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## **BENCH-SCALE DEMONSTRATION OF HOT-GAS DESULFURIZATION TECHNOLOGY**

### **Quarterly Technical Progress Report**

Submitted to

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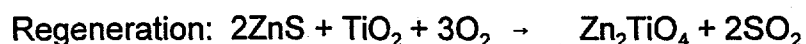
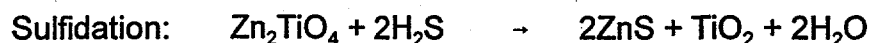
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## 1.0 INTRODUCTION AND SUMMARY

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:



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  $SO_2$ .

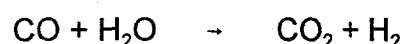
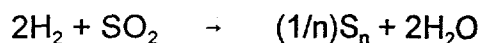
The  $SO_2$  in the regeneration offgas needs to be disposed of in an environmentally acceptable manner. Options for disposal include conversion to a solid

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<sub>2</sub> in the regenerator offgas directly to elemental sulfur.

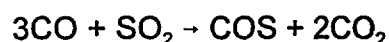
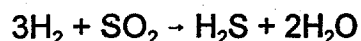
Research Triangle Institute (RTI) with DOE/FETC sponsorship has been developing zinc titanate sorbent technology since 1986. In addition, RTI has been developing the Direct Sulfur Recovery Process (DSRP) with DOE/FETC sponsorship since 1988. Fluidized-bed zinc titanate desulfurization coupled to the 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 750°C. In bench-scale development tests, zinc titanate sorbent EXSO3 (developed by Intercat and RTI) consistently reduced the H<sub>2</sub>S 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 650°C.

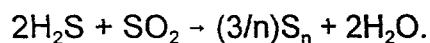
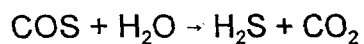
In the DSRP,  $\text{SO}_2$  is catalytically reduced to elemental sulfur using a small slip stream of the coal gas at the pressure and temperature conditions of the regenerator offgas. A near-stoichiometric mixture of offgas and raw coal gas (2 to 1 mol ratio of reducing gas to  $\text{SO}_2$ ) reacts in the presence of a selective catalyst to produce elemental sulfur directly:



The above reactions occur in Stage I of the two-stage (as originally conceived) process, and convert up to 96% of the inlet  $\text{SO}_2$  to elemental sulfur. The sulfur is recovered by cooling the outlet gas to condense out the sulfur as a molten solid. All of the  $\text{H}_2$  and  $\text{CO}$  is consumed in the first reactor, with some  $\text{H}_2\text{S}$  and  $\text{COS}$  forming according to the following reactions:



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  $\text{H}_2\text{S}$  and  $\text{COS}$  produced by the reactions above yields an ( $\text{H}_2\text{S} + \text{COS}$ ) to unconverted  $\text{SO}_2$  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% of the remaining sulfur species is converted to elemental sulfur, most probably via these reactions:



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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>.

## 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<sub>2</sub> 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

A limited amount of project planning liaison with the Southern Company Services (SCS) at PSDF took place. At the end of this reporting period the paperwork was not yet in place to authorize expenditure by SCS on DSRP field test activities (see Open Items, below). Items discussed were emergency procedures associated with liquid sulfur dioxide supply tank, and material of construction for cooling water piping.

Development of the engineering specifications and detailed design requirements for the high-temperature electric heat tracing continued. Direct contact with the manufacturer's engineering department was required, to obtain detailed design information and computer program for the sizing calculations.

A detailed review of the piping and instrumentation diagrams (P&IDs) and the accompanying pipe run data base was completed in order to develop a definitive list of hand valves and special fittings to be ordered.

Tentative plans were made for project planning meeting at the PSDF site in mid December, but the meeting was postponed.

### **2.3.2. Equipment Acquisition**

The order was placed for the furnace for the simulated regeneration off-gas feed preheat coil (HX-090), HTR-091. This the last furnace required on the DSRP skid. The only significant item of equipment that has not yet been ordered is HX-225, the coal gas sample conditioning water condenser system. The last potentially long lead item is the heat tracing, for which the specifications are still be developed.

### **2.3.3. Fabrication/Construction**

The junction boxes for the process control wiring (24-volt analog and discrete signals) between the skid and the trailer/control room were received and installed. Carolina Instrumentation Corp. (CIC) came on-site to make the permanent connections of those junction boxes to the PLC control panel that they had earlier supplied. The temporary field connections at PSDF will be made using custom-fabricated multiconductor cables with plugs joining to receptacles in the junction boxes, which were installed on the outside of the trailer and on the DSRP skid.

Additional work was completed on the sulfur collection canister, V-188, to install it on the DSRP skid with appropriate fittings that will make it possible for this vessel to be routinely disconnected from the pressurized system, and be opened for removal of the collected elemental sulfur.

The thermocouples and thermocouple protection heads were installed on the skid for all the equipment and lines that are in place. The necessary calibration equipment was acquired, calibrations ranges were determined, and each transmitter

was calibrated using a thermocouple simulator.

The support ring inside HTR-141 was rebuilt so that HX-140 could be installed properly. This work was necessary to correct a manufacturing problem that had not been identified earlier. It was determined that it would be more cost-effective to repair the problem, rather than spend the effort to make a warranty claim.

The furnace for the off-gas re-heat coil (HX-160), HTR-161, was relocated on the skid to give additional clearance to V-188. This change (which involved fabricating new brackets and re-routing the process tubing) became necessary after V-188 (sulfur canister) was put in place, and it became clear that the original process equipment layout (intended for the Enviropower test situation) would not be feasible with the on-skid sulfur canister that is being used for the PSDF test arrangement.

### 3.0 OPEN ITEMS

The current project schedule, as reported in the Milestone Plan for FY2000, calls for the RTI equipment to move to Wilsonville, AL, in January 2000, and to be fully hooked up and ready for slip-stream testing in February 2000. As of the end of this reporting period, however, an extension to the cooperative agreement between SCS and DOE had not been finalized. As a result, SCS was only able to provide limited resources to the project. Thus, the preparation of the detailed process interface between the RTI equipment and PSDF equipment has not been accomplished and the proposed project schedule cannot be met.

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.

## 4.0 PLANS FOR NEXT QUARTER

The following activities are planned for the next quarter:

- Continue the construction activities associated with the modification and renovation of the control room in the Mobile Laboratory.
- 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.
- Place the order for the hydrogen analysis chromatography software and PC interface hardware.
- Place the order for the sample conditioning system.
- Complete the engineering design and purchase specifications for the custom-designed heat tracing elements and place the order.
- Continue installation of temperature transmitters, and thermocouple wiring.
- Install the control system cable receptacle junction boxes.
- Install the wiring between the field instruments and the control system cable receptacle junction boxes.
- Receive, install, and test the control system operator interface computer and software.
- Receive and install HTR-091.
- Fabricate and install HX-090 coil inside HTR-091, and install connecting process tubing, thermocouples, and hand valves.
- Receive and install all remaining hand valves for the DSRP skid.