DOE/MC/30010 -- 5024
Distribution Category UC-106

Bench-Scale Demonstration of Hot Gas Desulfurization Technology

RECEIVED
NOV 21 1995
OSTI

Quarterly Report
January - March 1995

Santosh K. Gangwal
Jeffrey W. Portzer

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

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

By
Research Triangle Institute
P.O. Box 12194
Research Triangle Park, North Carolina 27709

April 1995

DLC

TABLE OF CONTENTS

Section **Page**

LIST OF TABLES

LIST OF FIGURES

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 last quarterly report described the results of the October slipstream test of the Zinc Titanate Fluid Bed Desulfurization/Direct Sulfur Recovery Process (ZTFBD/DSRP) using the RTI trailer at the METC gasifier. Although the run had to be shortened due to mechanical problems with the METC gasifier, there was sufficient on-stream time to demonstrate highly successful operation of both the ZTFBD and the DSRP with actual coal gas. The fluidizable zinc titanate formation, ZT-4L demonstrated 99+ percent removal of hydrogen sulfide (H_2S) from actual coal gas and up to 20 lbs sulfur per 100 lbs sorbent loading capacity. The DSRP demonstrated up to 99% sulfur recovery during lined out operation in a single reaction stage. Also, the multimetals (Method 29), NH_3, and HCl/HF impinger trains were successfully used during the run to determine the level of trace contaminants. In short term testing (20-25 hours) of each process, separately as well as in an integrated manner, no significant effect of the trace contaminants were detected.

The TGA capacity of reacted ZT-4L from the RTI trailer and from the Enviropower pilot plant did show some reduction, up to 10%. To further evaluate the influence of trace contaminants, several metals were analyzed in the ZT-4L sorbent from the trailer, METC-MGCR, and Enviropower pilot plant. The purity of the DSRP sulfur was also examined using a differential scanning calorimeter (DSC).

2.1.1 Trace Contaminants in ZT-4L

The sulfided ZT-4 sorbent from the RTI trailer was subjected to regeneration using RTI's standard regeneration procedure of 2% O_2 at 650 °C in an atmospheric pressure TGA. Compared to a typical ZT-4L sulfided using simulated coal gas, it appeared that the RTI trailer ZT-4L sulfided using actual coal gas, regenerated slower. Some poisoning of the regeneration active sites due to trace contaminants was suspected. Several trace contaminants were measured on the sulfided ZT-4L and the results are compared in Table 1.

Table 1. Trace Contaminants in ZT-4L Sulfided with Actual Gas (µg/g)

	ZT-4L Fresh	ZT-4L Sulfided Enviropower	ZT-4L Sulfided (600 °C) RTI Trailer, 10/26/94	ZT4-94 MGC-10 (Sulfided METC-MGCR)
As	0.7	5.1	8.4	N/A
Ba	12.7	N/A	19.8	35.4
Be	1.4	N/A	2.0	2.7
Cd	10.6	N/A	11.6	10.2
Cr	<10	N/A	<10.0	<10.0
Pb	<30	N/A	49.6	45.2
Mn	4.2	N/A	11.2	9.4
V	192	N/A	192	171
Se	<0.57	2.9	0.72	N/A
Cl	N/A	N/A	38	N/A

The increase in concentration of As, Pb, or other metals in the sulfided materials is noteworthy and could have contributed to the slower regenerability. However, controlled tests on ZT-4L with H_2S and metal vapor addition are needed to ascertain this. The estimated gaseous concentrations based on the measurements is about 100 µg/m^3 for As and 10-40 µg/m^3 for Se. No Hg was detected in the gas or sorbents.

2.1.2 Sulfur Purity

The sulfur purity of the DSRP sulfur was examined using a differential scanning calorimeter (DSC). DSC profile of pure sulfur obtained from the drug store is compared to those for sulfur obtained from the DSRP condensers in Figure 1. There are three phase

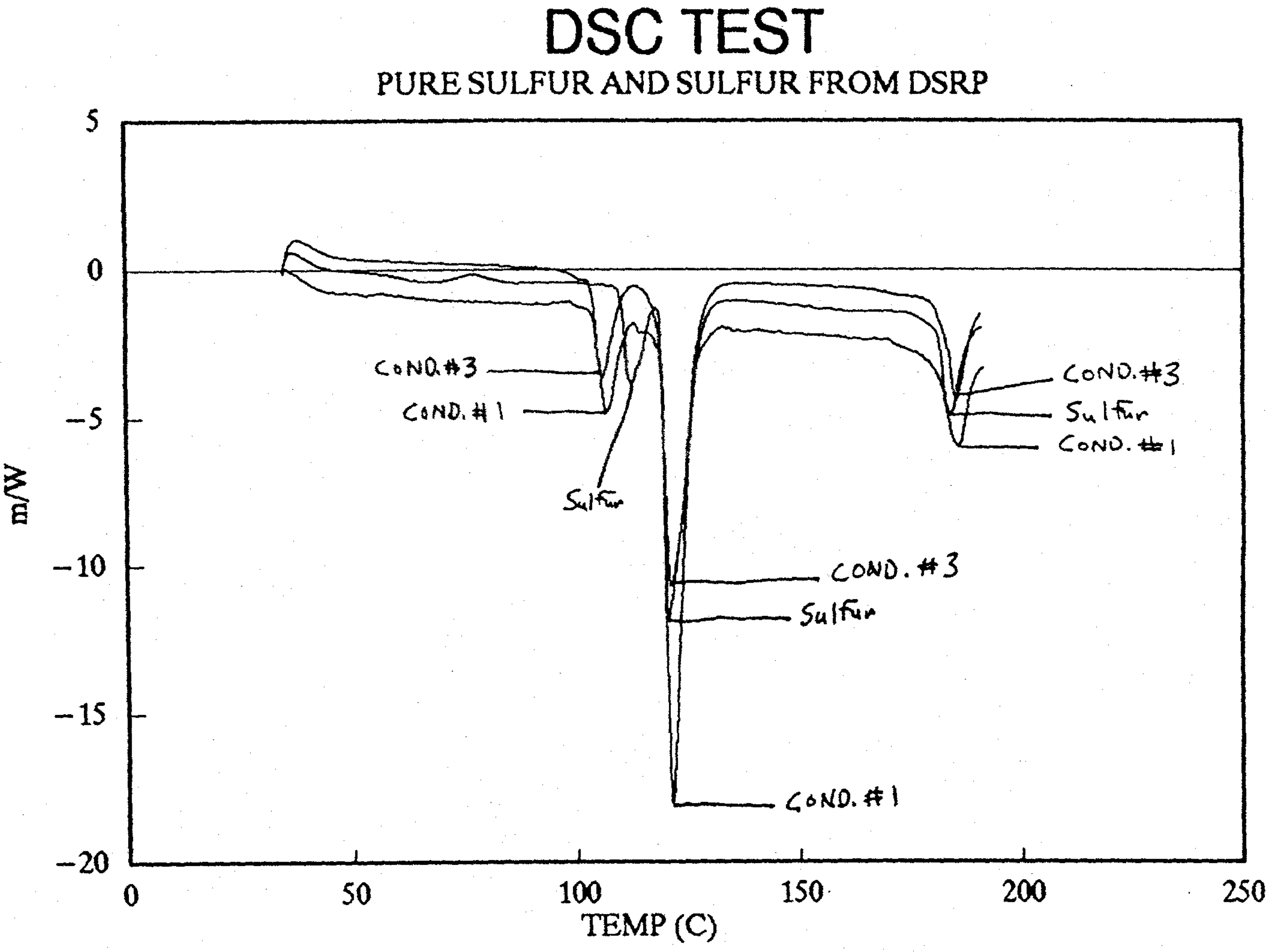

Figure 1. Comparison of DSC Profiles of DSRP Sulfur and Pure Sulfur

transitions which are typical of sulfur. The middle transition due to melting occurs at the same temperature for all samples. There is a slight shift in the other two transitions for the DSRP sulfur versus the drugstore sulfur. This could be due to small amounts of undissolved metal impurities in the DSRP sulfur from corrosion of the stainless steel vessel or due to metal vapor in coal gas (such as AsH_3 or H_2Se) dissolving in the sulfur. The more likely possibility can be ascertained by melting a relatively large sample of the sulfur and examining the melted sulfur for undissolved impurities.

2.1.3 Future Slip-Stream Test

Based on the interrupted October field test, a decision was made to conduct a slipstream test of 160 hours. This test is currently scheduled to begin on July 17, 1995 and will include:

(i) A 160-hour test of single-stage DSRP with actual coal gas and simulated regeneration off gas.

(ii) A 100-hour test of NH_3 decomposition at 850 °C and 150 psia.

The ZTFBD system will be modified for NH_3 decomposition testing. The 2-stage DSRP system will be modified to a single stage with improved control of stoichiometric ratio of reducing gas to SO_2 entering the reactor. The requirements for the modification were described in the previous quarterly report. All long-lead items requiring up to 12-weeks delivery have been ordered. Coordination meetings for the test and NH_3 analysis have been held at METC. Also a paper was presented at the Houston AIChE meeting.

2.2 SCALED-UP DSRP REACTOR SYSTEM

Two detailed meetings have been held, one on-site in Finland and one at Tampella Power offices in Atlanta with METC and Enviropower. Significant accomplishments have been made during the quarter towards the goal of supplying the reactor system to Enviropower. These are highlighted below.

- The PFD and P&ID have been completed and frozen. Material balances have been completed.
- Preliminary pressure vessel drawings have been completed.
- Control panels have undergone preliminary design and a potential vendor has been identified to supply the panels.
- Operating procedures have been developed to enable Enviropower to successfully conduct a hazop of the process.
- The responsibilities of RTI and Enviropower have been clearly defined.
- A preliminary schedule has been developed for supply of the DSRP system. Delays have been experienced due to the highly stringent and detailed pressure vessel and safety requirements at Enviropower.

3.0 PLANS FOR NEXT QUARTER

1. Order all long lead items.
2. Complete design and secure Finnish authorities approval of pressure vessels.
3. Select vendors for the scaled-up DSRP system and begin skid construction.
4. METC contractor's meeting paper/presentation.
5. All required preparations for the field test at METC.

SKG/jks-12.25666J-M.QTR

Figure 1. Comparison of DSC Profiles of DSRP Sulfur and Pure Sulfur