

Bench-Scale Demonstration of Hot-Gas Desulfurization Technology

Quarterly Report

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

RECEIVED

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

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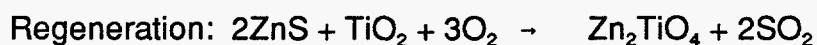
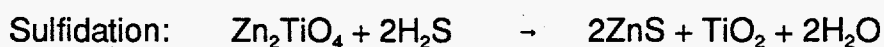
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1.0 INTRODUCTION AND SUMMARY

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:



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.

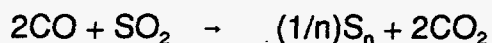
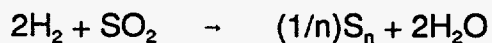
The SO_2 in the regeneration offgas needs to be disposed of in an environmentally acceptable manner. Options for disposal include recycle to the gasifier in which an in-bed desulfurization sorbent such as dolomite or limestone is being employed, conversion to sulfuric acid, and conversion to elemental 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 SO₂ 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 SO₂) 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 SO₂ 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 H₂S and COS produced (by the reactions: 3H₂ + SO₂ → H₂S + 2H₂O, and 3CO + SO₂ → COS + 2CO₂) yields an (H₂S + COS) to SO₂ 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 + H₂O → H₂S + CO₂ and 2H₂S + SO₂ → (3/n)S + 2H₂O. 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

No work was carried out on this task during this quarter.

2.2 SCALED-UP DSRP REACTOR SYSTEM

Construction on the skid-mounted, 6-fold larger ("6X") DSRP test unit continued. The furnaces were mounted on custom-fabricated brackets and frames. The pressure vessels were welded up and mounted in the furnaces, again with custom-fabricated brackets, as required. The pneumatically operated shutoff and control valves were mounted, as were the flow meter orifice runs. The field instrumentation (pressure transducers, pressure gages) is being installed. Some process tubing runs have been put in place. Fabrication is occurring more slowly than originally scheduled, but is still expected to be complete by the end of the Fiscal Year.

2.3 EXPOSURE TEST

As of the beginning of this quarter, the catalyst removed from the reactor in the RTI trailer was at the GE pilot gasifier in Schenectady, N.Y., where it was being exposed to coal gas at high temperature and pressure (downstream of the moving bed desulfurizer). The exposed catalyst was received back at RTI and it was tested in the bench-scale DSRP unit to determine if an acceptable activity level had been maintained.

EXPERIMENTAL RESULTS

Table 1 summarizes the results from operating the DSRP bench unit with the "canister" catalyst that came back from the exposure test at GE. The single number that is most interesting is the conversion to elemental sulfur, expressed as percent of inlet sulfur dioxide. While only 86% conversion was obtained initially, by the end of the series

SUMMARY OF "CANISTER TEST" RESULTS

Run No.	Bed Temp. (°C)	Press. (atm. abs.)	Inlet Space Velocity (hr ⁻¹)	Inlet SO ₂ Conc'n (vol %)	Outlet Gas Composition (Dry)			Conv. to Sulfur (%)
					H ₂ S (ppmv)	COS (ppmv)	SO ₂ (ppmv)	
2	575	19.7	4858	2.15	1995	361	717	85.69
3A	618	19.7	4907	2.46	1528	276	731	89.76
3B	610	19.7	8187	2.24	1130	1008	1484	83.72
4A	630	19.7	5114	3.84	1377	491	1627	90.84
4B	632	19.7	3963	3.71	1987	457	1101	90.40
4C	628	19.7	3905	3.09	2272	390	1033	87.86
4D	628	19.7	3914	3.17	798	385	698	93.95
5A	638	19.7	5137	3.57	538	1111	1104	92.09
5B	633	19.7	3983	3.49	810	587	504	94.45
6A	642	19.7	2789	5.42	896	680	1021	94.88
6B	630	19.7	2692	5.39	656	632	864	95.90

the conversion was up to 96%. This value compares to 98% that was achieved using the same catalyst during the July, 1995, METC campaign.

The idea of the canister exposure test was that the DSRP catalyst would have 200 hours of additional exposure to actual coal gas (beyond that which was achieved during the METC 160-hour campaign) so that the effect, if any, of the trace contaminants could be determined. In normal DSRP operation, the catalyst is exposed to a mixture of gases containing about 15% coal gas. Assuming that concentration and exposure time are directly related, 200 hours of pure coal gas would be equivalent to 1330 hours of diluted (15%) coal gas.

It was planned that the coal gas would be relatively particulate-free, and to that end the canister was installed downstream of the desulfurizer at the GE pilot plant. Nevertheless, when the catalyst was received back from GE it was covered with soot and tar. It is possible that the tar has had an effect on conversion, as noted below.

The variables studied in the bench unit runs were as follows:

- Catalyst bed temperature (over a narrow range around 630 °C previously determined to be optimum)
- Space velocity, expressed as standard cc per hour of gas per cc of catalyst (hence, units of hr^{-1}) at the bed inlet, over the range of 2700 to 8100. This compares to the July trailer test where the space velocity was 5100 hr^{-1} .
- Inlet SO_2 concentration, expressed as volume percent, over the range of 2.1 to 5.4%.

Examining the data, it is difficult to determine the effect of any of these variables, because of the overwhelming effect of an uncontrolled variable: operating time.

The attached graph plots the conversion to elemental sulfur from each run, in chronological order. Run 1 was a shakedown run conducted with an unoptimized fresh catalyst, whereas Runs 2 through 6 were carried out with the "canister" catalyst. One can see that, independent of the changes of the controlled variables, the conversion to elemental sulfur improves steadily with increasing operating time. This effect was especially noted on day 4 where the conditions are quite similar between runs 4B and 4D, yet 4D had more than 3 percent greater conversion to sulfur. This improved operation was noted with no change in operating parameters.

The hypothesis is that the soot and tar buildup on the catalyst pellets initially inhibited the sulfur reduction reactions. With additional exposure time to the sulfur dioxide reaction mixture, however, there was a gradual removal, and the catalyst regained some lost activity. The highest activity (96% conversion) was somewhat lower than the previous level achieved in the trailer runs (98%). It is possible that with more run time the activity would improve further and reach its original value.

CONCLUSIONS

There was an apparent loss of catalyst activity after 200 hours of exposure to coal gas in the GE pilot plant. The pure coal gas exposure of 200 hours is equivalent to exposure at DSRP conditions of around 1330 hours. Thus, total exposure of the catalyst including the 160-hour test at METC is approximately 1500 hours.

The loss of activity could be due to the tar and soot covering the catalyst as received from GE. However, following an induction period, a significant portion of the

activity was restored. The data taken after 5 DSRP runs of approximately 4 hours each with the canister catalyst indicate that the induction period was not complete even after nearly 22 hours of tests in the bench-scale unit. The activity is likely to improve to its original value of 98% sulfur recovery with further run time. A surface cleaning phenomenon is apparently occurring leading to removal of impurities and improved activity. This run demonstrates that the DSRP catalyst is quite rugged in the presence of tar laden coal gas even after 1330 equivalent hours of exposure.

3.0 PLANS FOR NEXT QUARTER

1. Complete mechanical construction of the 6-fold larger DSRP system.
2. Prepare a presentation and write and submit the paper for the Contractors's Review Meeting.

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