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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), 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 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 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:

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

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

The sulfidation/regeneration cycle can be carried out in 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:

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

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

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

The above reactions occur in Stage I of the process, and convert up to 96% of the inlet 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: $3H_2 + SO_2 \rightarrow H_2S + 2H_2O$, and $3CO + SO_2 \rightarrow COS + 2CO_2$) yields an ($H_2S$ + 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 most probably via $COS + H_2O \rightarrow H_2S + CO_2$ and $2H_2S + SO_2 \rightarrow (3/n)S_n + 2H_2O$. 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 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 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 ~80 μm). 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.

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.

2.0 TECHNICAL DISCUSSION

2.1 FIELD TESTING OF ZTFBD/DSRP AT METC

The modifications to the DSRP bench-scale unit in the ZTFBD/DSRP Mobile Laboratory ("RTI trailer") currently located at METC were completed in early July, 1995. The work was done in time for the on-schedule start of the gasifier run on July 17, 1995. As described in the previous Quarterly Technical Progress Report, the equipment in the ZTFBD/DSRP Mobile Lab was modified somewhat from the 1994 configuration. The DSRP unit was modified to have only a single stage of reaction, the coal gas flow control system was improved, and several improvements were made to the off-gas processing. The fluid bed reactor previously used for sorbent testing (the ZTFBD reactor) was loaded with fixed-bed ammonia decomposition catalyst and operated at a higher temperature but lower pressure. Gas sampling and "wet" analytical methods were used to measure trace metals, chlorides, and ammonia content in the DSRP and ZT units.

The primary objective of the test program, exposure of the DSRP catalyst to 160 hours of actual coal gas, was achieved. The percent conversion of sulfur dioxide to elemental sulfur was the same at the beginning of the run as at the end: 99+ % conversion of SO_2 and 98+% conversion of all sulfur compounds to elemental sulfur.

Actual Operating Parameters:

- DSRP unit operated at
  - -- 180 to 260 psig
  - -- 780-630 °C
  - -- 70 SLPM of synthetic regeneration off-gas with 1.4 to 4.9% SO_2
  - -- 7.5 - 16 SLPM of actual coal gas

- -- Space velocity of 5100 scc/cc•hr

- ZTFBD unit operated by NH_3 decomposition test at
  - -- 150 psig
  - -- 780 °C
  - -- 68 SLPM of actual coal gas
  - -- Space velocity of 5000 scc/cc•hr
- DSRP Catalyst exposure to coal gas for 16 hours.
- DSRP took coal gas 91% of the time it was available from METC.
- DSRP operated with simulated regeneration off-gas (liquid SO_2 flowing; producing molten sulfur) for 9 periods during run, totaling 44 hours.
- NH_3 Decomposition Catalyst exposed to coal gas for 102 hours.

Preliminary Evaluation of Results:

- Single-stage DSRP design resulted in high conversion of sulfur compounds to elemental sulfur - 98+% during lined-out operation.
- No effect of trace contaminants in actual coal gas over duration of run: conversion at end was as high as at beginning.
- Measured NH_3 decomposition ranged from 85 to 9% (depending on analytical technique).
- No effect of exposure time on NH_3 decomposition.

The ammonia decomposition catalyst experiments are described in more detail in the Monthly Report for DOE/METC Contract No. DE-AC21-92MC29011.

A paper was presented at the Pittsburgh Coal Conference on September 14, 1995 covering the DSRP slipstream testing in 1994 and 1995. A copy was included with the

previous Quarterly Technical Progress Report. The presentation included some preliminary results of the July test run that were not in the preprint.

2.2 SCALED-UP DSRP REACTOR SYSTEM

The following accomplishments were made in this quarter with respect to the large scale DSRP system.

- The special furnace designs (to satisfy the Enviropower site safety requirements) were approved and fabrication is underway.
- The steel support frame was fabricated and painted in preparation for having the equipment mounted.
- The electrical control panel is essentially complete and is being temporarily stored at the subcontractor's facility.
- The design check and minor redesign of the pressure vessels was completed, and all parts are on hand for the final welding.
- Except for the furnaces and the pressure vessels (noted above), all other long lead equipment items, such as valve, filters, and orifice flow meters, have been received.

3.0 PLANS FOR NEXT QUARTER

1. Continue construction of the scaled-up DSRP system.
2. Continue analyzing the data from the July slipstream test.
3. Prepare for and meet with M.W. Kellogg Technology Company personnel to discuss commercialization of the DSRP technology.

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