DOE Contract No. DE-AC21-93MC30010--32
RTI Project No. 93U-5666
April 1, 1999 to June 30, 1999

BENCH-SCALE DEMONSTRATION OF HOT-GAS DESULFURIZATION TECHNOLOGY

Quarterly Technical Progress 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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1.0 INTRODUCTION AND SUMMARY

The U.S. Department of Energy (DOE), Federal Energy Technology Center (FETC), 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/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 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 FETC 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 FETC’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. <u>Project Planning</u>

As was described in the last quarter's report, the process design and documentation is complete for the "self-contained" portion of the process – that is, the portion of the RTI scope of work that is inside the trailer or is fully on the skid. The design of the interface of the RTI process with the PSDF process and utility lines is still not complete. The "site access agreement" between RTI and Southern Company Services (SCS) is not in place, and no liaison staff has been assigned by SCS to assist with the details of the process interface. (See Open Items.)

Minor modifications were made (as fabrication proceeded) to the mechanical designs for the several equipment items that were redesigned or had to be added to the RTI scope when the test site was identified to be the PSDF:

- the re-designed reactor vessel (to incorporate fluid-bed, as well as fixed-bed testing);

- C the sulfur separator pot; and,
- C the sulfur collection canister (not previously part of the RTI scope).

No additional planning action was taken regarding the process hazard analysis (safety review) that is planned, pending assignment by SCS of the liaison staff, and determination of the specific requirements.

2.3.2. **Equipment Acquisition**

Fabrication is 90% complete at the vendor's facility for the stand-alone control panel that will be required for remote control of the skid-mounted DSRP Unit. The control panel (to be mounted in the Mobile Laboratory trailer) houses a programmable logic controller (PLC) to provide the control and process interlock logic. The operator interface is a personal computer running National Instruments "Lookout" commercial software for supervisory control and data acquisition (SCADA) that includes data logging and trending.

Extensive communications with the panel vendor took place throughout the quarter in order to answer questions that arose during fabrication, and to insure that the control system will function as desired, including a fairly complex algorithm for tight stoichiometric control of the reaction.

Two RTI staff attended a National Instruments training seminar on the use of the Lookout software. With this training, on-the-fly changes to the SCADA system, during the field test, will be facilitated.

The specifications were developed for purchase of software and hardware to interface an existing Carle 400 GC (specially equipped to analyze for hydrogen) to the stoichiometric ratio control scheme. No orders were placed, pending approval to add these items to the contract authorized equipment list (see Open Items).

Specifications were also developed for fabrication of a heat exchanger coil, and purchase of an additional electric furnace to be added to the DSRP skid. These additional items (which form the SimROG preheater) will provide the capability for vaporization of liquid sulfur dioxide to provide a synthesized regeneration off-gas (ROG) stream, without removing the existing capability of the skid to handle an "actual" ROG stream. No orders were placed, pending approval to add these items to the contract authorized equipment list (see Open Items).

Additionally, with the finalization of the process design for the analytical system, the need to add a sample conditioning system (for the moist coal gas sample) became apparent. An appropriate commercial unit was identified, but no order was placed, pending approval to add this item to the contract authorized equipment list (see Open Items).

2.3.3. Fabrication/Construction

Construction activities during this quarter focused on the erection of the canopy shed over the DSRP skid in its temporary location at the RTI shops (Figure 1). Also, some additional vessel fabrication work took place: The reactor vessel was modified to have a flanged top so that a catalyst "cage", enabling fluid-bed as well as fixed-bed testing, can be inserted. The sulfur collection pot was fabricated with a specially-designed nozzle-impinger designed to enhance the coalescing and separation of the aerosol droplets of molten sulfur. The sulfur collection canister design was completed and all parts either on-hand or ordered for this pressure vessel designed to hold a 1-gallon paint can (suitable for collecting 24 hours' production of molten sulfur).

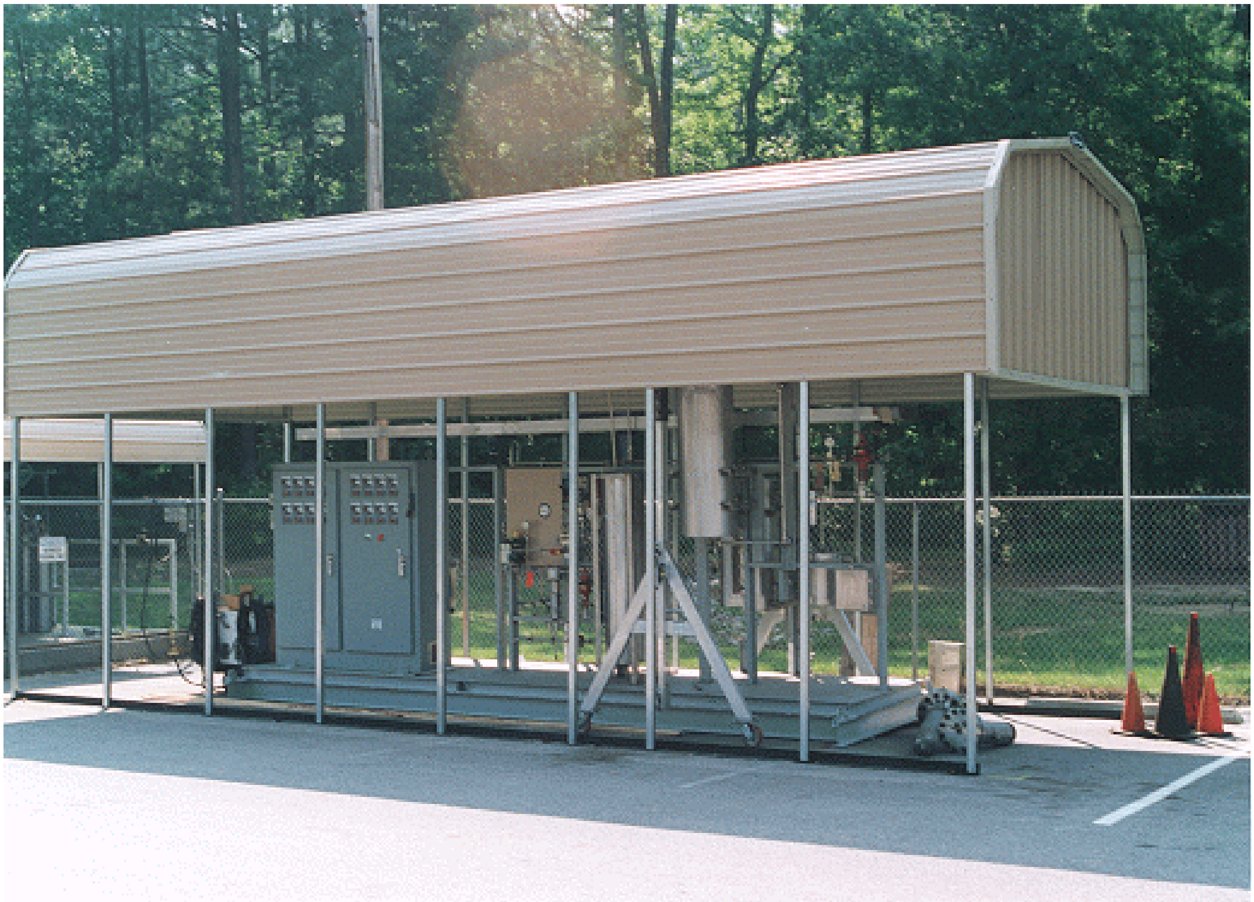

Figure 1. The weather-protection canopy has been installed over the enlarged Skid-Mounted DSRP unit while it is at RTI undergoing final fabrication. This same canopy will be used during the field test at PSDF.

3.0 OPEN ITEMS

As has been reported previously, the operative schedule is currently estimated to call for the RTI equipment to move to Wilsonville, AL, in November of this calendar year, and to be fully hooked up and ready for slip-stream testing starting after January 2000. However, the site access agreement is still not in place with SCS at PSDF, and no liaison staff from SCS have been assigned. Thus, the preparation of the proper process interface between the RTI equipment and PSDF equipment has not been accomplished. Unless that activity can be started very soon, the field test schedule will be in jeopardy.

Certain key items of equipment (notably the Sim ROG preheater coil and furnace, the hydrogen analysis chromatography software and PC interface hardware, and the coal gas sample conditioning system) have not been ordered because they were not on the original contract equipment list. Approval for a modification to that list has not been received, yet; timely receipt of the required items may be jeopardized.

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 Receive (from the vendor) and install the PLC-based control panel in the Mobile Laboratory.
- C Conduct a hazard and operability analysis (HAZOP) of the RTI-supplied equipment, based on the piping and instrumentation diagrams (P&ID's) prepared, as part of the previous task noted above. Revise the equipment design and control system, as required.
- C Provide technical support, as needed, to the RTI Office of Research Contracts so that the site access agreement with Southern Company Services can be put in place.
- C Complete the fabrication of the catalyst cage for the modified reactor vessel, and fabricate the sulfur collection canister.
- C Install the rebuilt reactor vessel, and sulfur collection canister on the equipment skid.
- C Finalize the specifications and place the order for the additional heater (furnace) required for the Sim ROG system.
- C Place the order for the hydrogen analysis chromatography software and PC interface hardware.
- C Place the order for the sample conditioning system.
- C Prepare the engineering design and purchase specifications for the custom-designed heat tracing elements.
- C Prepare the thermocouple wiring design, develop the purchase specifications, and place the orders for the thermocouples and temperature transmitters.

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