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DOE Contract No. DE-AC21-93MC30010
RTI Project No. 96U-5666
October 1, 1993 to December 31, 1993

BENCH-SCALE DEMONSTRATION OF HOT-GAS DESULFURIZATION TECHNOLOGY

Quarterly Technical Progress Report

Submitted to

U.S. Department of Energy
Morgantown 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), Morgantown Energy Technology Center (METC), is sponsoring research in advanced methods for controlling contaminants in hot coal gasifier gas (coal gas) streams of integrated gasification combined-cycle (IGCC) power systems. The programs focus on hot-gas particulate removal and desulfurization technologies that match or nearly match the temperatures and pressures of the gasifier, cleanup system, and power generator. The purpose is 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 which can reduce the sulfur in coal 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 fixed-bed, moving-bed, or fluidized-bed reactor configuration, and all three types of reactors are slated for demonstration in the DOE Clean Coal Technology program. 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 . However, a durable

attrition-resistant sorbent in the 100- to 400- μm size range is needed for successful fluidized-bed operation.

The SO_2 in the regeneration offgas needs to be disposed of in an environmentally acceptable manner. Options for disposal include recycle to the gasifier in which an in-bed desulfurization sorbent such as dolomite or limestone is being employed, conversion to sulfuric acid, and conversion to elemental sulfur. All three options are being pursued and/or proposed in the Clean Coal Technology program. Elemental sulfur recovery is the most attractive option because sulfur can be easily transported, stored, or disposed. However, elemental sulfur recovery using conventional methods from an offgas containing low levels of SO_2 (typically 3%) is an expensive proposition. 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/METC sponsorship has been developing zinc titanate sorbent technology since 1986. In addition, RTI has been developing the Direct Sulfur Recovery Process (DSRP) with DOE/METC sponsorship since 1988. Fluidized-bed zinc titanate desulfurization coupled to the DSRP is currently the most advanced and attractive technology for sulfur removal/recovery for IGCC systems, and it has recently been proposed in a Clean Coal Technology project.

RTI has developed a durable fluidized-bed zinc titanate sorbent, ZT-4, which has shown excellent durability and reactivity over 100 cycles of testing at 750 to 780°C. In bench-scale development tests, it consistently reduced the H_2S in simulated coal gas to <20 ppmv and demonstrated attrition resistance comparable to fluid cracking catalysts. The sorbent is manufactured by a commercially scalable granulation technique using commercial equipment available in sizes up to 1,000 L. The raw materials used are relatively

inexpensive, averaging about \$1.00/lb. It is anticipated that the impact on cost of electricity (COE) due to sorbent replacement for attrition will be less than 0.5 mil/kWh. ZT-4 has recently been tested independently by the Institute of Gas Technology (IGT) for Enviropower/Tampella Power, 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:

The above reactions occur in Stage I of the process, and convert up to 96% of the inlet sulfurous gases ($\text{H}_2\text{S} + \text{SO}_2$) to elemental sulfur, which is recovered by cooling the outlet gas to condense out the sulfur. 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: $3\text{H}_2 + \text{SO}_2 \rightarrow \text{H}_2\text{S} + 2\text{H}_2\text{O}$, and $3\text{CO} + \text{SO}_2 \rightarrow \text{COS} + 2\text{CO}_2$) yields an $\text{H}_2\text{S} + \text{COS}$ to 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 via $\text{COS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{CO}_2$ and $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow (3/n)\text{S}_n + 2\text{H}_2\text{O}$. The overall sulfur recovery is projected at 99.5%.

The DSRP technology is also currently at the bench-scale development stage with

a skid-mounted system ready for field testing. Very recently, the process has been extended to fluidized-bed operation in the Stage I reactor. Fluidized-bed operation has proved to be very successful with conversions up to 94% at space velocities ranging from 8,000 to 15,000 scc/cc-h. Overall conversion in the two stages following interstage sulfur and water removal has ranged up to 99%.

A preliminary economic study 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 Direct Sulfur Recovery Process (DSRP) technologies have been shown to be technically and economically attractive. The demonstrations to date, however, have 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 is currently unknown. Furthermore, the zinc titanate work to date has emphasized sorbent durability development rather than database development to permit design of large-scale reactors. Discussions with fluidized-bed experts have indicated that data from a larger reactor than the present are required for scaleup, especially if the material does not have particle sizes similar to fluid catalytic cracking catalysts (typically $\sim 80\text{ }\mu\text{m}$). The fluidized-bed zinc titanate technology uses 100- to 400- μm particles. Finally, the zinc titanate desulfurization unit and DSRP have not been demonstrated in an integrated manner.

1.1 PROJECT OBJECTIVES

The goal of this project is to continue further development of the zinc titanate desulfurization and DSRP technologies by

- Scaling up the zinc titanate reactor system;
- Developing an integrated skid-mounted zinc titanate desulfurization-DSRP reactor system;
- Testing the integrated system over an extended period with real coal-gas from an operating gasifier to quantify the degradative effect, if any, of the trace contaminants present in coal gas;
- Developing an engineering database suitable for system scaleup; and
- Designing, fabricating and commissioning a larger DSRP reactor system capable of operating on a six-fold greater volume of gas than the DSRP reactor used in the bench-scale field test.

1.2 MILESTONE ACCOMPLISHMENTS FOR CURRENT QUARTER

During this reporting period the Construction Permit Application was completed and approved by the Process Safety Committee, and a final revised Application has been submitted to DOE/METC. A draft Test Plan for the field test was formulated. Finally, progress was made in the reactor system fabrication with the submission of purchase orders for nearly all major equipment, and with the final design of the trailer (mobile laboratory).

2.0 TECHNICAL DISCUSSION

2.1 CONSTRUCTION PERMIT APPLICATION PACKAGE

The first half of this reporting period was occupied by the Construction Permit Application, included as part of DOE/METC's Safety Analysis and Review System (SARS). RTI and DOE/METC's Process Safety Committee (PSC) met on November 15, 1993, for a formal review of the application. The PSC voted unanimously to approve the SARS package and issue a Construction Permit after changes and corrections are made and documented to the PSC Secretary. These changes and corrections have been completed and a final revised Construction Permit Application, along with a cover memo documenting the revisions, was submitted to DOE/METC on December 17, 1993.

2.2 DRAFT TEST PLAN

A draft Test Plan, detailing the frequency and types of analyses to be performed as part of the Field Test, was prepared.

2.3 REACTOR SYSTEM FABRICATION

Since approval of the SARS package, RTI has made progress on the reactor system fabrication. Nearly all major equipment has been ordered, including the continuous, on-line H₂S monitor; the high-temperature control and shut-off valves; the toxic-gas sensors and alarms; and the continuous trace-O₂ monitor. The remaining major equipment, the experiment-control panel and the trailer, has been specified. Requisitions will be submitted in early January, 1994.

The trailer layout has been modified since the previous Quarterly Progress Report as a result of the SARS meeting, and because of the heating, ventilation and air-conditioning (HVAC) requirements. The new trailer layout is attached in Appendix A. The major revisions are the addition of the partition in the trailer and the change in placement of the 7 ft. x 7 ft. roll-up door. The partition adds a measure of safety to ensure that the experiment is separately enclosed and ventilated from the control and

instrumentation room, in which RTI operators will remain the great majority of time. Entry to the experiment room will be permitted for periodic maintenance during actual field testing. To satisfy the requirements of separate ventilation systems for the two rooms, and the increased air exchange rate in the experiment room, the trailer HVAC system was modified. One 4-ton HVAC system will be mounted on the trailer's back end to provide ventilation for the control and instrumentation room at four air exchanges per hour. Two 5-ton units will be mounted on the trailer's hitch end to supply cooled, outdoor air to the experiment room at six air exchanges per hour. The mounting of the 5-ton units forced the roll-up door to be moved to the side of the trailer. These changes will not interfere with the conduct of the experiment shakedown or field test.

3.0 PLANS FOR NEXT QUARTER

During the next reporting period we will progress through Tasks 1 and 2 by:

1. Finalizing the submitted Draft Operation and Test Plan detailing the test sequence and number of tests to be conducted at the test sight;
2. Constructing the zinc titanate desulfurization unit;
3. Receiving from vendors all major components of the experiment, including the mobile laboratory, safety and control panel, toxic-gas alarms, trace-oxygen analyzer, continuous H₂S analyzer, and high-temperature control valves;
4. Developing start-up, run-time, and shut-down strategies for the field test;
and
5. Designing and constructing the gas-analysis sampling system.

APPENDIX A

(A) 7

(B) 7

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