Bench-Scale Demonstration of Hot-Gas Desulfurization Technology

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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$_2$TiO$_4$ 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$_2$TiO$_4$ during the desulfurization (sulfidation)-regeneration cycle are shown below:

- **Sulfidation**: $\text{Zn}_2\text{TiO}_4 + 2\text{H}_2\text{S} \rightarrow 2\text{ZnS} + \text{TiO}_2 + 2\text{H}_2\text{O}$
- **Regeneration**: $2\text{ZnS} + \text{TiO}_2 + 3\text{O}_2 \rightarrow \text{Zn}_2\text{TiO}_4 + 2\text{SO}_2$

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 SO₂ 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 EXS03 (developed by Intercat and RTI) consistently reduced the H₂S 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:

\[
\begin{align*}
2H_2 + SO_2 & \rightarrow (1/n)S_n + 2H_2O \\
2CO + SO_2 & \rightarrow (1/n)S_n + 2CO_2 \\
CO + H_2O & \rightarrow CO_2 + H_2
\end{align*}
\]

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$_2$S and COS forming according to the following reactions:

\[
\begin{align*}
3H_2 + SO_2 & \rightarrow H_2S + 2H_2O \\
3CO + SO_2 & \rightarrow COS + 2CO_2
\end{align*}
\]

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$_2$S and COS produced by the reactions above yields an (H$_2$S + 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:

\[
\begin{align*}
COS + H_2O & \rightarrow H_2S + CO_2 \\
2H_2S + SO_2 & \rightarrow (3/n)S_n + 2H_2O.
\end{align*}
\]
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 SO₂ 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

With the acceptance of the proposal by RTI for follow-on work on this task, activities commenced with preparations for coal gas exposure testing of the DSRP fixed bed catalyst at the Power Systems Development Facility (PSDF) in Wilsonville, Alabama. Southern Company Services (SCS), the on-site contractor, reviewed RTI's canister design and offered suggestions for improvement. The planned location is inside the high temperature particulate control device (PCD) (i.e., coal gas filter) vessel, on the “clean” side.

Incorporating SCS's suggestions, RTI fabricated two rectangular canisters of perforated stainless steel, approximately 3 x 3 x 15 in., including hold-down straps. Two samples of DSRP catalyst will be exposed; two different methods of pretreatment will be used. One sample will be pretreated at RTI in the bench-scale sorbent test unit. The other sample will be treated by a commercial vendor of catalyst treatment services following a different protocol. An appropriate quotation for those services was received, and plans were made to ship a quantity of catalyst.

2.2 BENCH-SCALE FLUID-BED TESTING WITH HIGH-SO₂ CONCENTRATION FEED STREAMS

A potential source of substrate that could be used to prepare a fluidizable DSRP catalyst was located. Characterization and attrition tests were conducted on a small sample that was supplied at no charge; the results looked favorable.

Subsequently, a large quantity of substrate for the fluidizable DSRP catalyst was obtained (sufficient for use with the 6X unit, as well as with the bench unit tests). A vendor was selected to prepare the catalyst support with the proprietary active components of the
DSRP catalyst. The initial batch of substrate was sent out for preparation. Work started on developing the test plan and conditions for the bench unit run.
3.0 PLANS FOR NEXT QUARTER

The following activities are planned for the next quarter:

- Obtain pre-treated fixed-bed DSRP catalyst from the commercial vendor.
- Pre-treat a second batch of DSRP catalyst at RTI.
- Obtain the special shipping container for the canisters (that will allow shipping and storage under an inert nitrogen gas atmosphere), charge the canisters with the pre-treated catalyst samples, and ship the canisters to PSDF for installation in their process vessel.
- Obtain the impregnated DSRP fluidizable catalyst and set up the bench-scale runs.
- Conduct the planned fluid-bed experiments with high concentrations (up to 14 vol%) of SO$_2$ in the simulated regeneration off-gas.
- Start preparing for the annual contractors conference that will be held in July, 1997.
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