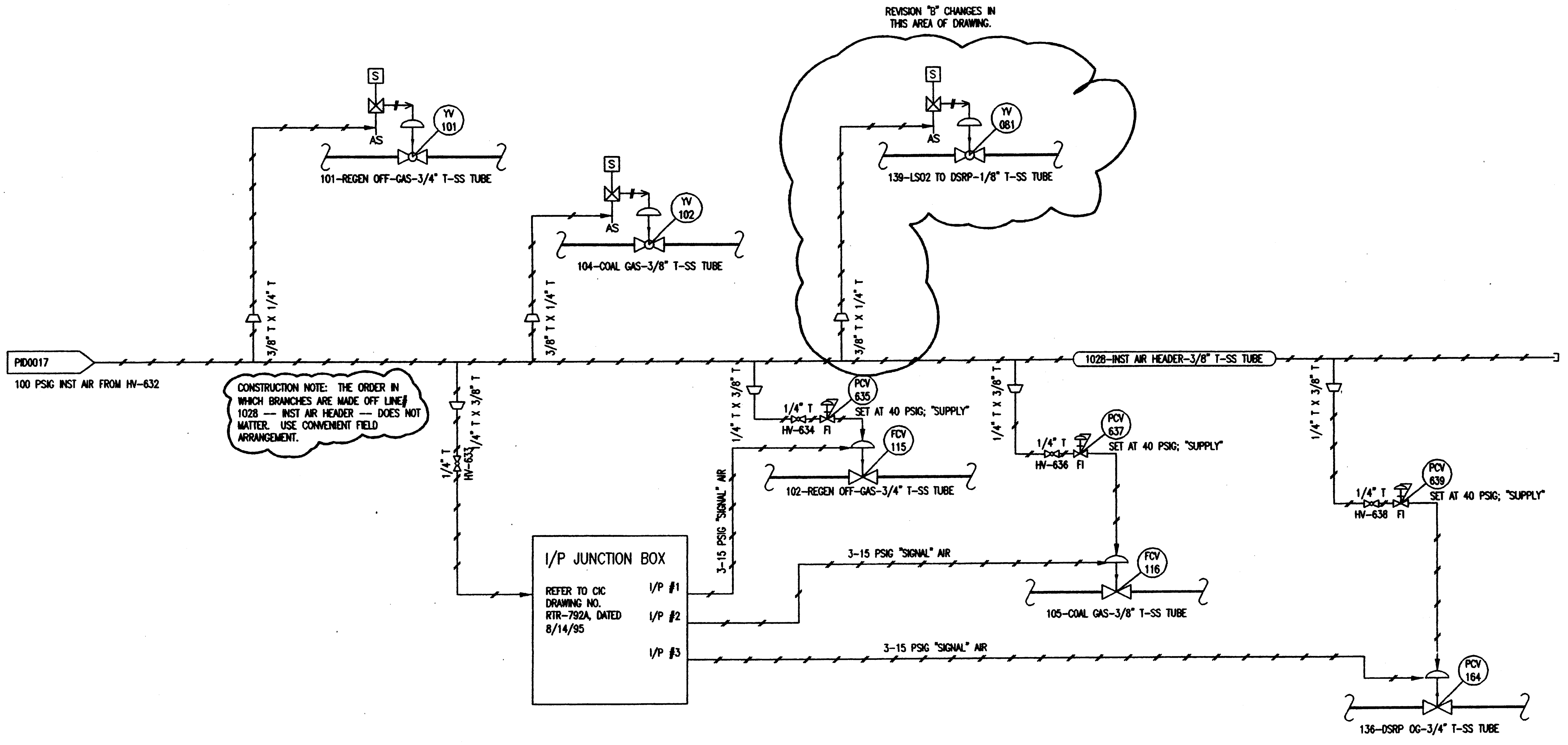
CADFILE-PSOFTEST\



DHR REVIEW
3 AUG 2000

TAG NUMBERS USED:
633 - 639

LINE NUMBERS USED:
1028

APPENDIX II, II-11

ENGINEERING RECORD	DATE	DWG. NO.	REFERENCE DRAWINGS	NO.	DATE	BY	REVISIONS	APP
DRN: JMP	08/16/99	RTR-792A	ENVIROPOWER DSRP I/P JUNCTION BOX (CIC DRAWING)	A	12/14/99	JMP	UPDATED #1028 LINE SIZE	
CHK:				B	03/31/00	JMP	ADDED YV-081	
APP:								
W.O.: 5666								
SCALE: NONE								

DSRP FIELD TEST PILOT UNIT
P&ID – INSTRUMENT AIR
Direct Sulfur Recovery Unit
Wilsonville, AL

DOE/FETC

DWG. NO. PID0020
REV B

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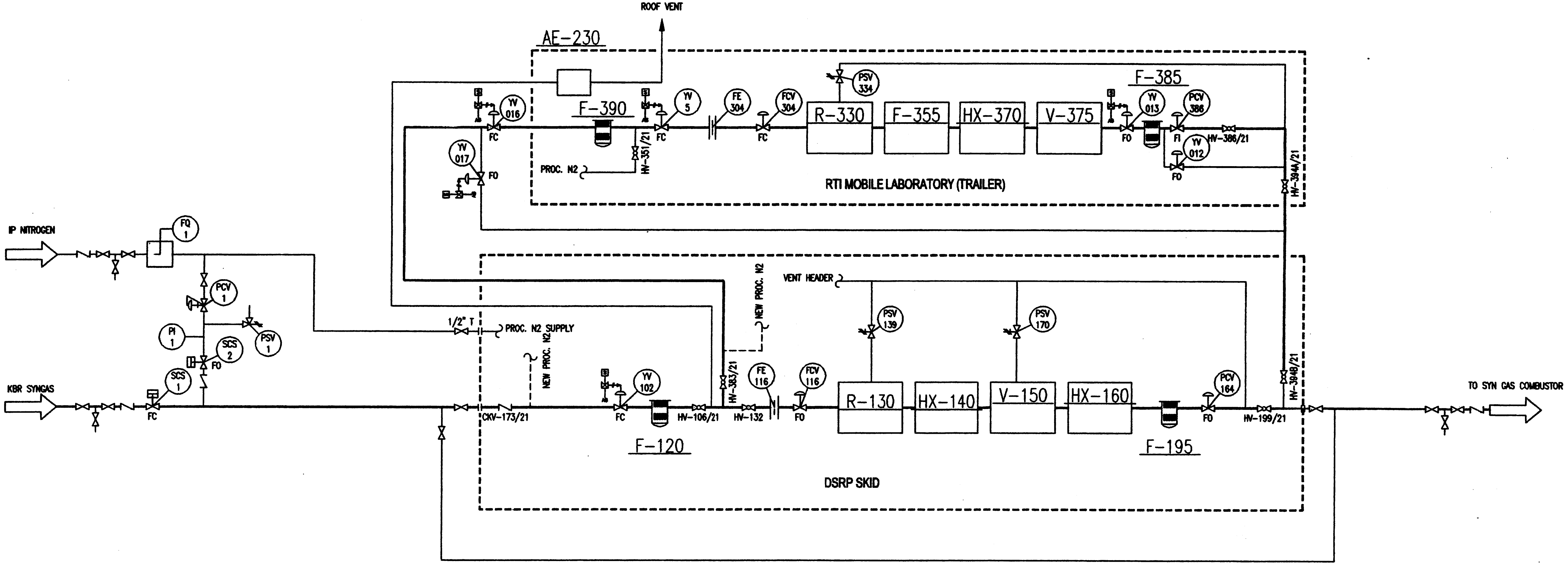
C-55

CADFILE-DSRP_FTU\P
W.O.L.- 03/31/00

AE-230	F-390	R-330	F-355	HX-370	V-375	F-385
CO/CO2 ANALYZER	COAL GAS FILTER	FLUID-BED REACTOR	SULF'N FILTER	WATER CONDENSER	CONDENSATE POT	SULF'N BALSTON



DHR REVIEW
REFERENCE

F-120	R-130	HX-140	V-150	HX-160	F-195
COAL GAS FILTER	DSRP REACTOR	SULFUR CONDENSER	SULFUR SEPARATOR POT	REHEATER COIL	DSRP OFF-GAS FILTER

APPENDIX II, II-12

NO.	DATE	BY	REVISIONS	APP.
A			ISSUED FOR APPROVAL	

REFERENCE DRAWINGS
DWG. NO.

ENGINEERING RECORD
DRN: JWP
CHK:
APP:
DATE
08/07/00
W.O.:5666 & 5669
SCALE: NONE

PSDF FIELD TEST
P&ID - SYN GAS LINES
DSRP + AHGP
Wilsonville, AL
DOE-FETC
DWG. NO. PID0021
REV

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APPENDIX A

PROCESS DESCRIPTION
(Direct Sulfur Recovery Process/Advanced Hot Gas Process)

Direct Sulfur Recovery Process

- Catalyst Development
- Literature Studies and Thermodynamic Evaluation
- Sorbent Development
- Specialized Process Testing
- Material Characterization
- Process Development
- Process Research Home

TECHNOLOGY
SURVEY & STATISTICS
ENVIRONMENT
HEALTH & PHARMACEUTICALS
PUBLIC POLICY

Sponsor: Department of Energy

The DSRP was originally developed to treat the regeneration off-gas from metal oxide sorbent-based coal gas desulfurization processes. In these processes, the regeneration of the sorbent produces a diluted sulfur dioxide off-gas that is available at elevated pressure and temperature. Depending on the specifics of the regeneration conditions, the SO_2 content can vary. Simplified chemistry is as follows, where MO represents a generic metal oxide sorbent:

Desulfurization: $MO + H_2S \dashrightarrow MS + H_2O$

Regeneration: $MS + O_2 \dashrightarrow MO + SO_2$

The DSRP uses a stream of a reducing gas -- typically a slipstream of coal gas containing CO and H_2 in the case of coal gas desulfurization -- to convert sulfur dioxide to elemental sulfur. The feed gas is at elevated temperature and pressure, and the following (simplified) reaction takes place in a gas phase, single-stage catalytic reactor:

$SO_2 + 2H_2$ (or 2 CO) --> $2H_2O$ (or $2CO_2$) + S

Figure 1, a simplified process flow diagram, shows how the DSRP can be integrated with hot gas desulfurization to produce a clean process gas and an elemental sulfur by-product.

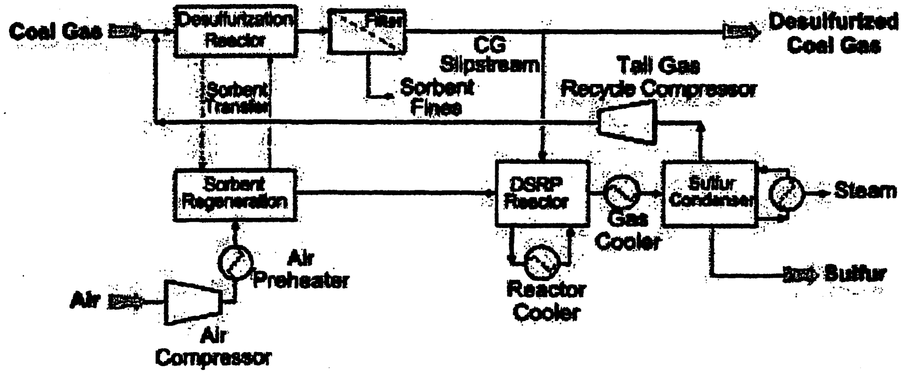

Figure 1. Conceptual DSRP integrated with hot coal gas desulfurization.

A main advantage of the DSRP is that it is a simple (single-stage) stand-alone process. It can be adapted to a variety of SO_2-containing feed gas compositions and, combined with sorbent-based desulfurization, can process a variety of H_2S-containing process gases. The disadvantage is that a valuable synthesis gas (H_2 and CO) is consumed in proportion to the amount of elemental sulfur produced. The DSRP has been extensively tested at the bench scale in the laboratory and in the field, using both simulated and actual coal gas streams. Rugged catalysts for the reaction are commercially available.

DSRP Process Development:

- Lab-scale proof-of-concept
- Laboratory testing - bench scale
- Field testing -- bench scale
- Field testing -- pilot scale.

Laboratory -- Scale Proof-of-Concept

In the late 1980s, the U.S. Department of Energy (DOE) initiated a program to develop the hot coal gas desulfurization concept. The most promising results were obtained with mixed metal oxide-based refractory sorbents. Regeneration of those sorbents with air resulted in the production of a dilute, SO_2-containing off-gas. While investigating several process concepts for the treatment of that stream, RTI's discoveries led to the concept of the Direct Sulfur Recovery Process.

The initial proof-of-concept studies were conducted in a 1-inch diameter, fixed-bed, tubular reactor ("laboratory" scale) containing 25 to 50 cm^3 of catalyst. The focus of these studies was on optimizing the operating conditions of temperature, pressure, space velocity, gas composition, and feed stoichiometry. Pressure was the most important variable, with higher pressures (over the range of 1.5 to 20 atmospheres) leading to significantly greater single-stage conversions of SO_2 to elemental sulfur. Higher temperatures (over the range of 675 to 925 K) also led to higher conversions. The DSRP reaction, unlike similar reactions encountered with the well-known Claus process for sulfur recovery, was insensitive to the steam content of the reaction mixture over the range studied.

Laboratory Testing -- Bench Scale

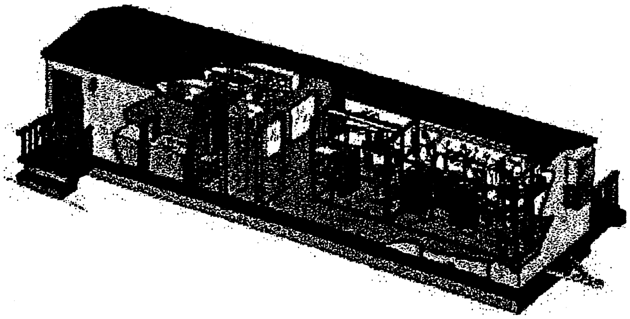

Figure 2. Artist's Conception of Mobile Laboratory showing Analytical/Control Room and Process Equipment Room.

Following the success with laboratory-scale testing, a larger apparatus was built in the early 1990s to include two stages of reaction with intermediate cooling and condensate removal. With 4-inch diameter reactor vessels holding 2-inch or 3-inch catalyst "cages," this apparatus could accommodate up to 1000 cm^3 of catalyst per reactor. It was used to screen several different catalyst formulations and to further refine the operating parameters. Various molten sulfur recovery strategies were evaluated empirically. The two reaction stages, with a different catalyst in the second stage, were integrated on the same process equipment skid, and runs of several hours' duration were achieved. In addition to the fixed-bed configuration, fluidized-bed concepts were tested.

Field Testing -- Bench Scale

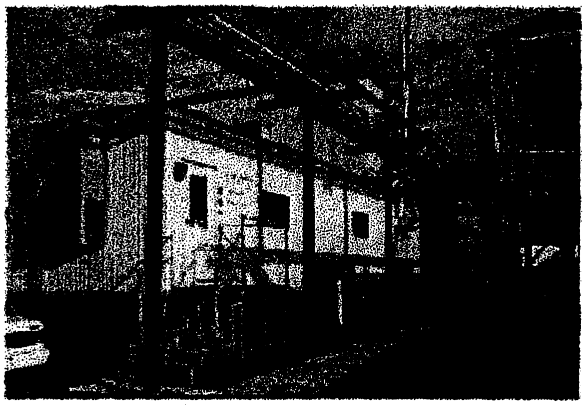

Figure 3. Mobile Laboratory in place at DOE-FETC (Morgantown).

To meet the objective of testing the DSRP catalyst and process concept with actual coal gas (from a working gasifier) RTI built a Mobile Laboratory to house the already-constructed bench-scale test apparatus, control system, and gas analyzers. Constructed in a modified office trailer, the portable unit was outfitted at RTI's site in North Carolina, then transported to DOE's pilot gasifier in Morgantown, West Virginia. Testing was conducted during several gasifier campaigns, over a period of two years, and led to two important conclusions:

- a simple, single-stage process provided acceptable conversion of SO_2 to elemental sulfur (>98%)
- the presence of trace contaminants in coal gas had no deleterious effect on catalyst activity (over the time period studied).

Field Testing -- Pilot Scale

To accomplish larger scale testing of the DSRP, a skid-mounted unit with a 6.0-inch diameter reactor was designed and fabricated, as the photographs show. The current emphasis is on development of a fluid-bed reactor-based process to handle the highly exothermic DSRP reactions. The SO_2 concentration in the sorbent regeneration off-gas in the more-recent hot gas desulfurization process designs is higher, resulting in higher heat densities in the DSRP reaction. In addition, demonstration of extended operation with actual coal gas and consistent production of elemental sulfur is necessary to gain commercial acceptance of the technology.

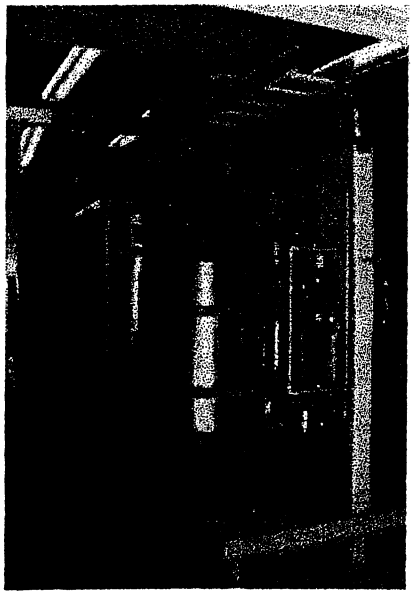

Figure 4. DSRP Field Test Pilot Unit being fabricated in RTI shop: gas inlet end of unit.

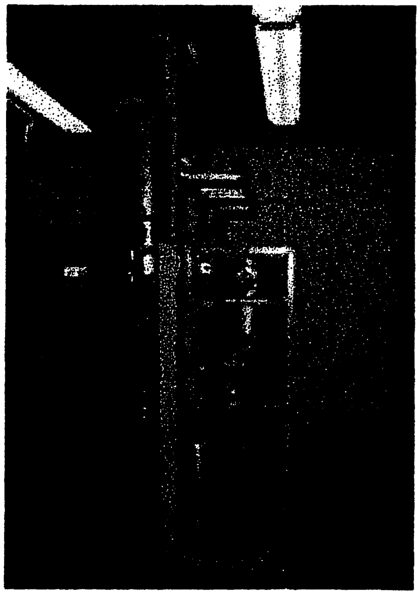

Figure 5. DSRP Field Test Pilot Unit being fabricated in RTI shop: gas outlet end of unit.

For field testing it is planned that the DSRP skid, under a shed roof, will sit alongside the Mobile Laboratory, which is being refitted to be used as a control room, shown below in Figure 6.

Preparations are actively under way for conducting a long-duration field test of the skid-mounted DSRP in the fluid-bed mode, with a slipstream of actual coal gas at the Power Systems Development Facility (PSDF) in Wilsonville, Alabama. Modifications of the skid-mounted DSRP unit are being made in the RTI shop, consistent with specific site requirements. The Mobile Laboratory refitting is also being done at RTI, and it, along with the skid-mounted DSRP will be moved to Wilsonville, Alabama, for the testing to be conducted in the 1999 - 2000 time frame.

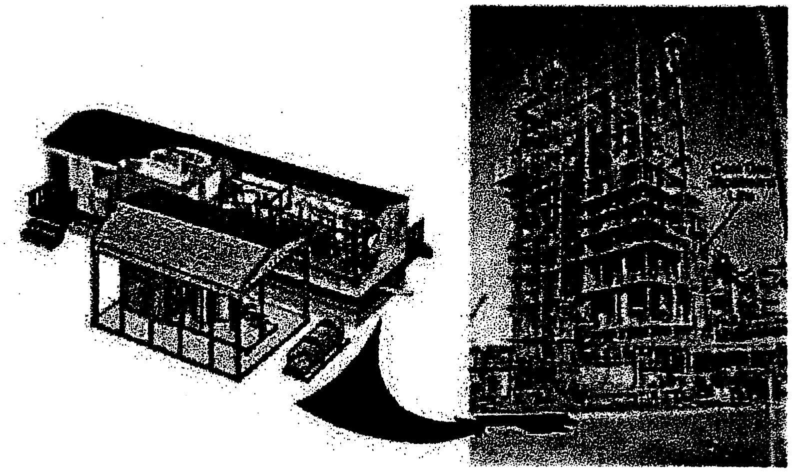

Figure 6. Planned field test of the DSRP at DOE's Power System Development Facility in Wilsonville, AL.

Contacts:

- Santosh Gangwal, phone:(919) 541-8033, fax:(919)541-8000, skg@rti.org
- Jeffrey Portzer, phone:(919)541-8025, fax:(919)541-8000, jwp@rti.org

References:

PATENTS:

Dorchak, T.P., S.K. Gangwal, and S.M. Harkins, U.S. Patent 5,366,717. Method for Producing Elemental Sulfur from Sulfur-Containing Gases. Nov. 11, 1994.

Dorchak, T.P., S.K. Gangwal, and S.M. Harkins, U.S. Patent 5,798,088. Method for Producing Elemental Sulfur from Sulfur-Containing Gases. Aug. 25, 1998.

PUBLICATIONS:

Dorchak, T.P., S.K. Gangwal, and W.J. McMichael. 1991. The Direct Sulfur Recovery Process. *Environmental Progress* 10(2):68.

Portzer, J.W., and S.K. Gangwal. 1994. "Slipstream Testing of the Direct Sulfur Recovery Process" in *Proceedings of the Coal-Fired Power System 94-Advances in IGCC and PFBC Review Meeting*, 246-255. DOE/METC-94/1008, Vol. 1.

NTIS/DE94012252. Springfield, VA: National Technical Information Service.

Portzer, J.W., and S.K. Gangwal. 1995. "Slipstream Testing of Hot-Gas Desulfurization with Sulfur Recovery." In *Proceedings of the Advanced Coal-Fired Power Systems '95 Review Meeting*, 220-228. DOE/METC-95/1018, Vol. 1. NTIS/DE95009732. Springfield, VA: National Technical Information Service.

Portzer, J.W., B.S. Turk, and S.K. Gangwal. 1996. "Durability Testing of the Direct Sulfur Recovery Process." In *Proceedings of the Advanced Coal-Fired Systems Review Meeting July 16-19, 1996.* (CD-ROM). U.S. Department of Energy, Morgantown, WV.

Portzer, J.W., and S.K. Gangwal. 1997. "Bench-Scale Demonstration of Hot-Gas Desulfurization Technology." In *Proceedings of the Advanced Coal-Based Power and Environmental Systems '97 Conference. July 22-24, 1997.* (CD-ROM). DOE/FETC-97/1046. U.S. Department of Energy, Federal Energy Technology Center.

Portzer, J.W., and S.K. Gangwal. 1998. "Bench-Scale Demonstration of Hot-Gas Desulfurization Technology." In *Proceedings of the Advanced Coal-Based Power and Environmental Systems '98 Conference.* July 21-23, 1998.

Catalyst Development | Literature Studies and Thermodynamic Evaluation

Sorbent Development | Specialized Process Testing

Material Characterization | Process Development

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Process Research Program
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Advanced Hot Gas Process

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Specifically oriented to H_2S-containing process gas streams, such as coal gas in an IGCC power plant, the Advanced Hot Gas Process (AHGP) combines metal oxide sorbent-based desulfurization with special sorbent regeneration for **direct production of elemental sulfur.** The intermediate, dilute SO_2 stream -- which arises from oxygen regeneration of the sulfided sorbent -- that the DSRP is designed to treat is eliminated, as is the slipstream of coal gas needed for the reduction reaction. In the AHGP a recycle stream of high concentration SO_2 oxidizes the absorbed hydrogen sulfide directly to elemental sulfur. In addition, a portion of the sorbent is regenerated with oxygen (introduced into the recycle SO_2 stream) in a "polishing" regeneration that also produces sulfur dioxide to balance the consumption. The simplified overall reactions are as follows (where MO represents a generic metal oxide sorbent):

Desulfurization: $MO + H_2S \text{ --> } MS + H_2O$

SO_2 regeneration: $2\ MS + SO_2 \text{ --> } 2\ MO + 3\ S$

O_2 regeneration: $MS + 3/2\ O_2 \text{ --> } MO + SO_2$

Figure 7 shows a conceptual process design for the AHGP to regenerate the desulfurization sorbent directly to elemental sulfur with minimal consumption of coal gas. In this process, a zinc-iron sorbent is used and the regeneration is carried out in two stages with SO_2 and O_2, respectively. The iron sulfide is regenerated by SO_2 in one stage to elemental sulfur. In the other stage, zinc sulfide and any remaining iron sulfide are regenerated by O_2 to provide the required SO_2. The sorbent is then returned to the desulfurizer.

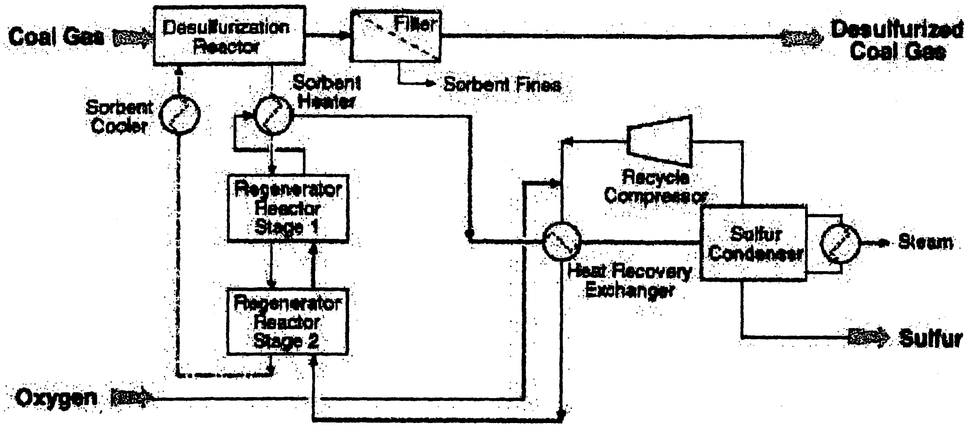

Figure 7. AHGP Conceptual Process Flow Diagram.

The key chemical reactions of interest are as follows:

1. Sulfidation

   $Fe_2O_3 + 2H_2S + H_2 \text{-->} 2FeS + 3H_2O$

   $ZnO + H_2S \text{-->} ZnS + H_2O$

2. SO_2 regeneration

   $4FeS + 3SO_{2 \text{-->}} 2Fe_2O_3 + 7/2\ S_2$

3. O_2 regeneration

   $2FeS + 7/2\ O_2 \text{-->} Fe_2O_3 + 2SO_2$

   $ZnS + 3/2\ O_{2 \text{-->}} ZnO + SO_2.$

AHGP Process Development

- lab-scale proof-of-concept
- laboratory testing -- bench scale
- engineering analysis

Laboratory-Scale Proof-of-Concept

The feasibility of SO_2 regeneration of combined zinc-iron sorbents was demonstrated using a thermogravimetric analyzer and high-pressure microreactor. Zinc sulfide shows essentially no SO_2 regeneration at temperatures of interest (500 to 600 degrees C), but zinc is needed to act as a polishing agent in the desulfurizer.

Laboratory Testing -- Bench Scale

A number of sorbents were prepared and tested at the bench scale ove multiple cycles. Based on these tests, a highly attrition-resistant sorbent (R-5-58) was prepared and the process was demonstrated over 50 cycles in a 7.5-cm I.D. bench-scale fluidized bed reactor.

The results showed that R-5-58 removed H_2S down to 50- to 100-ppm levels with stable desulfurization activity over the duration. The surface area and pore volume of the sorbent did not change appreciably and the attrition index before and after the test was 3.6% and 1.2%, respectively. Sulfur balances were adequate and the SO_2 regeneration step accounted for up to 70% of the total regeneration of the sorbent. This compares to a theoretical limit of approximately 80%, assuming complete regeneration by SO_2 of the iron component

Engineering Analysis

An engineering and economic evaluation of the DSRP and AHGP for large-scale IGCC plants was conducted in partnership with the Chemical Engineering Department at North Carolina State University (NCSU) using ASPEN PLUS® computer process simulation software and published generalized cost estimating methods (Gangwal*et al.* 1998) . For both processes the scope of the equipment and process steps included in the simulations were the same: coal gas desulfurization (but not the high temperature particulate removal), regeneration of the desulfurizing sorbent, and production, isolation, and short term storage of elemental sulfur.

The recovered sulfur was assumed to have a market value, and thus generate a cost credit. Coal gas consumed in the process was evaluated at a cost based on the potential power generation that was lost. High pressure steam generated in the process was assumed to provide a cost credit based on the power that could be recovered from it. Base case simulations of both processes assumed 0.85 mol% H_2S in the coal-gas feed. Such an H_2S concentration in the coal gas would be produced by an oxygen-blown Texaco gasification using a roughly 3.6 wt% sulfur-containing coal. Both base cases generate 260 MWe from the clean coal gas.

Figure 8 summarizes the results of the engineering analysis. The ASPEN simulations of DSRP and AHGP revealed the complexity of both hot gas desulfurization processes.

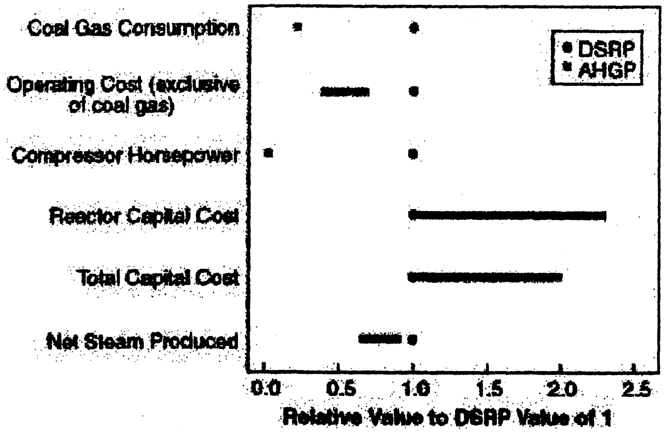

Figure 8. Comparison of key elements of AHGP and DSRP.

The AHGP appears to be the more difficult process to operate and may require more employees than the DSRP. Capital costs for the AHGP are higher than those for the DSRP--development of DSRP is also much closer to commercialization than AHGP. However, annual operating costs for the AHGP appear to be considerably less than those of the DSRP. Preliminary economic comparison shows that the total cost (capital plus cumulative operating cost) of implementing AHGP will be less than that of implementing DSRP after as little as 2 years of operation. Thus, despite its greater complexity, the potential savings with the AHGP encourage further development and scaleup of this advanced process.

<u>References</u>:

Gangwal, S.K., B.S. Turk, and R.Gupta. 1995. "Advanced Sulfur Control Concepts." In *Proceedings of the Advanced Coal-Fired Power Systems '95 Review Meeting*, pp. 622-630, DOE/METC-95/1018, Vol. 2, NTIS/DE 95009733. Springfield, VA.

Gangwal, S.K., J.W. Portzer, B.S. Turk, and R.Gupta. 1996. "Advanced Sulfur Control Processing." In *Proceedings of the Advanced Coal-Fired Systems Review Meeting July 16--19, 1996.* (CD-ROM). U.S. Department of Energy, Morgantown, WV.

Gangwal, S.K., J.W. Portzer, G.W. Roberts, and S.C. Kozup. 1998. "Engineering Evaluation of Hot-Gas Desulfurization with Sulfur Recovery." Topical Report. DOE Contract No. DE-AC21-94MC31258. Research Triangle Institute. Research Triangle Park, NC.

Portzer, J.W., A.S. Damle, and S.K. Gangwal. 1997. "Hot Gas Desulfurization with Sulfur Recovery." In *Proceedings of the Advanced Coal-Based Oiwer and Environmental Systems '97 Conference. July 22-24, 1997.* (CD-ROM). DOE/FETC-97/1046. U.S. Department of Energy, Federal Energy Technology Center.

Portzer, J.W., S.K. Gangwal, and T.P. Dorchak. 1998. "Advances in Hot Gas Desulfurization with Elemental Sulfur

Recovery." In *Proceedings of the Fifteenth Annual International Pittsburgh Coal Conference*. September 14-18, 1998. (CD-ROM). University of Pittsburgh, Pittsburgh, PA.

Portzer, J.W., and S.K. Gangwal. 1998. "Hot-Gas Desulfurization with Sulfur Recovery." In *Proceedings of the Advanced Coal-Based Power and Environmental Systems '98 Conference*. July 21-23, 1998. Available on the U.S. Department of Energy, Federal Energy Technology Center web site.

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Engineering and Environmental Technology (CEET)

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General inquiries may be directed tolisten@rti.org.
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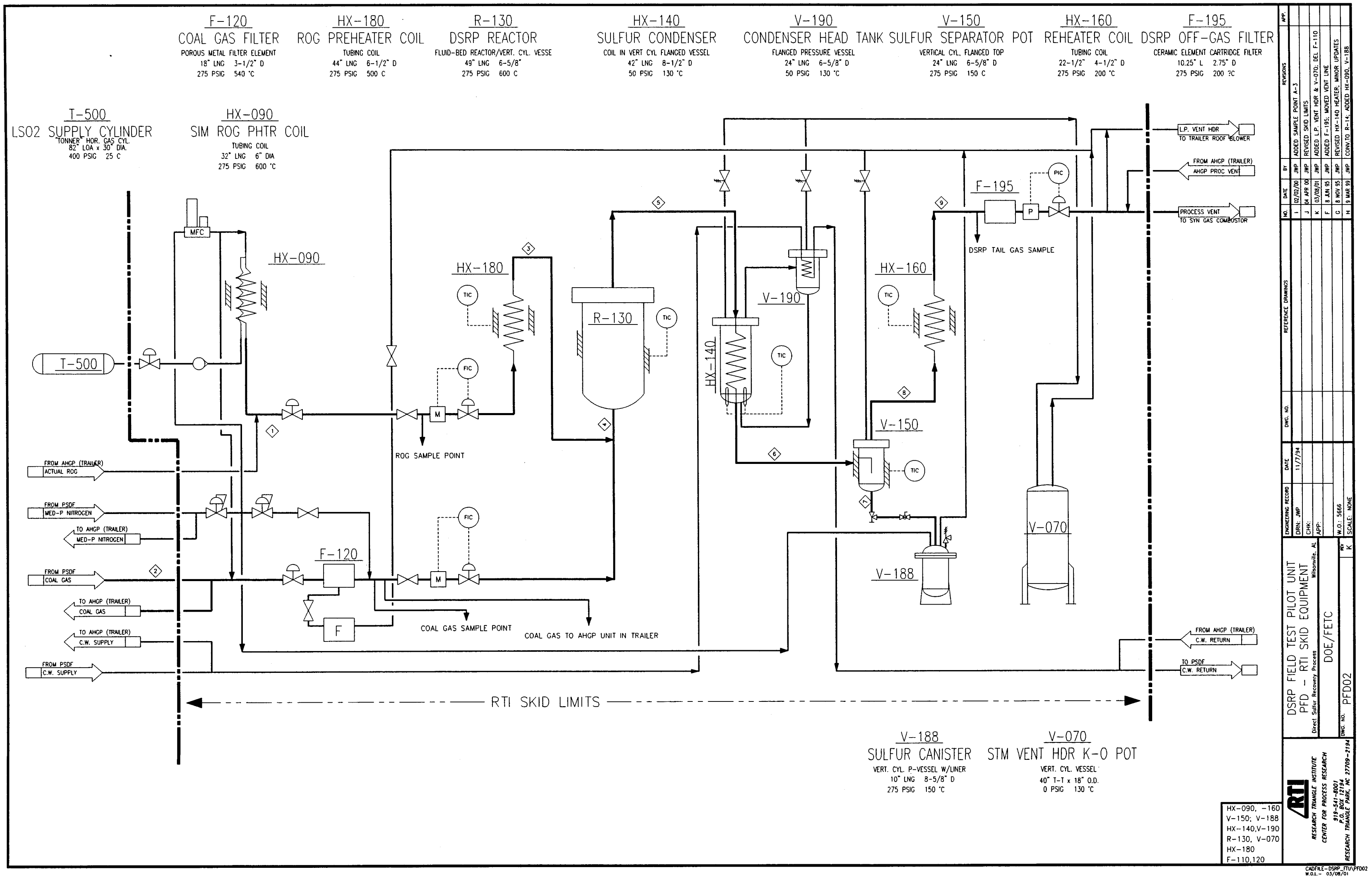
Research Triangle Institute, 3040 Cornwallis Road, Research Triangle Park, North Carolina 27709 USA
Telephone: 919-541-6000

Appendix D

Piping and Instrumentation Diagrams


F-120
COAL GAS FILTER
POROUS METAL FILTER ELEMENT
18" LNG 3-1/2" D
275 PSIG 540 °C
HX-180
ROG PREHEATER COIL
TUBING COIL
44" LNG 6-1/2" D
275 PSIG 500 C
R-130
DSRP REACTOR
FLUID-BED REACTOR/VERT. CYL. VESSE
49" LNG 6-5/8"
275 PSIG 600 C
HX-140
SULFUR CONDENSER
COIL IN VERT CYL FLANGED VESSEL
42" LNG 8-1/2" D
50 PSIG 130 °C
V-190
CONDENSER HEAD TANK
FLANGED PRESSURE VESSEL
24" LNG 6-5/8" D
50 PSIG 130 °C
V-150
SULFUR SEPARATOR POT
VERTICAL CYL. FLANGED TOP
24" LNG 6-5/8" D
275 PSIG 150 C
HX-160
REHEATER COIL
TUBING COIL
22-1/2" 4-1/2" D
275 PSIG 200 °C
F-195
DSRP OFF-GAS FILTER
CERAMIC ELEMENT CARTRIDGE FILTER
10.25" L 2.75" D
275 PSIG 200 °C
T-500
LSO2 SUPPLY CYLINDER
TONNER HOR. GAS CYL.
82" LOA x 30" DIA.
400 PSIG 25 C
HX-090
SIM ROG PHTR COIL
TUBING COIL
32" LNG 6" DIA
275 PSIG 600 °C
T-500
MFC
HX-090
HX-180
TIC
FIC
M
R-130
TIC
HX-140
TIC
V-190
HX-160
TIC
V-150
TIC
F-195
P
PIC
DSRP TAIL GAS SAMPLE
V-188
V-070
F-120
F
FIC
M
ROG SAMPLE POINT
COAL GAS SAMPLE POINT
COAL GAS TO AHGP UNIT IN TRAILER
1
2
3
4
5
6
8
9
FROM AHGP (TRAILER) ACTUAL ROG
FROM PSDF MED-P NITROGEN
TO AHGP (TRAILER) MED-P NITROGEN
FROM PSDF COAL GAS
TO AHGP (TRAILER) COAL GAS
TO AHGP (TRAILER) C.W. SUPPLY
FROM PSDF C.W. SUPPLY
L.P. VENT HDR TO TRAILER ROOF BLOWER
FROM AHGP (TRAILER) AHGP PROC VENT
PROCESS VENT TO SYN GAS COMBUSTOR
FROM AHGP (TRAILER) C.W. RETURN
TO PSDF C.W. RETURN
RTI SKID LIMITS
V-188
SULFUR CANISTER
VERT. CYL. P-VESSEL W/LINER
10" LNG 8-5/8" D
275 PSIG 150 °C
V-070
STM VENT HDR K-O POT
VERT. CYL. VESSEL
40" T-T x 18" O.D.
0 PSIG 130 °C
HX-090, -160
V-150; V-188
HX-140,V-190
R-130, V-070
HX-180
F-110,120
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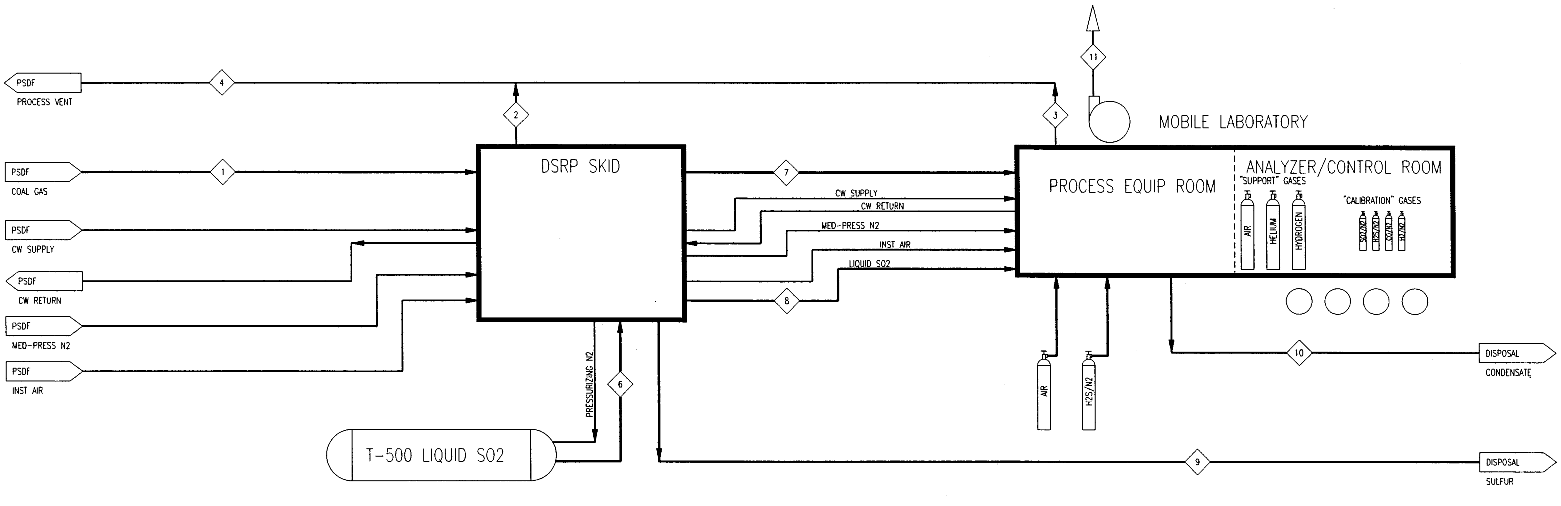
919-541-8001
P.O. BOX 12194
RESEARCH TRIANGLE PARK, NC 27709-2194
DSRP FIELD TEST PILOT UNIT
PFD - RTI SKID EQUIPMENT
Direct Sulfur Recovery Process
Wilsonville, AL
DOE/FETC
DWG. NO. PFD02
REV K
ENGINEERING RECORD
DATE
DRN: JWP
11/7/94
CHK:
APP:
W.O.: 5666
SCALE: NONE
DWG. NO.
REFERENCE DRAWINGS
NO.
DATE
BY
REVISIONS
APP.
I 02/02/00 JWP ADDED SAMPLE POINT A-3
J 04 APR 00 JWP REVISED SKID LIMITS
K 03/08/01 JWP ADDED L.P. VENT HDR & V-070; DEL F-110
F 8 JUN 95 JWP ADDED F-195; MOVED VENT LINE
G 8 NOV 95 JWP REVISED HX-140 HEATER; MINOR UPDATES
H 9 MAR 99 JWP CONV.TO R-14; ADDED HX-090, V-188
CADFILE-DSRP_FTU\PFD02
W.O.L.- 03/08/01



STREAM NUMBER	1	1	2	3	3	3	4	4	4	4	6	6	7	8	9	10	11
MODE	A,C,D	B	A	B	C	D	A	B	C	D	A	C	B	C	A,B,C,D	B	A,B,C,D
STREAM NAME	TOT COAL GAS	TOT COAL GAS	DSRP VENT	AHGP VENT	AHGP VENT	AHGP VENT	PROC VENT	PROC VENT	PROC VENT	PROC VENT	LIQ SO2	LIQ SO2	AHGP CG	AHGP LSO2	SULFUR	CONDENSATE	TRLR VENT
COMPOSITION, VOL%																	
CO	18.5%	18.5%	0.0%	19.6%	0.0%	0.0%	0.0%	5.4%	0.0%	0.0%	0.0%	0.0%	18.5%	0.0%	0.0%	0.0%	TRACE
CO_2	8.0%	8.0%	12.6%	8.5%	0.0%	0.0%	12.6%	11.5%	8.9%	8.9%	0.0%	0.0%	8.0%	0.0%	0.0%	0.0%	TRACE
H_2O	8.0%	8.0%	10.4%	0.0%	0.0%	0.0%	10.4%	7.6%	7.4%	7.4%	0.0%	0.0%	8.0%	0.0%	0.0%	100.0%	TRACE
H_2	14.0%	14.0%	0.0%	14.9%	0.0%	0.0%	0.0%	4.1%	0.0%	0.0%	0.0%	0.0%	14.0%	0.0%	0.0%	0.0%	TRACE
H_2S	0.050%	0.050%	0.23%	0.00%	0.00%	0.0%	0.23%	0.17%	0.00%	0.2%	0.0%	0.0%	0.050%	0.0%	0.0%	0.0%	TRACE
SO_2	0.0%	0.0%	0.11%	0.00%	50.0%	0.67%	0.11%	0.08%	14.67%	0.28%	100.0%	100.0%	0.0%	100.0%	0.0%	0.0%	TRACE
S			TRACE		TRACE	0.0%	TRACE	TRACE	TRACE	TRACE					100.0%		
O_2	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	21.0%
N_2	51.5%	51.5%	76.6%	57.0%	50.0%	99.3%	76.6%	71.2%	68.9%	83.2%	0.0%	0.0%	51.5%	0.0%	0.0%	0.0%	79.0%
FLOW RATE, LB/HR	6	11	15	5	10	6	15	20	25	21	2.81	9.62	5.15	6.81	1.35	0.30	
FLOW RATE, SCFH	94	174	198	75	82	81	198	274	280	280			82				400 SCFM
FLOW RATE, GAL/HR											0.25	0.84		0.60		0.036	
TEMPERATURE, °F	1000	1000	400	85	260	300	400	313	359	371	70	70	1000	70	70	85	70
TEMPERATURE, °C	538	538	204	29	127	149	204	156	182	188	21	21	538	21	21	29	21
PRESS, PSIG	279	279	15	15	15	15	15	15	15	15	350	350	279	350	0	0	2" WC

SUFFIX LETTER	OPERATING MODE:	EXPECTED DURATION:
A	DSRP SKID ONLY	500 HOURS MINUS TIME FOR MODES B,C,&D
B	DSRP + AHGP-SULFIDATION	50 CYCLES @ 1 HR
C	DSRP + AHGP-SO2 REGENERATION	50 CYCLES @ 2HR
D	DSRP + AHGP-AIR REGENERATION	50 CYCLES @ 0.5 HR

NO.	DATE	BY	REVISIONS	APP.
A	02/02/00	JWP	REVISED T-500 TAG NO.	

DWG. NO.	REFERENCE DRAWINGS

ENGINEERING RECORD	DATE
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CHK:	
APP:	
W.O.: 5666 & 5869	
SCALE: NONE	

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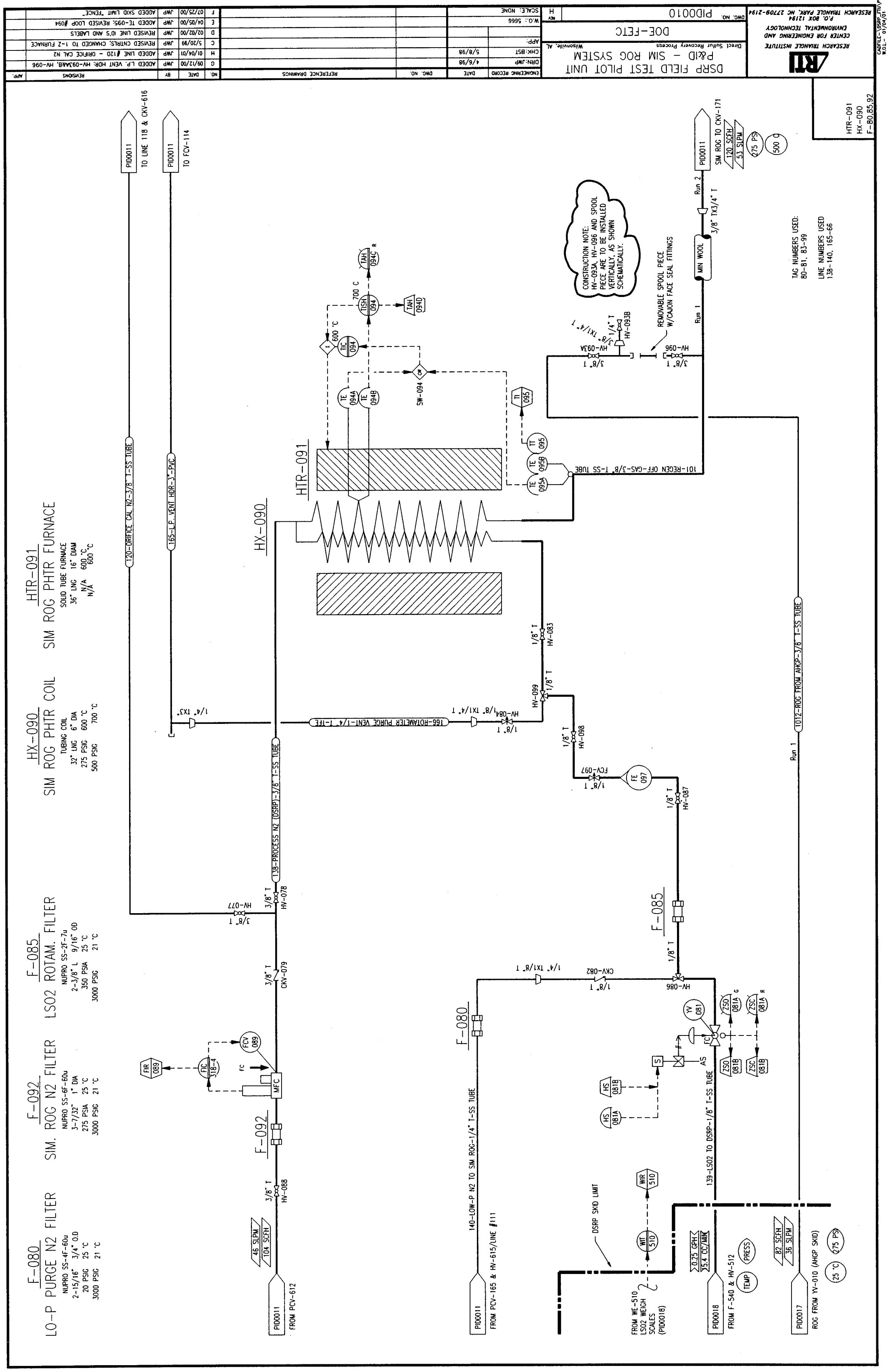
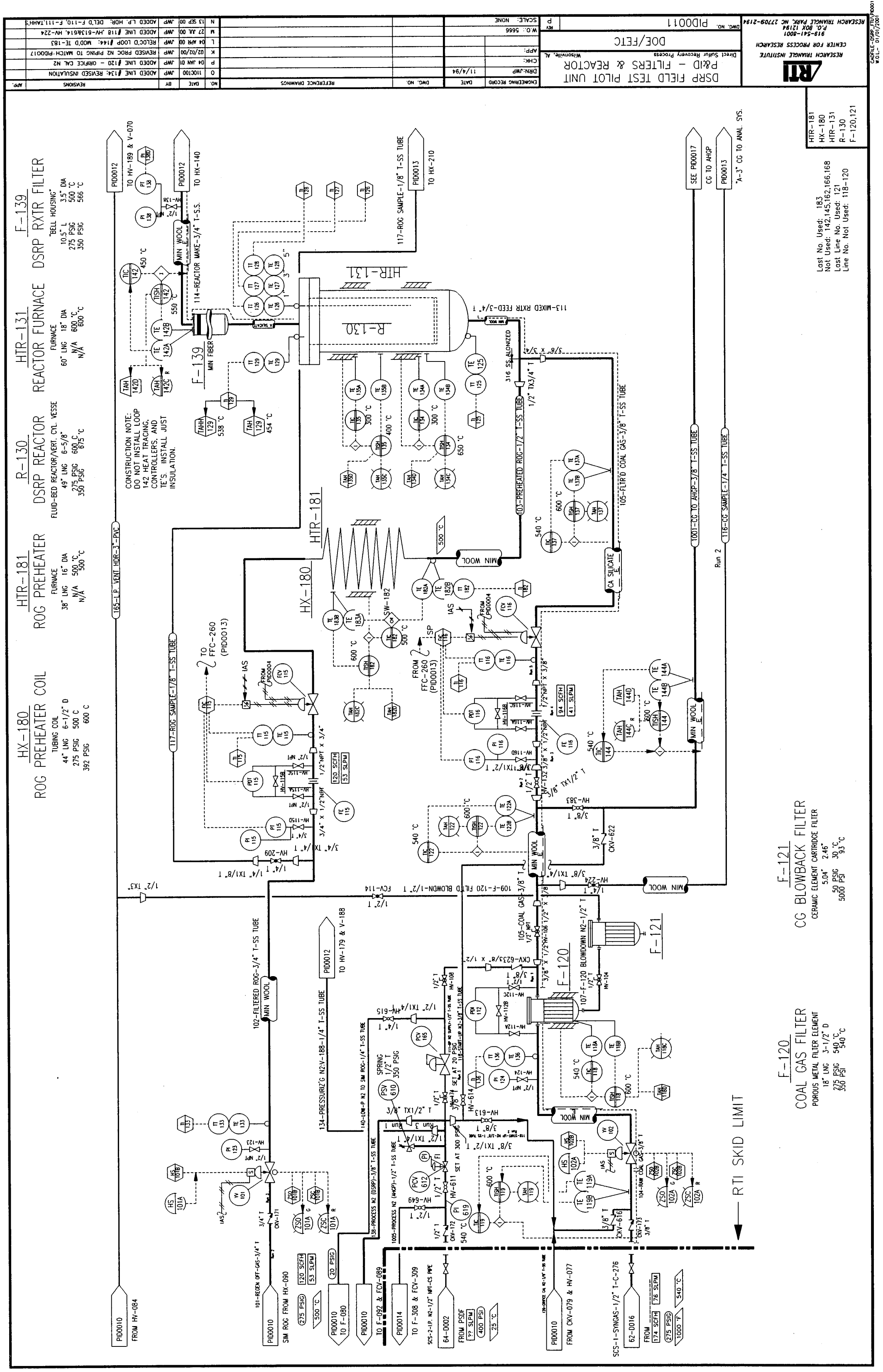
PSDF FIELD TEST
PFD - RTI SKID & TRAILER
DSRP + AHGP
Wilsonville, AL
DOE-FETC
DWG. NO. PFD04
RV A

CADFILE-\PSDFTEST\PFD04
W.O.L.- 02/02/00



DSRP FIELD TEST PILOT UNIT
P&ID – SIM ROG SYSTEM
Direct Sulfur Recovery Process
Wilsonville, AL
DOE-FETC
PID0010
RTI
RESEARCH TRIANGLE INSTITUTE
CENTER FOR ENGINEERING AND ENVIRONMENTAL TECHNOLOGY
P.O. BOX 12194
RESEARCH TRIANGLE PARK, NC 27709-2194
DRN: JWP 4/6/98
CHK: BST 5/8/98
W.O.: 5666
SCALE: NONE
REV H
G 09/12/00 JWP ADDED L.P. VENT HDR: HV-093A&B, HV-096
H 01/04/01 JWP ADDED LINE #120 – ORIFICE CAL N2
C 5/20/99 JWP REVISED CNTRLS, CHANGED TO 1-Z FURNACE
D 02/02/00 JWP REVISED LINE ID'S AND LABELS
E 04/05/00 JWP ADDED TE-095; REVISED LOOP #094
F 07/25/00 JWP ADDED SKID LIMIT "FENCE"
HTR-091 HX-090 F-80,85,92
LO-P PURGE N2 FILTER F-080 NUPRO SS-4F-60u 2-15/16" 3/4" O.D 20 PSIG 25 °C 3000 PSIG 21 °C
SIM. ROG N2 FILTER F-092 NUPRO SS-6F-60u 3-7/32" 1" DIA 275 PSIA 25 °C 3000 PSIG 21 °C
LSO2 ROTAM. FILTER F-085 NUPRO SS-2F-7u 2-3/8" L 9/16" OD 350 PSIA 25 °C 3000 PSIG 21 °C
SIM ROG PHTR COIL HX-090 TUBING COIL 32" LNG 6" DIA 275 PSIG 600 °C 500 PSIG 700 °C
SIM ROG PHTR FURNACE HTR-091 SOLID TUBE FURNACE 36" LNG 16" DIAM N/A 600 °C N/A 600 °C
PID0011 FROM PCV-612
46 SLPM 104 SCFH
HV-088 3/8" T
F-092
MFC FC FCV 089 FIC 118-4 FIR 089
CKV-079 3/8" T
HV-078 3/8" T
HV-077 3/8" T
138-PROCESS N2 (DSRP)-3/8" T-SS TUBE
120-ORIFICE CAL N2-3/8" T-SS TUBE
PID0011 TO LINE 118 & CKV-616
165-L.P. VENT HDR-3"-PVC
PID0011 TO FCV-114
1/4" TX3"
166-ROTAMETER PURGE VENT-1/4" T-TFE
HV-084 1/8" TX1/4" T 1/8" T
PID0011 FROM PCV-165 & HV-615/LINE #111
140-LOW-P N2 TO SIM ROG-1/4" T-SS TUBE
F-080
DSRP SKID LIMIT
FROM WE-510 LSO2 WEIGH SCALES (PID0018)
WIT 510 WIR 510
PID0018 FROM F-540 & HV-512
0.25 GPH 15.4 CC/MIN TEMP PRESS
139-LSO2 TO DSRP-1/8" T-SS TUBE
HS 081A HS 081B S AS
YV 081 FC ZSO 081A ZSC 081A ZSO 081B ZSC 081B
HV-086 CKV-082 1/8" T 1/4" TX1/8" T
F-085 1/8" T
HV-087 1/8" T
FE 097 FCV-097 1/8" T
HV-098 1/8" T
HV-099 1/8" T
HV-083 1/8" T
HX-090
HTR-091
TE 094A TE 094B SW-094 CX
TIC 094 I 600 °C
TISH 094 700 °C TAH 094C TAH 094D
TE 095A TE 095B TI 095 TI 095
101-REGEN OFF-GAS-3/8" T-SS TUBE
HV-093A 3/8" T HV-093B 1/4" T 3/8" TX1/4" T
REMOVABLE SPOOL PIECE W/CAJON FACE SEAL FITTINGS
HV-096 3/8" T
CONSTRUCTION NOTE: HV-093A, HV-096 AND SPOOL PIECE ARE TO BE INSTALLED VERTICALLY, AS SHOWN SCHEMATICALLY.
Run 1 Run 2
MIN WOOL
3/8" TX3/4" T
PID0011 SIM ROG TO CKV-171 120 SCFH 57 SLPM 275 PSI 500 °C
TAG NUMBERS USED: 80-81, 83-99
LINE NUMBERS USED: 138-140, 165-66
1012-ROG FROM AHGP-3/8" T-SS TUBE
PID0017 ROG FROM YV-010 (AHGP SKID)
82 SCFH 36 SLPM 25 °C 275 PSI


DSRP FIELD TEST PILOT UNIT
P&ID - FILTERS & REACTOR
DOE/FETC
PID0011
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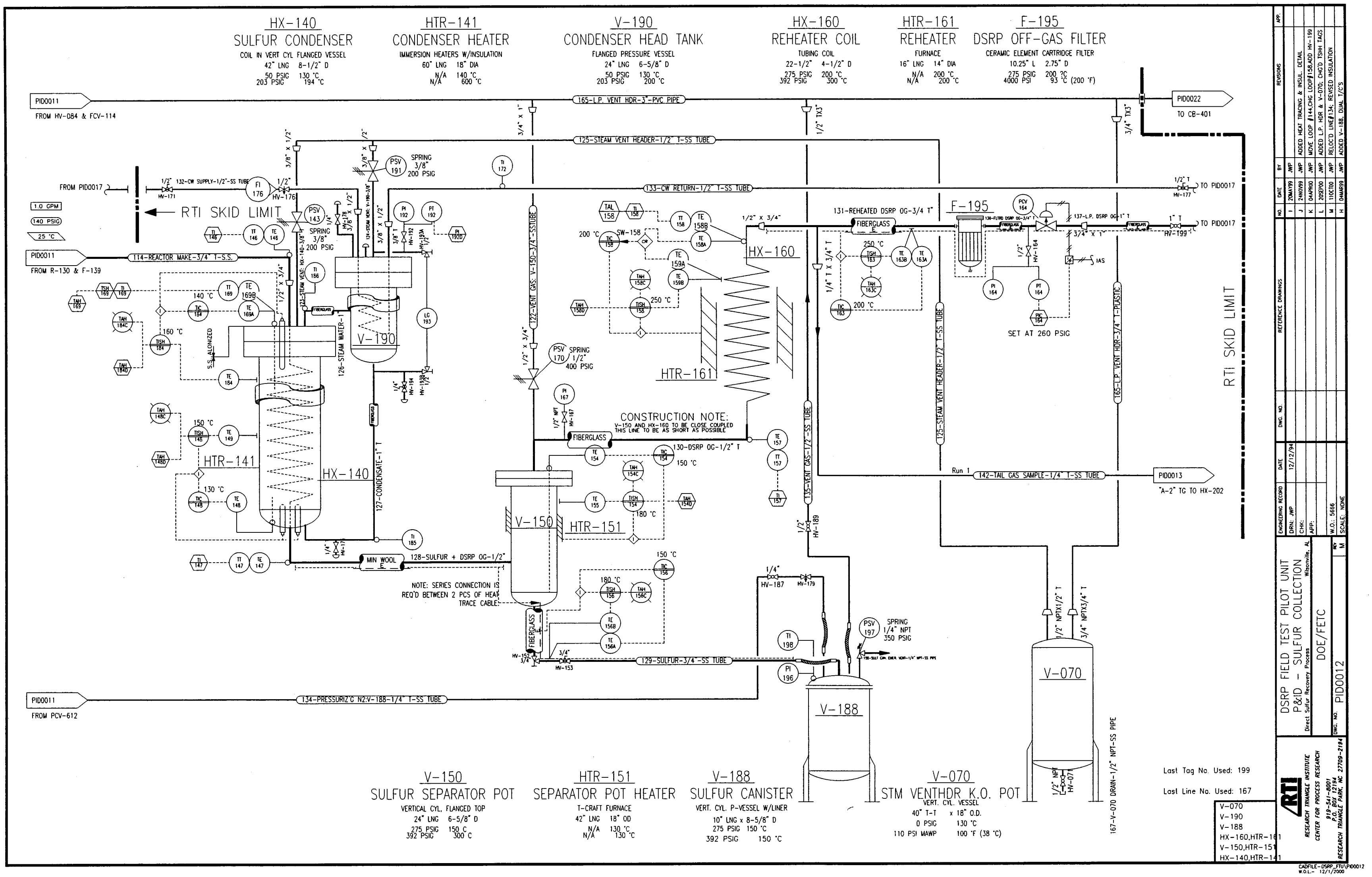
Direct Sulfur Recovery Process
Wilsonville, AL
DRN: JWP 11/4/94
W.O.: 5666
SCALE: NONE
HX-180
ROG PREHEATER COIL
TUBING COIL
44" LNG 6-1/2" D
275 PSIG 500 C
392 PSIG 600 C
HTR-181
ROG PREHEATER
FURNACE
38" LNG 16" DIA
N/A 500 °C
N/A 500 °C
R-130
DSRP REACTOR
FLUID-BED REACTOR/VERT. CYL VESSE
49" LNG 6-5/8"
275 PSIG 600 C
350 PSIG 675 °C
HTR-131
REACTOR FURNACE
FURNACE
60" LNG 18" DIA
N/A 600 °C
N/A 600 °C
F-139
DSRP RXTR FILTER
"BELL HOUSING"
10.5" L 3.5" DIA
275 PSIG 500 °C
350 PSIG 566 °C
F-120
COAL GAS FILTER
POROUS METAL FILTER ELEMENT
18" LNG 3-1/2" D
275 PSIG 540 °C
350 PSI 540 °C
F-121
CG BLOWBACK FILTER
CERAMIC ELEMENT CARTRIDGE FILTER
5.04" 2.46"
50 PSIG 30 °C
5000 PSI 93 °C
RTI SKID LIMIT
CONSTRUCTION NOTE:
DO NOT INSTALL LOOP
142 HEAT TRACING,
CONTROLLERS, AND
TE'S. INSTALL JUST
INSULATION.
Last No. Used: 183
Not Used: 142,145,162,166,168
Last Line No. Used: 121
Line No. Not Used: 118-120
HTR-181
HX-180
HTR-131
R-130
F-120,121
MIN WOOL
MIN FIBER
CA SILICATE
PID0010
FROM HV-084
PID0012
TO HV-179 & V-188
TO HV-189 & V-070
TO HX-140
PID0013
TO HX-210
SEE PID0017
CG TO AHGP
"A-3" CG TO ANAL SYS.
TO FFC-260 (PID0013)
FROM FFC-260 (PID0013)
SIM ROG FROM HX-090
TO F-080
TO F-092 & FCV-089
PID0014
TO F-308 & FCV-309
64-D002
FROM PSDF
FROM CKV-079 & HV-077
62-D016
101-REDCN OFF-GAS-3/4" T
102-FILTERED ROG-3/4" T-SS TUBE
109-F-120 FILT'D BLOWDN-1/2" T
113-MIXED RXTR FEED-3/4" T
114-REACTOR MAKE-3/4" T-S.S.
117-ROG SAMPLE-1/8" T-SS TUBE
134-PRESSURIZ'G N2/V-188-1/4" T-SS TUBE
105-COAL GAS-3/8" T
105-FLTR'D COAL GAS-3/8" T-SS TUBE
107-F-120 BLOWDOWN N2-1/2" T
116-CG SAMPLE-1/4" T-SS TUBE
1001-CG TO AHGP-3/8" T-SS TUBE
165-L.P. VENT HDR-3"-PVC
SCS-1-SYNGAS-1/2" T-C-276
SCS-2-I.P. N2-1/2" NPT-CS PIPE
103-PREHEATED ROG-1/2" T-SS TUBE
316 SS ALONIZED
Run 1
Run 2
Run 3
SPRING 1/2" T 350 PSIG
SET AT 300 PSIG
IAS
SP
540 °C
600 °C
300 °C
400 °C
650 °C
450 °C
550 °C
538 °C
454 °C
500 °C
120 SCFH
53 SLPM
94 SCFH
41 SLPM
174 SCFH
76 SLPM
275 PSIG
400 PSI
1000 °F
HV-209
HV-383
HV-224
HV-104
HV-613
HV-614
HV-615
HV-649
CKV-171
CKV-616
CKV-622
CKV-623
FCV-114
PCV 165
PCV 612
PSV 610
SW-182


HX-140
SULFUR CONDENSER
COIL IN VERT CYL FLANGED VESSEL
42" LNG 8-1/2" D
50 PSIG 130 °C
203 PSIG 194 °C
HTR-141
CONDENSER HEATER
IMMERSION HEATERS W/INSULATION
60" LNG 18" DIA
N/A 140 °C
N/A 600 °C
V-190
CONDENSER HEAD TANK
FLANGED PRESSURE VESSEL
24" LNG 6-5/8" D
50 PSIG 130 °C
203 PSIG 200 °C
HX-160
REHEATER COIL
TUBING COIL
22-1/2" 4-1/2" D
275 PSIG 200 °C
392 PSIG 300 °C
HTR-161
REHEATER
FURNACE
16" LNG 14" DIA
N/A 200 °C
N/A 200 °C
F-195
DSRP OFF-GAS FILTER
CERAMIC ELEMENT CARTRIDGE FILTER
10.25" L 2.75" D
275 PSIG 200 °C
4000 PSI 93 °C (200 °F)
PID0011
FROM HV-084 & FCV-114
165-L.P. VENT HDR-3"-PVC PIPE
PID0022
TO CB-401
125-STEAM VENT HEADER-1/2" T-SS TUBE
133-CW RETURN-1/2" T-SS TUBE
FROM PID0017
132-CW SUPPLY-1/2"-SS TUBE
HV-171
HV-176
RTI SKID LIMIT
1.0 GPM
140 PSIG
25 °C
PID0011
FROM R-130 & F-139
114-REACTOR MAKE-3/4" T-S.S.
PSV 143
SPRING 3/8" 200 PSIG
PSV 191
SPRING 3/8" 200 PSIG
S.S. ALONIZED
126-STEAM WATER-1"
127-CONDENSATE-1" T
MIN WOOL
128-SULFUR + DSRP OG-1/2"
NOTE: SERIES CONNECTION IS REQ'D BETWEEN 2 PCS OF HEAT TRACE CABLE
122-VENT GAS: V-150-3/4"-SSTUBE
PSV 170 SPRING 1/2" 400 PSIG
FIBERGLASS
CONSTRUCTION NOTE:
V-150 AND HX-160 TO BE CLOSE COUPLED THIS LINE TO BE AS SHORT AS POSSIBLE
130-DSRP OG-1/2" T
131-REHEATED DSRP OG-3/4 T"
SW-158
200 °C
250 °C
HX-160
HTR-161
HX-140
HTR-141
V-190
V-150
HTR-151
135-VENT GAS-1/2"-SS TUBE
HV-189
HV-187
HV-179
129-SULFUR-3/4"-SS TUBE
HV-152
HV-153
PSV 197 SPRING 1/4" NPT 350 PSIG
F-195
PCV 164
137-L.P. DSRP OG-1" T
HV-199
TO PID0017
HV-177
IAS
SET AT 260 PSIG
142-TAIL GAS SAMPLE-1/4" T-SS TUBE
Run 1
PID0013
"A-2" TG TO HX-202
165-L.P. VENT HDR-3/4" T-PLASTIC
PID0011
FROM PCV-612
134-PRESSURIZ'G N2:V-188-1/4" T-SS TUBE
V-188
V-070
3/4" NPTX3/4" T
1/2" NPTX1/2" T
HV-071
167-V-070 DRAIN-1/2" NPT-SS PIPE
V-150
SULFUR SEPARATOR POT
VERTICAL CYL. FLANGED TOP
24" LNG 6-5/8" D
275 PSIG 150 °C
392 PSIG 300 °C
HTR-151
SEPARATOR POT HEATER
T-CRAFT FURNACE
42" LNG 18" OD
N/A 130 °C
N/A 130 °C
V-188
SULFUR CANISTER
VERT. CYL. P-VESSEL W/LINER
10" LNG x 8-5/8" D
275 PSIG 150 °C
392 PSIG 150 °C
V-070
STM VENTHDR K.O. POT
VERT. CYL. VESSEL
40" T-T x 18" O.D.
0 PSIG 130 °C
110 PSI MAWP 100 °F (38 °C)
Last Tag No. Used: 199
Last Line No. Used: 167
V-070
V-190
V-188
HX-160,HTR-161
V-150,HTR-151
HX-140,HTR-141
RTI
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919-541-8001
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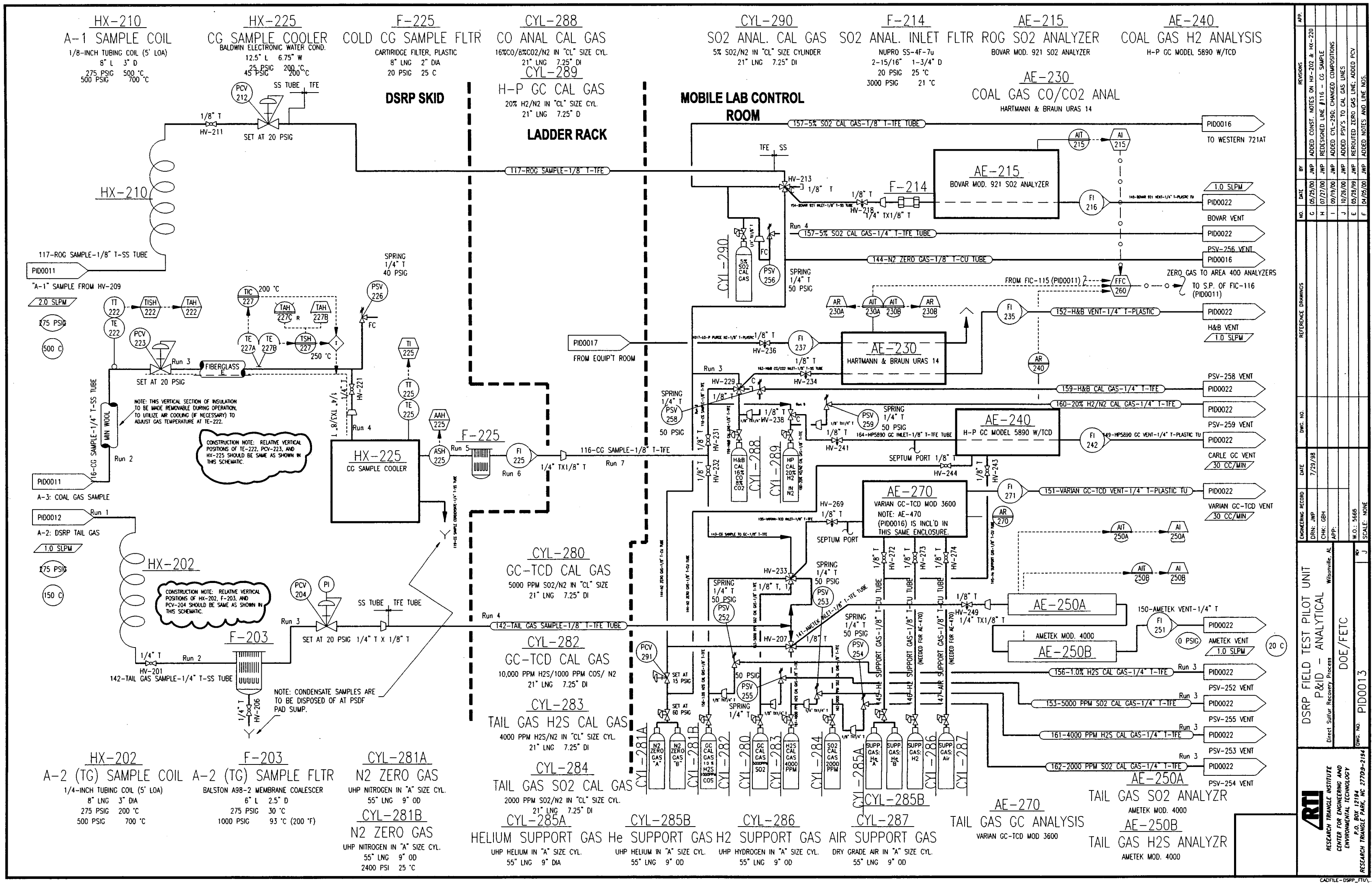
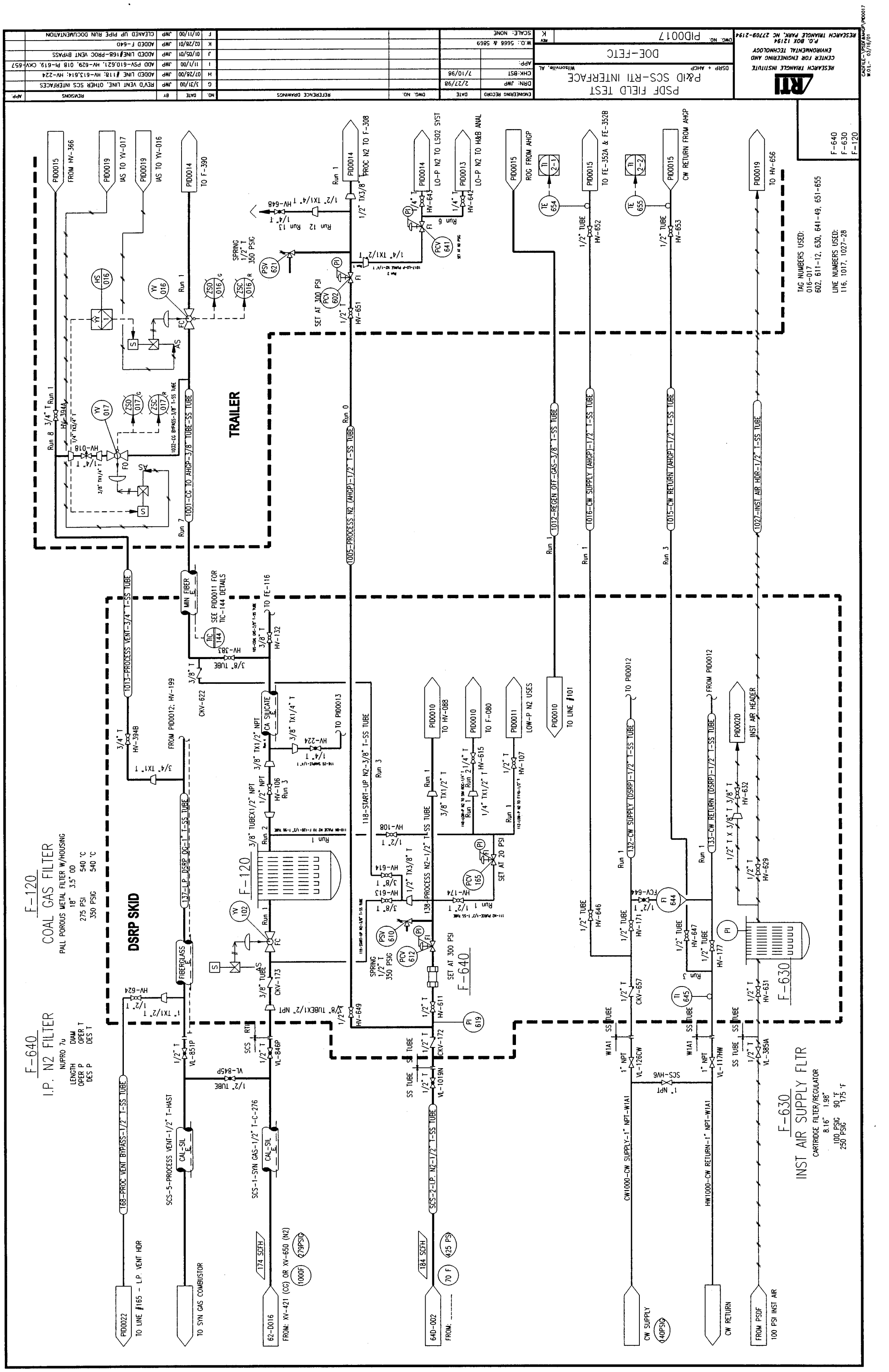
DSRP FIELD TEST PILOT UNIT
P&ID - SULFUR COLLECTION
Direct Sulfur Recovery Process
Wilsonville, AL
DOE/FETC
DWG. NO. PID0012
REV M
ENGINEERING RECORD
DRN: JWP 12/12/94
CHK:
APP:
W.O.: 5666
SCALE: NONE
DWG. NO.
REFERENCE DRAWINGS
NO. DATE BY REVISIONS APP.
I 20MAY99 JWP
J 24NOV99 JWP ADDED HEAT TRACING & INSUL. DETAIL
K 04APR00 JWP MOVE LOOP #144,CHG LOOP#158,ADD HV-199
L 20SEP00 JWP ADDED L.P. HDR & V-070; CHG'D TSHH TAGS
M 11OCT00 JWP RELOC'D LINE#134; REVISED INSULATION
H 04MAR99 JWP ADDED V-188, DUAL T/C'S
CADFILE-DSRP_FTU\PID0012
W.O.L.- 12/1/2000



CADFILE-DSRP_FTU\...\PID0013
W.O.L.- 12/1/2000


RTI
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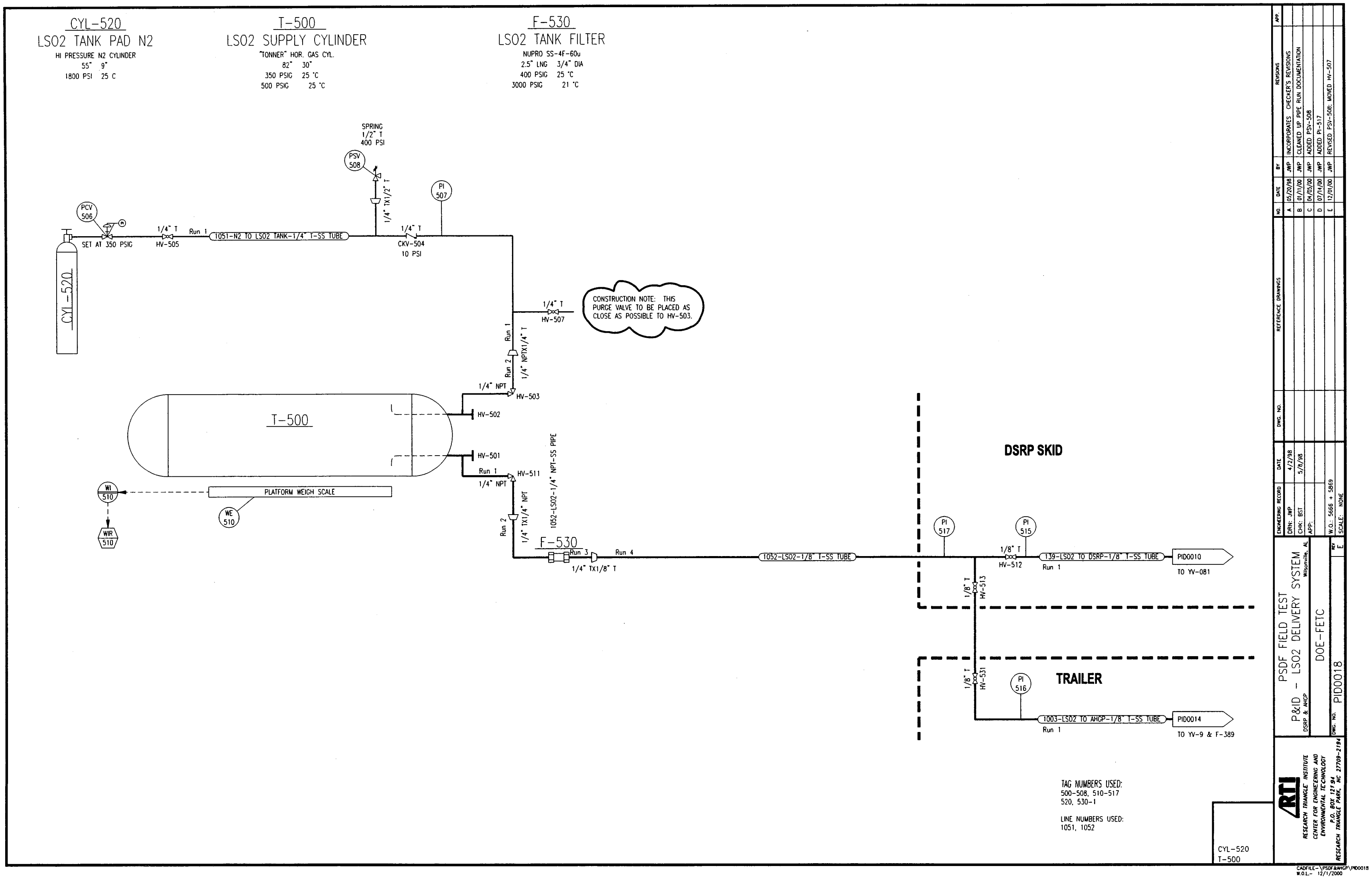
CENTER FOR ENGINEERING AND ENVIRONMENTAL TECHNOLOGY
P.O. BOX 12194
RESEARCH TRIANGLE PARK, NC 27709-2194
PSDF FIELD TEST
P&ID SCS-RTI INTERFACE
DOE-FETC
PID0017
SCALE: NONE
W.O.: 5666 & 5869
DSRP + AHGP
Wilsonville, AL
DRN: JWP 2/27/98
CHK: BST 7/10/98
REVISIONS
CLEANED UP PIPE RUN DOCUMENTATION
ADDED F-640
ADDED LINE 168-PROC VENT BYPASS
ADDED PSV-610,621, HV-629, 018 PI-619, CKV-657
ADDED LINE 118, HV-613,614, HV-224
REV'D VENT LINE, OTHER SCS INTERFACES
F-640
F-630
F-120
TAG NUMBERS USED:
016-017
602, 611-12, 630, 641-49, 651-655
LINE NUMBERS USED:
116, 1017, 1027-28
TRAILER
DSRP SKID
F-120
COAL GAS FILTER
PALL POROUS METAL FILTER W/HOUSING
18" 3.5" OD
275 PSI 540 °C
350 PSIG 540 °C
F-640
I.P. N2 FILTER
NUPRO 7u
F-630
INST AIR SUPPLY FLTR
CARTRIDGE FILTER/REGULATOR
100 PSIG 90 °F
250 PSIG 175 °F
PID0015 FROM HV-366
PID0019 IAS TO YV-017
PID0019 IAS TO YV-016
PID0014 TO F-390
PID0014 PROC N2 TO F-308
PID0014 LO-P N2 TO LS02 SYST
PID0013 LO-P N2 TO H&B ANAL
PID0015 ROG FROM AHGP
PID0015 TO FE-352A & FE-352B
PID0015 CW RETURN FROM AHGP
PID0019 TO HV-656
1001-CG TO AHGP-3/8" TUBE-SS TUBE
1005-PROCESS N2 (AHGP)-1/2" T-SS TUBE
1012-REGEN OFF-GAS-3/8" T-SS TUBE
1016-CW SUPPLY (AHGP)-1/2" T-SS TUBE
1015-CW RETURN (AHGP)-1/2" T-SS TUBE
1022-INST AIR HDR-1/2" T-SS TUBE
1013-PROCESS VENT-3/4" T-SS TUBE
132-LP DSRP OG-1" T-SS TUBE
118-START-UP N2-3/8" T-SS TUBE
138-PROCESS N2-1/2" T-SS TUBE
132-CW SUPPLY (DSRP)-1/2" T-SS TUBE
133-CW RETURN (DSRP)-1/2" T-SS TUBE
168-PROC VENT BYPASS-1/2" T-SS TUBE
SCS-5-PROCESS VENT-1/2" T-HAST
SCS-1-SYN GAS-1/2" T-C-276
SCS-2-LP. N2-1/2" T-SS TUBE
CW1000-CW SUPPLY-1" NPT-W1A1
HW1000-CW RETURN-1" NPT-W1A1
PID0010 TO HV-088
PID0010 TO F-080
PID0011 LOW-P N2 USES
PID0010 TO LINE 101
TO PID0012
FROM PID0012
PID0020 INST AIR HEADER
PID0022 TO LINE 165 - LP VENT HDR
TO SYN GAS COMBUSTOR
62-D016 FROM: XV-421 (CG) OR XV-650 (N2)
174 SCFH
1000F
279PSIG
64D-002 FROM: ____
184 SCFH
70 F
425 PSI
CW SUPPLY
140PSIG
CW RETURN
FROM PSDF 100 PSI INST AIR
SET AT 300 PSI
SET AT 20 PSI
SPRING 1/2" T 350 PSIG
SEE PID0011 FOR TIC-144 DETAILS
TO FE-116
FROM PID0012; HV-199
TO PID0013



NO.	DATE	BY	REVISIONS	APP.
A	05/20/98	JWP	INCORPORATES CHECKER'S REVISIONS	
B	01/11/00	JWP	CLEANED UP PIPE RUN DOCUMENTATION	
C	04/05/00	JWP	ADDED PSV-508	
D	07/14/00	JWP	ADDED PI-517	
E	12/01/00	JWP	REVISED PSV-508; MOVED HV-507	

REFERENCE DRAWINGS	DWG. NO.

ENGINEERING RECORD	DATE
DRN: JWP	4/2/98
CHK: BST	5/8/98
APP:	
W.O.: 5666 + 5869	
SCALE: NONE	

PSDF FIELD TEST
P&ID - LSO2 DELIVERY SYSTEM
DSRP & AHGP
Wilsonville, AL
DOE-FETC
DWG. NO. PID0018
REV E

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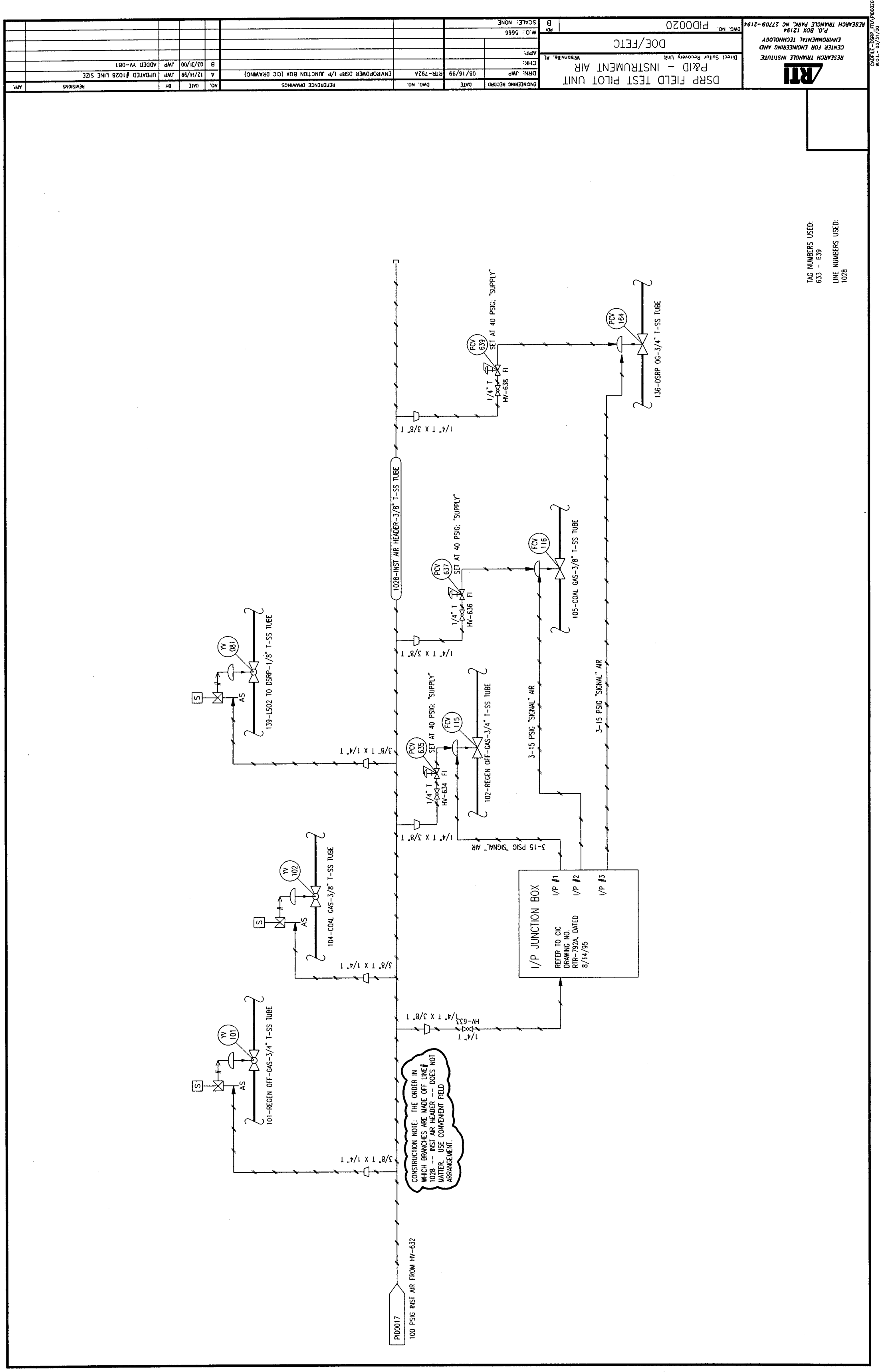
CADFILE-\PSDF&AHGP\PID0018
W.O.L.- 12/1/2000


DSRP FIELD TEST PILOT UNIT
P&ID – INSTRUMENT AIR
Direct Sulfur Recovery Unit Wilsonville, AL
DOE/FETC
DWG. NO. PID0020
REV B
SCALE: NONE
W.O.: 5666
RESEARCH TRIANGLE INSTITUTE
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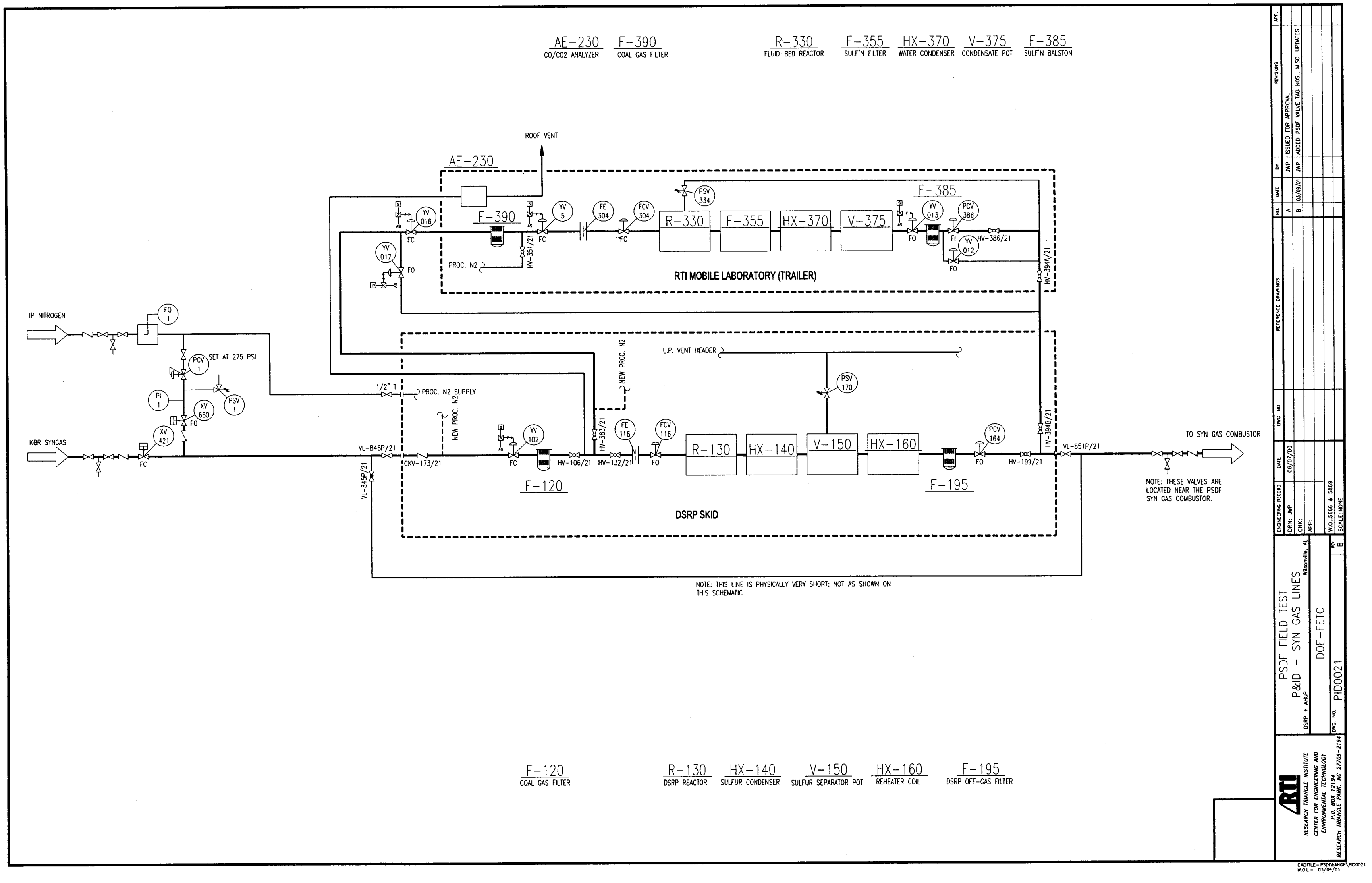
P.O. BOX 12194
RESEARCH TRIANGLE PARK, NC 27709-2194
ENGINEERING RECORD
DRN: JWP 08/16/99
CHK:
APP:
REFERENCE DRAWINGS
RTR-792A ENVIROPOWER DSRP I/P JUNCTION BOX (CIC DRAWING)
REVISIONS
A 12/14/99 JWP UPDATED #1028 LINE SIZE
B 03/31/00 JWP ADDED YV-081
CADFILE-DSRP_FTU\PID0020
W.O.L.- 03/31/00
TAG NUMBERS USED: 633 - 639
LINE NUMBERS USED: 1028
PID0017
100 PSIG INST AIR FROM HV-632
1028-INST AIR HEADER-3/8" T-SS TUBE
CONSTRUCTION NOTE: THE ORDER IN WHICH BRANCHES ARE MADE OFF LINE # 1028 -- INST AIR HEADER -- DOES NOT MATTER. USE CONVENIENT FIELD ARRANGEMENT.
I/P JUNCTION BOX
REFER TO CIC DRAWING NO. RTR-792A, DATED 8/14/95
I/P #1
I/P #2
I/P #3
3-15 PSIG "SIGNAL" AIR
HV-633
1/4" T
1/4" T X 3/8" T
3/8" T X 1/4" T
YV 101
101-REGEN OFF-GAS-3/4" T-SS TUBE
YV 102
104-COAL GAS-3/8" T-SS TUBE
YV 081
139-LS02 TO DSRP-1/8" T-SS TUBE
AS
S
PCV 635
SET AT 40 PSIG; "SUPPLY"
HV-634 FI
FCV 115
102-REGEN OFF-GAS-3/4" T-SS TUBE
PCV 637
HV-636 FI
FCV 116
105-COAL GAS-3/8" T-SS TUBE
PCV 639
HV-638 FI
PCV 164
136-DSRP OG-3/4" T-SS TUBE


AE-230 CO/CO2 ANALYZER
F-390 COAL GAS FILTER
R-330 FLUID-BED REACTOR
F-355 SULF'N FILTER
HX-370 WATER CONDENSER
V-375 CONDENSATE POT
F-385 SULF'N BALSTON
ROOF VENT
AE-230
F-390
F-385
YV 016
YV 5
FE 304
FCV 304
PSV 334
YV 013
PCV 386
YV 012
YV 017
FC
FO
FI
HV-351/21
HV-386/21
HV-394A/21
PROC. N2
RTI MOBILE LABORATORY (TRAILER)
IP NITROGEN
FQ 1
PCV 1
SET AT 275 PSI
PI 1
PSV 1
XV 650
XV 421
KBR SYNGAS
1/2" T
PROC. N2 SUPPLY
NEW PROC. N2
L.P. VENT HEADER
PSV 170
VL-846P/21
CKV-173/21
VL-845P/21
YV 102
HV-106/21
HV-383/21
HV-132/21
FE 116
FCV 116
R-130
HX-140
V-150
HX-160
PCV 164
HV-199/21
HV-394B/21
VL-851P/21
F-120
F-195
DSRP SKID
TO SYN GAS COMBUSTOR
NOTE: THESE VALVES ARE LOCATED NEAR THE PSDF SYN GAS COMBUSTOR.
NOTE: THIS LINE IS PHYSICALLY VERY SHORT; NOT AS SHOWN ON THIS SCHEMATIC.
F-120 COAL GAS FILTER
R-130 DSRP REACTOR
HX-140 SULFUR CONDENSER
V-150 SULFUR SEPARATOR POT
HX-160 REHEATER COIL
F-195 DSRP OFF-GAS FILTER
NO. DATE BY REVISIONS APP.
A JWP ISSUED FOR APPROVAL
B 03/09/01 JWP ADDED PSDF VALVE TAG NOS.; MISC. UPDATES
REFERENCE DRAWINGS
DWG. NO.
ENGINEERING RECORD DATE
DRN: JWP 06/07/00
CHK:
APP:
W.O.:5666 & 5869
SCALE: NONE
PSDF FIELD TEST
P&ID - SYN GAS LINES
DSRP + AHGP
Wilsonville, AL
DOE-FETC
DWG. NO. PID0021
REV B
RTI
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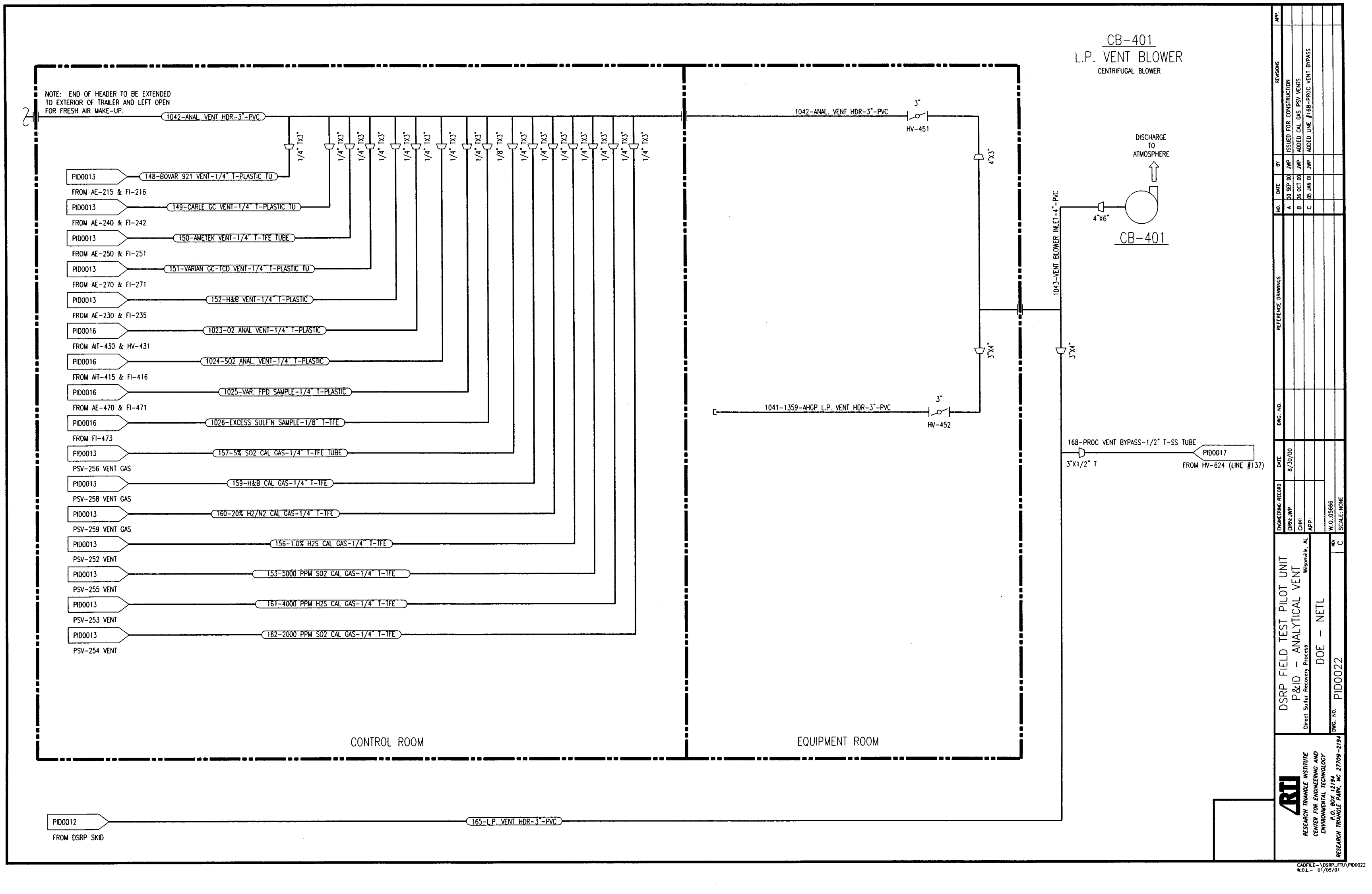
P.O. BOX 12194
RESEARCH TRIANGLE PARK, NC 27709-2194
CADFILE - PSDF&AHGP\PID0021
W.O.L.- 03/09/01


NOTE: END OF HEADER TO BE EXTENDED TO EXTERIOR OF TRAILER AND LEFT OPEN FOR FRESH AIR MAKE-UP.
1042-ANAL. VENT HDR-3"-PVC
1/4" TX3"
1/4" TX3"
1/4" TX3"
1/4" TX3"
1/4" TX3"
1/4" TX3"
1/4" TX3"
1/4" TX3"
1/8" TX3"
1/4" TX3"
1/4" TX3"
1/4" TX3"
1/4" TX3"
1/4" TX3"
1/4" TX3"
1/4" TX3"
PID0013
148-BOVAR 921 VENT-1/4" T-PLASTIC TU
FROM AE-215 & FI-216
PID0013
149-CARLE GC VENT-1/4" T-PLASTIC TU
FROM AE-240 & FI-242
PID0013
150-AMETEK VENT-1/4" T-TFE TUBE
FROM AE-250 & FI-251
PID0013
151-VARIAN GC-TCD VENT-1/4" T-PLASTIC TU
FROM AE-270 & FI-271
PID0013
152-H&B VENT-1/4" T-PLASTIC
FROM AE-230 & FI-235
PID0016
1023-02 ANAL VENT-1/4" T-PLASTIC
FROM AIT-430 & HV-431
PID0016
1024-SO2 ANAL. VENT-1/4" T-PLASTIC
FROM AIT-415 & FI-416
PID0016
1025-VAR. FPD SAMPLE-1/4" T-PLASTIC
FROM AE-470 & FI-471
PID0016
1026-EXCESS SULF'N SAMPLE-1/8" T-TFE
FROM FI-473
PID0013
157-5% SO2 CAL GAS-1/4" T-TFE TUBE
PSV-256 VENT GAS
PID0013
159-H&B CAL GAS-1/4" T-TFE
PSV-258 VENT GAS
PID0013
160-20% H2/N2 CAL GAS-1/4" T-TFE
PSV-259 VENT GAS
PID0013
156-1.0% H2S CAL GAS-1/4" T-TFE
PSV-252 VENT
PID0013
153-5000 PPM SO2 CAL GAS-1/4" T-TFE
PSV-255 VENT
PID0013
161-4000 PPM H2S CAL GAS-1/4" T-TFE
PSV-253 VENT
PID0013
162-2000 PPM SO2 CAL GAS-1/4" T-TFE
PSV-254 VENT
CONTROL ROOM
1042-ANAL. VENT HDR-3"-PVC
3"
HV-451
4"X3"
3"X4"
1041-1359-AHGP L.P. VENT HDR-3"-PVC
3"
HV-452
EQUIPMENT ROOM
CB-401
L.P. VENT BLOWER
CENTRIFUGAL BLOWER
DISCHARGE TO ATMOSPHERE
4"X6"
CB-401
1043-VENT BLOWER INLET-4"-PVC
3"X4"
168-PROC VENT BYPASS-1/2" T-SS TUBE
3"X1/2" T
PID0017
FROM HV-624 (LINE #137)
PID0012
FROM DSRP SKID
165-L.P. VENT HDR-3"-PVC
NO.
DATE
BY
REVISIONS
APP.
A
20 SEP 00
JWP
ISSUED FOR CONSTRUCTION
B
26 OCT 00
JWP
ADDED CAL GAS PSV VENTS
C
05 JAN 01
JWP
ADDED LINE #168-PROC VENT BYPASS
REFERENCE DRAWINGS
DWG. NO.
ENGINEERING RECORD
DATE
DRN: JWP
8/30/00
CHK:
APP:
W.O.:05666
SCALE: NONE
DSRP FIELD TEST PILOT UNIT
P&ID - ANALYTICAL VENT
Direct Sulfur Recovery Process
Wilsonville, AL
DOE - NETL
DWG. NO.
PID0022
REV
C
RTI
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CADFILE-\DSRP_FTU\PID0022
W.O.L.- 01/05/01

Appendix E

Stoichiometric Flow Control Calculations

Orifice Flow Meters (FIC-115 and FIC-116)

Principle of Operation: The basis of the orifice flow meter calculation is defined by the following "practical working equation for weight rate of discharge, adopted by the ASME Research Committee on Fluid Meters for use with either gases or liquids," as quoted in *Perry's Chemical Engineers' Handbook* (6th Ed., Eqn. 5-14):

$$w = KYA_2\sqrt{2g_c(p_1 - p_2)\rho_1}$$

w = weight rate of discharge, lb/sec

K, Y are special coefficients, defined belowA_2 = cross sectional area of the orifice, ft^2

g_c = the gravitational constant (32.2 ft/sec^2)

p_1 = pressure at upstream static pressure tap, lb/ft^2

p_2 = pressure at downstream static pressure tap, lb/ft^2

ρ_1 = density of flowing fluid at upstream pressure and temperature, lb/ft^3

For the process control logic, the weight rate must be converted to "molar" or volumetric flow. The following equation applies:

$Q = w\,k / MW$

w = weight rate of discharge, lb/sec

k = conversion factor constants

MW is the molecular weight of the sample gas.

Application: The field instruments provide 3 measurements: the upstream gas temperature in degrees Fahrenheit (TE-115 and 116 for the regeneration offgas and coal gas loops, respectively), the upstream pressure in pounds per square inch (PT-115 and 116), and the pressure drop across the orifice in inches of water (PDT-115 and 116). With the appropriate conversion factors, these measurements can be plugged into the equation above.

Coefficients:

The K term is defined as follows:

$K = C/\sqrt{}(1-\beta^4)$, where

C = coefficient of discharge, dimensionless

β = ratio of the orifice diameter to the pipe diameter, dimensionless

C is the discharge coefficient and is empirically determined. From Figure 5-20 in Perry's, it appears that a typical value for the flow conditions that exist around the orifices on the DSRP skid should be 0.62.

β is the diameter ratio, and when raised to the fourth power, is a small number. Subtracting that value from 1.0, and then taking the square root results in a correction factor that is not much different from 1.0, so the algorithms that are programmed in the SCADA system ignore it. Similarly, the Y correction factor (for expansion of the gas across the orifice) is approximately 1.0 since this is a high pressure system with a very low orifice meter pressure drop. Thus, the KY term is approximately equal to C, which was stated above to be 0.62. This is an operator-adjustable term, as discussed in more detail below.

Constants:

A_2 comes from the mechanical design of the orifice. We have the following information about the orifice plates that are currently installed, but bear in mind that we may want to change out the plates, and enter new information into the calculation algorithms:

FE-115	Regenerable Offgas	0.2776 inches dia.	0.00042031 ft^2
FE-116	Coal Gas	0.1595 inches	0.00013875 ft^2

The $2g_c$ term is also a constant: 64.4 ft/sec^2.

Variables:

The DP transmitter directly measures the $(p_1 - p_2)$ term, except that the engineering units of the output (inches of water) has to have a conversion constant applied to get lb/ft^2 (multiply inches of water by 5.20).

The final step to complete the input to the mass flow calculation is to calculate the gas density. The gas density calculation utilizes the upstream pressure measurement, the gas temperature, and the molecular weight (MW). The molecular weight is not calculated continuously from field data; it is a keyboard input value and only needs to be changed by the operator if, during operation, the coal gas composition changes significantly from the design value.

The equation that applies is as follows:

$$\rho_1 = MW * P / (10.73 * (T + 459.6))$$

where ρ_1 is the density in lb/ft^3, P is the pressure in PSIA (the transmitter reading + 14.7), and T is the gas temperature in degrees Fahrenheit.

With the mass flow calculation complete, the final step is to convert the weight rate of discharge (w, calculated above) into volumetric (also called molar) flow. This calculation changes the units from "lb/sec" to "standard liters per minute" (SLPM) by applying the following equation:

w * (454 g/lb) * (60 sec/min) *(22.4 std L / mole) / (MW, g/mole) = w * 610,176 / MW

The calculated mass flow rate in SLPM becomes the "PV" or process value for feedback to the P-I-D controllers (FIC-115 and FIC-116, for regeneration off gas and coal gas respectively).

One final consideration in programming the mass flow calculation was providing the functionality to calibrate the orifice flow meter in the field by changing the value of the discharge coefficient. What the field crew successfully did during the commissioning activities was pass a known flow rate of nitrogen (measured in SLPM by an electronic mass flow controller) through the flow orifice and note the output value from the orifice meter calculations (after inputting the correct molecular weight). If the values did not match, the operator adjusted the orifice coefficient constant in order to force the values to match.

Stoichiometric Flow Ratio Calculation (FFC-260)

Principle of Operation: The flow ratio calculation starts with the output from the ROG orifice meter (FE-115) calculation, and applies a field instrument value to it to calculate the SO_2 component flow rate. Then the flow ratio controller applies a user-defined constant (the stoichiometric ratio; keyboard entry) to determine the required flow rate of the “reducing” components of the coal gas. Using two other field instrument values to define the current concentration of reducing components, the flow ratio controller determines the new set point for the coal gas flow controller (FIC-116).

Application: Figure A-1 diagrams the information flow for the flow ratio calculations that must be carried out to define the set point of the coal gas flow controller. Relevant equations are as follows:

$SO_2FLOW = ROGFLOW * \%SO_2$

$\%REDCOMP = \%H_2 + \%CO$

$REDCOMPF = STOICHR * SO_2FLOW$

$CGFLOW = REDCOMPF / \%REDCOMP$

where the terms, above, are defined as follows:

SO_2FLOW	Flow rate (in SLPM) of the sulfur dioxide component of the regeneration offgas.
ROGFLOW	Flow rate (in SLPM) of the regeneration offgas stream; output of the mass flow calculations of FIC-115
$\%SO_2$	Volume % sulfur dioxide in the ROG; output of AIT-215.
%REDCOMP	% of reducing components of the coal gas.
$\%H_2$	Volume % hydrogen in the coal gas; output of AR-240. [NOTE: this is a special signal and required special logical treatment, as described below.]
%CO	Volume % carbon monoxide in the coal gas; output of AIT-230.
REDCOMPF	Desired flow rate of reducing components (in SLPM).
STOICHR	The stoichiometric ratio of reducing components to SO_2; approximately equal to 2.0. THIS VALUE IS THE SET POINT OF FFC-260.
CGFLOW	Required coal gas flow to meet stoichiometry requirements. THIS VALUE IS THE OUTPUT OF FFC-260, and becomes the ”floating” set point of FIC-116.

The data acquisition and processing of the signals for all of the above was quite straightforward, with the exception of the $\%H_2$ signal. A gas chromatograph measures the hydrogen concentration (GC; AE-240). A GC is a ”batch” device, in that it receives a small sample of the process gas (the ”injection”), and then for a period of 20 or 30 minutes, passes that gas through a long, thin, heated (temperature-programmed) tube and past a detector. The detector generates a constantly varying voltage output that must have a considerable degree of signal processing in order to be made useful. A freestanding PC, running Hewlett-Packard Chemstations® software processes (*i.e.,* ”integrates”) that signal. Then a Labview® program extracts a single number – the H_2 concentration – from the Chemstation files, and outputs that number to a National Instruments analog-out board. That analog signal (4-20 mA) goes into the PLC of the DSRP control system. The whole combination of computer, two different software packages, and analog board is designated on the P&ID by the single bubble, AR-240.

The Labview® program generates a signal such that the H_2 concentration will have a fixed value for the duration of each sample. At the end of the injection, the integration calculations will take place, and a new H_2 concentration value will be calculated. That new value will be held for the duration of the next injection, and so on. During this time the carbon monoxide concentration in the coal gas could be changing, however, and the continuous CO analyzer will pick that up.

The concern in building a rugged control system for the field test, is that the GC can potentially (and, in fact, is somewhat likely to) generate spurious signals that will be integrated to give unlikely answers for the H_2 concentration. There is ”error trapping” to check that the calculated value is reasonable, before letting FFC-260 use that value in a fully automatic mode to determine the new value for the set point for the coal gas flow rate.

The overall process control has three levels of automatic control, as follows:

MANUAL	Valves FCV-115 and FCV-116 will have their position determined by the operator inputting "% open" values into FIC-115 and 116.
SEMI-AUTOMATIC	The PID loops for FCV-115 and FCV-116 will be operational, with the mass flow calculations operating, so that the operator can input a set point value (in SLPM) and the valve controller will strive to maintain that value. This mode of operation is equivalent to turning OFF the FFC-260. In this mode, the FFC-260 calculations will continue to be displayed on the screen, for de-bugging purposes, but the set point of FIC-116 will not be changed.
FULL AUTOMATIC	The stoichiometric flow ratio controller (FFC-260) is turned ON, and the coal gas set point is constantly modulated in response to the changing compositions of the ROG and CG so that the ratio of reducing gas components to the SO2 content is equal to the set point.