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

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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

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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).