DOE Contract No. DE-AC21-93MC30010--30
RTI Project No. 93U-5666
April 1, 2000 to June 30, 2000

BENCH-SCALE DEMONSTRATION OF HOT-GAS DESULFURIZATION TECHNOLOGY

Quarterly Technical Progress Report

Submitted to

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

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1.0 INTRODUCTION AND SUMMARY

The U.S. Department of Energy (DOE), National Energy Technology Laboratory (NETL), is sponsoring research in advanced methods for controlling contaminants in hot coal gasifier gas (coal-derived fuel-gas) streams of integrated gasification combined-cycle (IGCC) power systems. The hot gas cleanup 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 that can reduce the sulfur in coal-derived fuel-gas to less than 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:

Sulfidation: $Zn_2TiO_4 + 2H_2S$ 6 $2ZnS + TiO_2 + 2H_2O$

Regeneration: $2ZnS + TiO_2 + 3O_2$ 6 $Zn_2TiO_4 + 2SO_2$

The sulfidation/regeneration cycle can be carried out in a fixed-bed, moving-bed, or fluidized-bed reactor configuration. 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.

The SO_2 in the regeneration offgas needs to be disposed of in an environmentally acceptable manner. Options for disposal include conversion to a solid calcium-based waste using dolomite or limestone, conversion to sulfuric acid, and conversion to elemental sulfur. Elemental sulfur recovery is the most attractive option because sulfur can be easily transported, sold, stored, or disposed of. However, elemental sulfur recovery using conventional methods is a fairly complex, expensive process. 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/NETL sponsorship has been developing zinc titanate sorbent technology since 1986. In addition, RTI has been developing the Direct Sulfur Recovery Process (DSRP) with DOE/NETL sponsorship since 1988. Fluidized-bed zinc titanate desulfurization coupled to the DSRP is currently an advanced, attractive technology for sulfur removal/recovery for IGCC systems.

Under other contracts, RTI (with the help of commercial manufacturers) has developed durable fluidized-bed zinc titanate sorbents that showed excellent durability and reactivity over 100 cycles of testing at up to 750EC. In bench-scale development tests, zinc titanate sorbent EXSO3 (developed by Intercat and RTI) 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 was manufactured by a commercially scalable spray drying technique using commercial equipment. Previous RTI zinc titanate formulations, such as ZT-4, have been tested independently by the Institute of Gas Technology (IGT) for Enviropower/Tampella Power, and by others such as British Coal and Ciemat, and showed no reduction in reactivity and capacity after 10 cycles of testing at 650EC.

In the DSRP, SO_2 is catalytically reduced to elemental sulfur using a small slip stream 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:

$$2H_2 + SO_2 \quad 6 \quad (1/n)S_n + 2H_2O$$

$$2CO + SO_2 \quad 6 \quad (1/n)S_n + 2CO_2$$

$$CO + H_2O \quad 6 \quad CO_2 + H_2$$

The above reactions occur in Stage I of the two-stage (as originally conceived) process, and convert up to 96% of the inlet SO_2 to elemental sulfur. The sulfur is recovered by cooling the outlet gas to condense out the sulfur as a molten solid. All of the H_2 and CO is consumed in the first reactor, with some H_2S and COS forming according to the following reactions:

$$3H_2 + SO_2 \; 6 \; H_2S + 2H_2O$$

$$3CO + SO_2 \; 6 \; COS + 2CO_2$$

Adjusting the stoichiometric ratio of coal gas to regenerator offgas to 2 at the inlet of the first reactor also controls the Stage I effluent stoichiometry since any H_2S and COS produced by the reactions above yields an (H_2S + COS) to unconverted SO_2 ratio of 2 to 1. The effluent stoichiometry plays an important role in the Stage II DSRP reactor (operated at 275 to 300EC), where 80% to 90% of the remaining sulfur species is converted to elemental sulfur, most probably via these reactions:

$$COS + H_2O \; 6 \; H_2S + CO_2$$

$$2H_2S + SO_2 \; 6 \; (3/n)S_n + 2H_2O.$$

The prior laboratory work suggested that the overall sulfur recovery could be projected to be 99.5%.

At the start of the current project, the DSRP technology was at the bench-scale development stage with a skid-mounted system ready for field testing. The process had been extended to fluidized-bed operation in the Stage I reactor. Fluidized-bed operation proved to be very successful with conversions up to 94% at space velocities ranging from 8,000 to 15,000 scc/cc·h and fluidizing velocities ranging from 3 to 7 cm/s. Overall conversion in the two stages following interstage sulfur and water removal had ranged up to 99%.

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% 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, both fluidized-bed zinc titanate and DSRP technologies have been shown to be 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 off-gas. Thus, the effect of trace contaminants in real coal gases on the sorbent and DSRP catalyst was not known. Also, the zinc titanate desulfurization unit and DSRP had not been demonstrated in an integrated manner.

The overall goal of this project is to continue further development of the zinc titanate desulfurization and DSRP technologies by scale-up and field testing (with actual coal gas) of the zinc titanate fluidized-bed reactor system, and the Direct Sulfur Recovery Process.

By the end of the 1996 Fiscal Year, the following milestones had been achieved toward that goal:

- Construction of a larger, skid-mounted zinc titanate fluidized-bed desulfurization (ZTFBD) reactor system;
- Integration of the ZTFBD with the skid-mounted DSRP and installation of these process units into a specially-equipped office trailer to form a Mobile Laboratory;
- Transport to and installation of the ZTFBD/DSRP Mobile Laboratory at the NETL Morgantown site for testing with a slip stream of actual coal gas from the pilot gasifier located there;
- Shake-down and testing of the ZT-4 sorbent integrated with the 2-stage DSRP during September and October 1994;
- Discovery that in longer duration testing, the second stage of the DSRP did not aid overall conversion of the inlet SO_2 to elemental sulfur, and subsequent modification to the DSRP process equipment;
- Additional, longer duration (160 h) testing of the simplified, single-stage DSRP during July, 1995, and determination of no degradative effect of the trace contaminants present in coal gas over this time period;
- Exposure of the used DSRP catalyst to an additional 200 h of coal gas at the General Electric pilot plant gasifier, and subsequent testing of the exposed catalyst in a bench-scale DSRP in the RTI laboratory; and,
- Design and partial construction of six-fold larger (“6X”), single-stage DSRP process unit intended for additional field testing.

The plans for additional work in this project (in Fiscal Year 1997 and beyond) include the following:

- Additional long duration exposure of the DSRP catalyst to actual coal gas from the Kellogg-Rust-Westinghouse (KRW) gasifier at NETL’s Power Systems Development Facility (PSDF) in Wilsonville, Alabama, and subsequent testing in RTI's bench-scale DSRP;

- Additional development of 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;

- Modification of the ZTFBD/DSRP Mobile Laboratory for use as a portable control and analyzer room for the 6X DSRP;

- Completion of construction of the 6X DSRP process equipment in preparation for field testing; and

- Extended duration field testing of the 6X DSRP at PSDF with actual coal gas and high concentrations of SO_2.

2.0 TECHNICAL DISCUSSION

2.1 EXPOSURE TEST AT PSDF

No work was conducted on this task during this reporting period.

2.2 BENCH-SCALE FLUID-BED TESTING WITH HIGH-SO_2 CONCENTRATION FEED STREAMS

No work was conducted on this task during this reporting period.

2.3 SLIPSTREAM TESTING OF THE 6X DSRP UNIT AT PSDF

2.3.1. Project Planning

The P&IDs were revised, and updated revisions were issued, to better represent the interconnections of the piping between the DSRP skid and the Mobile Reactor (trailer), and to clarify the connections with PSDF lines.

The control scheme for the three furnaces that are used to heat tubing coils was revised to include the option of using a furnace-mounted thermocouple, or a process line-mounted thermocouple as the primary sensing element for the controller. Thus, a feed-forward or a feedback strategy can be implemented on the fly during the field test. The thermocouple wiring diagrams were revised to reflect these changes.

The design of the cable tray (ladder rack) that will be used to hold up the cables, sample lines, and process tubing from the skid to the trailer was finalized, and additional pieces of the cable tray were ordered. The terminations of the PSDF lines will occur on one end of this ladder rack; updated drawings were provided to SCS for their detailed engineering design of the site and the piping. The routing of the added lengths of the nitrogen supply line, and the coal gas line, was established.

Communication channels with PSDF staff remained open, with a steady e-mail correspondence covering various details of the design. Additional mass balance information was supplied for upset operating conditions, so that safety implications could be checked. Also, estimates of maximum nitrogen utilization were prepared so that the totalizer meter that SCS will install could be sized and ordered. Coordination is ongoing between SCS and RTI and a designated consultant for scheduling the Design Hazard and Operability Review (safety review/process hazard analysis). Originally schduled for June 19, that date had to slip pending DOE approval of the RTI add-on cost proposal that includes the consultant services.

A review and update of the Microsoft Project-based Gantt chart suggested that, in order to meet the November time frame for the shake-down test, the DSRP skid and Mobile Laboratory trailer had to be at PSDF on October 1, 2000. In a conference call in late May PSDF staff reported that the schedule for the gasifier tests has slipped by a month or so. However, to meet the on-site construction schedule they requested that the RTI should continue to maintain October 1 as the target date for having the DSRP skid on site. Table 1, below, updates the project schedule in light of this information.

Table 1. Updated Project Schedule.

Activity	Proposed Schedule based on information presented at February 9, 2000 meeting at PSDF	Revised Schedule based on information in teleconference on May 23, 2000
Modification and Refitting of Mobile Lab (trailer)	ongoing, until September 2000	Same
Modification and Completion of DSRP Equipment Skid	ongoing, until September 2000	Same
Installation of Trailer and CSRP skid at PSDF	October 2000	October - November 2000
Shakedown test (1 month)	November 2000	Mid-December 2000 or January 2001
Field Test	April - May 2001	May - June 2001
Demobilization of Trailer and Skid	June - July 2001	After Field Test
Data Analysis and Draft Final Report	August 2001 - November 2001	September - December 2001

Some additional effort was expended on the engineering of the heat tracing system and its connection to the heater control panel. Detailed instructions were worked up for the electrical crew that will be doing that work later this summer.

A review of the synthesis gas slipstream line piping plans, undertaken as part of the initial thinking for drafting the start-up and operating instructions, suggested that additional process piping will need to be added to the system to allow for more complete nitrogen purging before and after coal gas flow. This activity is the subject of ongoing discussion.

Based on the “as-built” length of the coal gas sample line, and the expected operating conditions, anticipated residence time (delay) of the gas sample between the sample point and the analyzer was calculated. Depending on system pressure, the delay was calculated to be 7 to 10 minutes. This may be too long for good process control. Some additional calculations are planned, and it may be necessary to replace the sample line with less rugged, smaller diameter tubing.

2.3.2. Equipment Acquisition

With the finalization of the skid pipe rack/cable tray design, it became apparent that an additional length of heat trace cable would need to be purchased. The decision was made to connect together into one circuit two of the cables already received, in order to free up a control circuit to use for the new cable. The additional heat cable was specified and orderdered/

Parts for the simulated regeneration off-gas (Sim ROG) preheater tubing coil, HX-090, were also ordered.

2.3.3. Fabrication/Construction

A significant number of construction tasks on the skid-mounted DSRP field test unit were completed this quarter:

- Instrument air tubing installed.
- Control panel (WIT-510) for the liquid sulfur dioxide (LSO_2) tank weigh scales was mounted on a panel on the DSRP skid.
- The nitrogen mass flow controller for the SimROG stream was mounted.
- The SimROG preheater furnace (HTR-091) was mounted. N_2 and LSO_2 lines were routed up to the furnace. The internal coil was fabricated and installed.
- The nitrogen piping was reworked to include the necessary tees, branches and valves to supply nitrogen to the Mobile Laboratory.
- The cooling water supply and return lines, including branches to the Mobile Lab, were installed.
- The "tee" connector piece of ladder rack was received and installed. This item facilitates routing lines from the skid to the Mobile Laboratory trailer, while also allowing supporting the lines that terminate at the "east" end of the skid.
- The hardware to implement the revised furnace control scheme (for the 3 tubing coil heater furnaces) was ordered and received. The thermocouple selector switches were installed in the thermocouple junction boxes on the skid.

- The replacement orifice plates for the coal gas and the regeneration off-gas (ROG) orifice flow meters were installed. (The new orifice plates were required because the gas flow rates that will be used at the PSDF test are different from what was originally planned when the DSRP skid was first assembled.)
- The panel to support the LSO_2 rotameter and flow control hand valves was designed and fabricated. The LSO_2 lines were installed.
- The flow control valves for the filter back-pulse/blowdown nitrogen (FCV-113 and 114) were received and installed.
- The panel for the cooling water rotameters was been fabricated, and the rotameters (FE-644 and FI-176) installed. Special, high pressure rotameters were required due to the potentially high pressure that can occur in the PSDF cooling water supply loop.
- The ROG sample line with air-cooled coil and block valve (HX-210 and HV-211) was installed.
- The additional pieces of piping support “ladder rack” were received and installed, in order to build a second level to hold all the process lines.
- The panel to support the LxSO) rotameter and flow control hand valves was fabricated, painted (color code: yellow), and installed on the skid. The rotameters and valves were mounted and connection of the tubing was completed.
- The panel for the cooling water rotameters was painted (color code: blue) and installed on the skid framework. The components were installed on the panel.
- Work continued on fabrication of the nitrogen back-pulse/purge system for the coal gas filter and the regeneration off-gas (ROG) filter with installation of the two flow control valves for de-pressurizing.
- The line regulator for the ROG sample line was installed on a custom-fabricated mounting bracket.
- The on-skid portion of the DSRP tail gas sample line hardware (PCV-204 and related items; sample point A-2) was completed. A new type filter (Balston membrane coalescing type, Model A98-2) was purchased and installed for this service (F-203). The expectation is that this unit will be able to handle the high condensate loading and sulfur aerosol particle concentration expected during the field test runs made with high SO_2 concentrations in the regeneration off-gas (ROG).
- The on-skid portion of the ROG sample line (sample point A-1) was complete.
- The DSRP tail gas line (line no. 137; also referred to as “DSRP Off-Gas.” in the project documentation) and the vent header (line no. 121) were extended to the skid limits and cross connected with the installation of isolation valve HV-199. The isolation valve was required for the installation of the skid at PSDF in order to isolate the RTI equipment from the back pressure of the PSDF vent header to which the skid discharge will be connected.

- For the skid-mounted mass flow controller (FCV-089) that controls nitrogen flow to the simulated regeneration off-gas (SimROG) system, the control box was modified and a custom cable was prepared.
- The coal gas sample conditioning system (HX-225; electronic water condenser) was installed in a convenient location on the skid. The sample line (#116) was installed, connected to the coal gas line on the skid, downstream of the Pall Filter (F-120).

With the completion of all but a few minor items of the process and instrumentation tubing on the skid (one or two thermocouples, etc.), the pressure testing got underway. As the skid is not electrically connected to the control panel in the Mobile Laboratory, temporary control power and instrument air supplies had to be rigged in order to operate the automatic valves. This set up was in addition to the compressed gases (nitrogen and helium) required for the actual pressure test.

As anticipated, the pressure testing uncovered a few fittings that were not leak tight. It also became apparent that there was a sealing problem with the main reactor flange. It was disassembled and sent out for additional machining of the custom-fabricated joint between the 6-inch 300-lb class pipe flange and the catalyst cage flange.

3.0 OPEN ITEMS

The scheduled date of the safety review of the DSRP field test unit and the accompanying analytical and control system in the Mobile Laboratory has been substantially postponed from the date assumed in the project schedule. If the review uncovers any concerns that will require substantial equipment or process modification, there is a good chance that the overall field test schedule could be negatively impacted.

4.0 PLANS FOR NEXT QUARTER

The following activities are planned for the next quarter:

- C Continue the construction activities associated with the modification and renovation of the control room in the Mobile Laboratory.
- C Conduct a process hazard analysis (PHA) of the RTI-supplied equipment, at RTI, using the services of an outside consultant/facilitator. Revise the equipment design and control system, as required.
- C Complete the installation of temperature transmitters, and thermocouple wiring.
- C Complete the installation of wiring between the field instruments and the control system cable receptacle junction boxes.
- C Conduct pressure test and repair all identified leaks.
- C Install heat trace cables. Prepare the insulation for later installation at PSDF (following on-site follow-up leak test).
- C Temporarily set up the hydrogen analysis hardware and software and test/debug the system.

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