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Bench-Scale Demonstration of Hot-Gas Desulfurization Technology

Quarterly Report
April 1 - June 30, 1998

By:
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Work Performed Under Contract No.: DE-AC21-93MC30010

For
U.S. Department of Energy
Office of Fossil Energy
Federal Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
Research Triangle Institute
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DOE Contract No. DE-AC21-93MC30010--25
RTI Project No. 93U-5666
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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

Of the several candidate fluid-bed catalysts that were tested at the bench scale (as previously reported in the Quarterly Technical Progress Report covering July through September, 1997), the most promising one, "B", was selected for further testing of physical properties. The "used" material showed only a small loss of total pore volume, but the surface area declined as the median pore size (diameter) increased. In separate testing, there was no measurable loss of the active metal species on the catalyst.

Table 1. Catalyst "B" Properties

	"Fresh"	"Used"
BET Surface area, m2/g	212	157
Hg Porosimetry pore volume, mL/g	0.41	0.385
Median pore diameter, A	70	92

2.3 SLIPSTREAM TESTING OF THE 6X DSRP UNIT AT PSDF

2.3.1. Project Planning

As the decision was made on the choice of CO and H_2 analyzers (see below), the Mobile Laboratory control room interior layout could be finalized. The emphasis was on continuing with the development of the process and control system documentation.

Table 2 is a list of the process flow diagrams (PFDs) and piping and instrumentation diagrams (P&IDs) that are currently under development for the RTI equipment that will be used in the field test. The reader should note that the list also includes those drawings that apply to the “Advanced Hot Gas Process” (AHGP) testing that is being conducted under contract 31258.

Discussions with Southern Company Services (SCS), the on-site contractor at the PSDF, continued with regard to planning for the field test. The revised site plan / equipment layout for the RTI-supplied equipment (Mobile Laboratory, 6X DSRP skid, and ancillary equipment) was accepted. The DSRP skid will be located alongside the Mobile Laboratory trailer, rather than at the end.

In previous field testing of the bench-scale DSRP equipment, heat tracing of the high temperature coal gas lines and the molten sulfur lines using laboratory-grade heat tapes was only partially successful. To alleviate those problems with the 6X DSRP skid, industrial-grade, heavy-duty heat tracing will be installed. Based on a lead from SCS, a vendor was located who can work with the small diameter tubing and piping of the pilot-scale field test unit, yet achieve the high temperatures required.

2.3.2. Equipment Acquisition

Decisions have been made on the choice of analyzers for the key components of the coal gas: hydrogen and carbon monoxide. The coal gas composition is expected to vary somewhat as the gasifier operation fluctuates. To achieve a high conversion efficiency in the DSRP, the active reducing components in the coal gas must be in exact stoichiometric ratio with the SO_2 composition being treated in the regeneration off-gas. Therefore, an accurate, timely analysis is essential.

A non-dispersive infrared (NDIR) analyzer was ordered to analyze continuously the CO content. It will also measure the CO_2 content of the coal gas that is supplied to the DSRP unit. The NDIR analyzer is expected to be a rugged, reliable, and accurate instrument for this application.

Continuous analysis of the hydrogen content, with the background of the other gases that make up coal gas, is problematical. Conventional continuous analyzers are based on thermal conductivity principles and may have relatively low accuracy if the sample matrix changes much from that on which the unit was calibrated. Because modestly-priced mass spectroscopic analyzers units have recently become available, they were considered for this application, as a way to get around the background gas problem. People with experience with the affordable units suggested, however, that a combination of software and hardware problems made them troublesome to operate in a field test situation. The more expensive units that are also available were reportedly more reliable, but their cost was deemed prohibitive for this field test application.

Therefore, for hydrogen analysis, the decision was made to use an existing Carle gas chromatograph. This unit will give an accurate measure of the hydrogen content against a varying sample matrix, but it will not be a continuous signal. Provision will need to be made in the process control system to incorporate a periodic, discrete H_2 analysis along with the continuous CO analysis.

2.3.3. Fabrication/Construction

Construction activities are proceeding inside the Mobile Laboratory, currently located at RTI. The bench tops and shelving were modified to increase the space available for computer consoles. A PC-based operator interface is planned for accessing the control system for the 6X DSRP unit and a comfortable operating station needed to be arranged. Additionally, space needed to be provided for the floor-standing control panel (containing the PLC, PID controllers, relays, and terminal strips) that will provide the hardware interface to the 6X DSRP skid.

2.3.4. Topical Report

A topical report was submitted for DOE review 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. This report will be submitted as an NTIS document.

2.3.5. Contractors Conference

A poster session was prepared for the annual contractors conference to be held in July at Morgantown. The development of the fluidized-bed catalyst material will be presented, in addition to the plans for the PSDF field test.

Table 2. Drawing Index.

DRAWING #	REV #	TITLE - 1ST LINE	TITLE – 2ND LINE	REMARKS	AREA CODE	DATE
PFD02	G	DSRP FIELD TEST PILOT UNIT	PFD – RTI SKID EQUIPMENT	AutoCAD Rel. 12		3/11/95
PFD03	A	AHGP FIELD TEST BENCH UNIT	PFD – RTI TRAILER EQUIPMENT			5/20/98
PFD04	--	PSDF FIELD TEST	PFD – RTI SKID & TRAILER	incl. mat'l balance		2/9/98
PID0010	A	DSRP FIELD TEST PILOT UNIT	P&ID – SIM ROG SYSTEM		000	5/20/98
PID0011	G	DSRP FIELD TEST PILOT UNIT	P&ID – FILTERS & REACTOR		100	5/27/98
PID0012	G	DSRP FIELD TEST PILOT UNIT	P&ID – SULFUR COLLECTION		100	5/28/98
PID0013		DSRP FIELD TEST PILOT UNIT	Analytical System	not drawn	200	
PID0014	A	AHGP FIELD TEST BENCH UNIT	P&ID–FEED GASES+PREHEATERS		300	6/23/98
PID0015	A	AHGP FIELD TEST BENCH UNIT	P&ID – REACTOR + PROD RECOV		300	6/5/98
PID0016		AHGP FIELD TEST BENCH UNIT	Analytical System	not drawn	400	
PID0017	A	PSDF FIELD TEST	P&ID – SCS-RTI INTERFACE		600	5/20/98
PID0018	A	PSDF FIELD TEST	P&ID – LSO2 DELIVERY SYSTEM		500	5/20/98

3.0 PLANS FOR NEXT QUARTER

The following activities are planned for the next quarter:

- C Continue to prepare the engineering design drawings for the modification of the skid-mounted DSRP to meet the site-specific requirements, and the overall site plan/interface points. Develop the control system strategy.

- C Continue the construction activities associated with the modification and renovation of the control room 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 Develop the purchase specifications for the process control system and place the order for the control panel.

- C Attend the annual contractors conference and present the poster session.

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