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Bench-Scale Demonstration of Hot-Gas Desulfurization Technology

Quarterly Report
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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:

$$\text{Sulfidation:} \quad Zn_2TiO_4 + 2H_2S \rightarrow 2ZnS + TiO_2 + 2H_2O$$

$$\text{Regeneration:} \quad 2ZnS + TiO_2 + 3O_2 \rightarrow Zn_2TiO_4 + 2SO_2$$

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 750°C. 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 650°C.

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:

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

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

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

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:

$$3H_2 + SO_2 \rightarrow H_2S + 2H_2O$$

$$3CO + SO_2 \rightarrow COS + 2CO_2$$

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 300°C), where 80% to 90% of the remaining sulfur species is converted to elemental sulfur, most probably via these reactions:

$$COS + H_2O \rightarrow H_2S + CO_2$$

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

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

The exposure test had been scheduled for October, 1998. However, the tentative schedule for operation of the gasifier has been delayed (as reported below), and the current plan is that the exposure test will take place in the summer or fall of 1999.

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

The initial results of the spectroscopic characterization of the two candidate fluid-bed catalysts were received, but the results were anomalous. Therefore, the analyses will be repeated at a different laboratory. Other than this activity, the subtask is essentially complete.

2.3 SLIPSTREAM TESTING OF THE 6X DSRP UNIT AT PSDF

2.3.1. Project Planning

Project planning, design, and engineering are in full swing for the planned field test at PSDF. Preliminary designs for the arrangement of the analytical instruments, control panels and computers in the office/control room side of the Mobile Laboratory have been prepared. The final arrangement will be made after the decision has been made on which cabon monoxide and hydrogen analyzer will be purchased.

A drawing was prepared of the overall site plan ("footprint") showing the layout and general arrangement of the RTI field test equipment. The drawing included sufficient detail to show the support racks and conduit that will be required for the interconnections of the control system low-voltage wiring, the gas sample lines, the utility gases, and the heat-traced coal gas slipstream line between the DSRP skid and the trailer. This drawing was reviewed by SCS staff at PSDF; they determined that there was insufficient space with the initial proposed arrangement in which the DSRP skid was placed at the end of the trailer.

The second, revised arrangement places the DSRP skid alongside the trailer, thus shortening and widening the footprint. This arrangement, shown in Figure 1, is currently being reviewed by Southern Company Services staff.

2.3.2. Equipment Acquisition

The project requirements and specifications were developed for the continuous analyzers that are to be purchased for the field test. The requirement is that the composition of the reducing gas components of the coal gas be continuously monitored and that this information become input to the coal gas flow control computation. The carbon monoxide content will most likely be measured using an analyzer based on non-dispersive infrared (NDIR) sensing. The hydrogen content will be analyzed using a thermal conductivity detector (TCD). Alternatively, a mass-spectrometer-based analyzer is being considered to measure the two target gases, as well as other components of the coal gas. Bids are currently being received on these equipment items.

2.3.3. Fabrication/Construction

Construction activities have started on the modification of the trailer interior with the removal of the "Liquid SO_2 closet". This small partitioned area used during the prior field tests to house the pressurized liquid SO_2 cylinder used to generate the simulated regeneration off-gas feed. The current test plan will use a pressurized reservoir of LSO_2 that will be maintained outside. Removal of the closet partition walls frees up additional floor space for construction of cabinets and lab benches.

2.3.4. Revised Field Test Schedule

The recent information that the PSDF gasifier test schedule has been delayed 9-12 months suggests that the project schedule will be as follows:

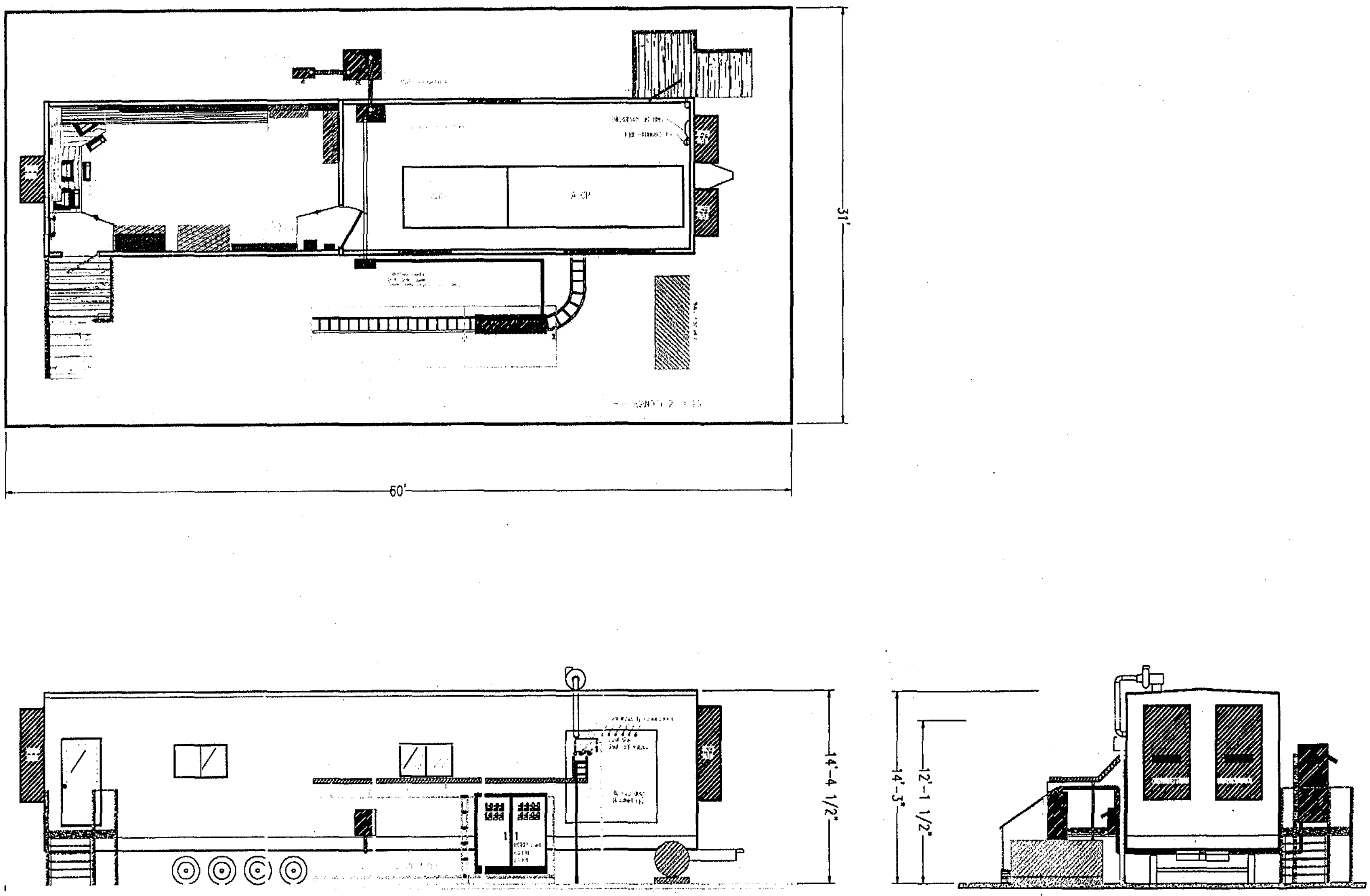
June 1998 — RTI ships catalyst canisters to PSDF for temporary storage, and later installation in particulate control device prior to start of commissioning run of transport gasifier.

June 1999	Commissioning of the transport gasifier (run GCT1) for approximately one month.
August 1999	Earliest possible date for start of long gasification run (TC03).
December 1999	Likely start date for run TC03.
Jan-Mar 2000	RTI staff on-site for continuous operation of the test unit.

2.3.4. Topical Report

A topical report has been drafted that covers the previous field testing of the DSRP using the Mobile Laboratory (1994 and 1995 campaigns). This report also describes the design basis and construction history of the DSRP skid-mounted unit that will be tested at PSDF.

Figure 1. General Arrangement of RTI Equipment for Field Test at PSDF.



3.0 PLANS FOR NEXT QUARTER

The following activities are planned for the next quarter:

- Continue to prepare the engineering design drawings for the Mobile Lab conversion to control room, the modification of the skid-mounted DSRP to meet the site-specific requirements, and the overall site plan/interface points.
- 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.
- Complete the data analysis of the fluid-bed catalyst testing program, including any followup material characterization that may be required.

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