

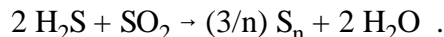
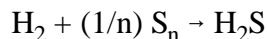
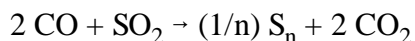
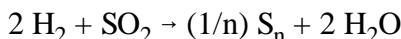
Durability Testing of the Direct Sulfur Recovery Process

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Introduction

Designs for advanced integrated gasification combined cycle (IGCC) power systems call for desulfurization of coal gasifier gas at high-temperature, high-pressure (HTHP) conditions using highly efficient, regenerable metal oxides such as zinc titanate. Regeneration of the sulfided sorbent using an oxygen-containing gas stream results in a sulfur dioxide (SO₂)-containing off-gas at HTHP conditions. The patented Direct Sulfur Recovery Process (DSRP) developed by the Research Triangle Institute (RTI) with Morgantown Energy Technology Center (METC) support is an attractive option for treatment of this regeneration off-gas. Using a slipstream of coal gas as a reducing agent, it efficiently converts the SO₂ to elemental sulfur, an essential industrial commodity that is easily stored and transported.

In the DSRP (Dorchak et al., 1991), the SO₂ tail gas is reacted with a slipstream of coal gas over a fixed bed of a selective catalyst to directly produce elemental sulfur at the HTHP conditions of the tail gas and coal gas. Overall reactions involved are shown below:



The DSRP was initially developed as a two-stage process using simulated coal gas in the laboratory. The original process concept employed two catalytic reactors in series, each followed by a sulfur condenser. Hot regeneration tail gas was mixed with a hot coal gas slipstream (to act as the reducing gas) and fed to the first DSRP reactor. Approximately 95 percent of the combined sulfur in the inlet stream to the first reactor was converted to elemental sulfur. The outlet gas of the first reactor was then cooled, condensing out the sulfur. The cooled gas stream was reheated and sent to the second DSRP reactor where 80 to 90 percent of the remaining

sulfur compounds were converted to elemental sulfur via the modified Claus reaction at high pressure. The total efficiency of the two reactors for the conversion of sulfur compounds to elemental sulfur was projected to be 99 percent.

However, based on the initial results from the slipstream tests with actual coal gas (Portzer and Gangwal, 1995) and additional data presented here, the second stage does not appear necessary. A sulfur recovery of 98 percent can be consistently achieved in a single stage with careful control of the stoichiometric ratio of the gas input. The single-stage process, as it would be proposed to be integrated with a metal oxide sorbent regenerator, is shown in Figure 1. There is a potential for "zero" sulfur emissions if the DSRP tail gas is recycled.

Objectives

Prior to the current project, the development of the DSRP was done in a laboratory setting, using synthetic gas mixtures to simulate the regeneration off-gas and coal gas feeds. The objective of the current work is to further the development of zinc titanate fluidized-bed desulfurization (ZTFBD), and the DSRP for hot-gas cleanup by testing with actual coal gas. There are three main goals of this project:

- Develop and test an integrated, skid-mounted, bench-scale ZTFBD/DSRP reactor system with a slipstream of actual coal gas;
- Test the DSRP over an extended period with a slipstream of actual coal gas to quantify the degradation in performance, if any, caused by the trace contaminants present in coal gas (including heavy metals, chlorides, fluorides, and ammonia); and
- Design and fabricate a six-fold larger-scale DSRP reactor system for future slipstream testing.

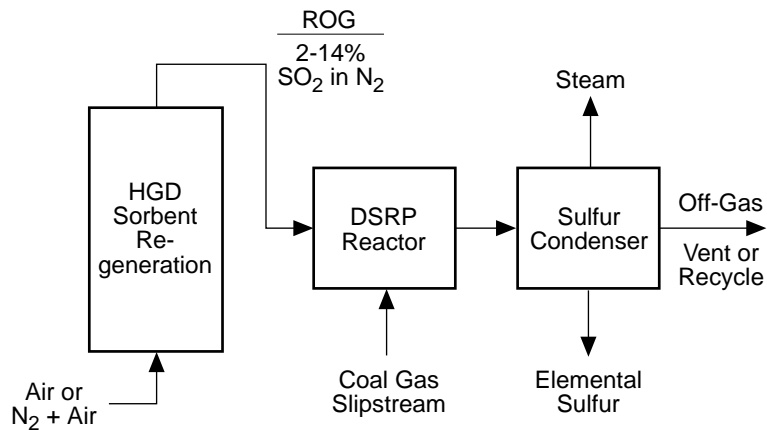


Figure 1. Sorbent Regeneration - DSRP Integration

Accomplishment of the first objective, testing of the DSRP with actual coal gas and integrated with hot-gas desulfurization, was described previously (Portzer and Gangwal, 1994, 1995). This paper describes the accomplishment of the second objective — an extended test period (durability testing) of the DSRP. One of the main reasons for testing the DSRP for an extended period with actual coal gas from an operating gasifier was to quantify the degradative effect, if any, of the trace contaminants present in coal gas.

Approach

Since coal gas is not available at RTI's laboratories in Research Triangle Park, North Carolina, other approaches were used to accomplish the desired DSRP testing. The first strategy — slipstream testing — moved the existing bench-scale DSRP apparatus to the coal gas source (METC 10-in. gasifier) using a mobile laboratory. At METC, the process equipment was operated to produce elemental sulfur using a small slipstream of the total gasifier output.

The second strategy — canister testing — moved only the catalyst to the source of the coal gas (General Electric [GE] pilot-plant gasifier) and exposed it for an extended period. The exposure was followed by testing in a second bench-scale DSRP unit at RTI that used simulated coal gas to verify the catalyst's efficacy.

Project Description

Figure 2 shows the equipment, consisting of RTI's ZTFBD/DSRP mobile laboratory (trailer), used for the slipstream testing at METC. It was described previously (Portzer and Gangwal, 1994). Following the 1994 slipstream test, a number of modifications were made to the bench-scale DSRP unit contained in the trailer. The second stage reactor and sulfur condenser were removed to convert the unit into a single-stage process. An improved-design sulfur separator pot was added to the steam-heated sulfur condenser. A temperature- and pressure-corrected orifice flow meter was added to the coal gas line feeding the DSRP. A PC-based flow controller was installed that compared the coal gas composition (continuous analyzer data from METC data network) with the regeneration off-gas SO_2 content and adjusted the mass flow of the coal gas in order to maintain the desired 2:1 stoichiometric ratio of the reducing components (H_2 and CO).

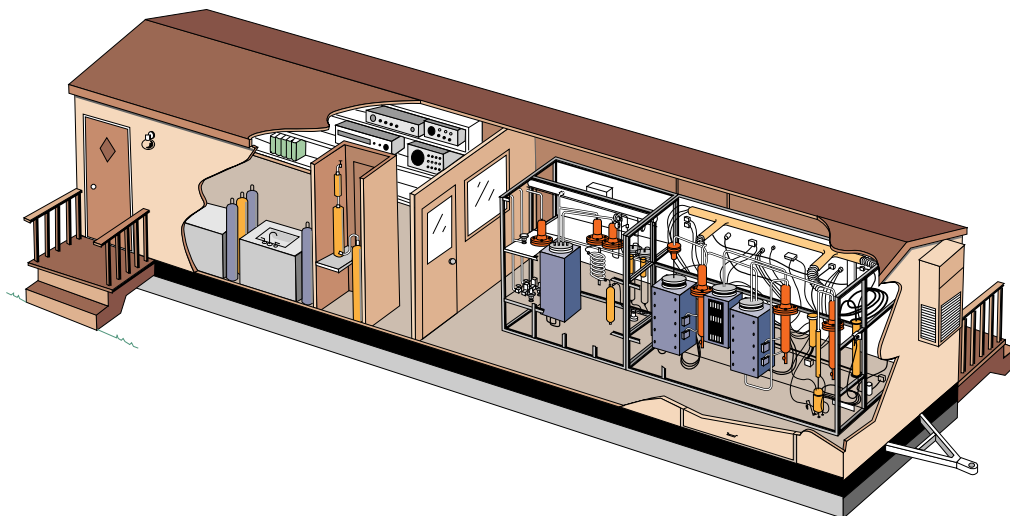


Figure 2. DSRP Mobile Laboratory.

The 1995 long duration slipstream test used simulated regeneration off-gas (ROG) to react with the actual coal gas. The ROG was prepared by evaporating liquid SO₂ from a pressurized transfer cylinder into a heated nitrogen stream. The cylinder was mounted on an electronic balance to monitor weight change. Flow was controlled by a rotameter with a manual needle valve. The mixed gas composition was analyzed continuously for input to the coal gas stoichiometric flow control.

The METC coal gasifier is a fluidized-bed gasifier providing approximately 4,750 std ft³/h of low-Btu coal gas from a nominal charge rate of 80 lb/h of coal. A heated slipstream, approximately 170 std ft³/h (80 std L/min), was directed to the RTI trailer. Of this, approximately 32 std ft³/h (15 std L/min) were used to operate the DSRP.

The DSRP was operated in conjunction with a 2-week gasifier campaign at METC in July 1995. During this period coal gas was flowing through the DSRP catalyst bed for 160 h. The simulated regeneration off-gas was fed to the catalyst bed for a total of 44 h, divided into nine separate periods of multihour operation. The duration of the runs with SO₂ flowing were limited by problems associated with solid sulfur plugging of the downstream vent lines. The METC coal gas was sampled several times for trace contaminants (volatile heavy metals) using a modified EPA “Method 29” protocol.

Several months following completion of the 160-h slipstream run, the DSRP catalyst was removed from the reactor, placed in a canister, and installed in a coal gas line at the GE pilot gasifier in Schenectady, New York. The canister was a simple fabrication of perforated stainless steel with a capacity of approximately 850 mL. Thus, the entire charge of 1 L of catalyst could not be subjected to this additional exposure. The canister was placed in the piping prior to the start of a 200-h gasifier campaign and was removed following completion of the campaign. No trace contaminant sampling of the GE gasifier gas was performed. Table 1 summarizes the exposure conditions. The canister and catalyst were shipped in tightly closed bottles that had been purged with dry nitrogen prior to filling; however, the bottles were not hermetically sealed.

Table 1. GE Exposure Test Conditions

-
- 20 atm (294 psia)
 - 482 to 538 °C (900 to 1,000 °F)
 - Illinois #6 Coal Gas
 - 200 h
 - Downstream of absorber
-

The idea of the canister exposure test was that the DSRP catalyst would have 200 h of additional exposure to actual coal gas (beyond what was achieved during the METC 160-h 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 percent coal gas. Assuming that concentration and exposure time are directly related, 200 h of pure coal gas would be equivalent to 1,330 h of diluted (15%) coal gas.

The most effective way to demonstrate the continued activity of the DSRP catalyst is to install it in an HTHP reactor and actually conduct the SO₂ reduction reaction using a reducing gas mixture. Thus, to determine if additional coal gas exposure of the catalyst had any deleterious effects, the doubly exposed catalyst was tested in a bench-scale DSRP unit set up in a laboratory

in RTI's main campus in Research Triangle Park. The reactor design was essentially identical to that of the trailer-mounted unit; the sulfur condenser design was identical. The coal gas was simulated by using a purchased custom gas mixture, and the regeneration off-gas was generated similarly to the method used in the trailer: vaporization of liquid SO₂ under pressure. The continuous H₂S/SO₂ tail gas analyzer used in the Mobile Laboratory was moved to RTI for the duration of the bench-scale testing.

Results

Table 2. Reactor Test Conditions

Table 2 summarizes the operating conditions of the DSRP reactor in the Mobile Laboratory (1995 slipstream test) and compares them to the conditions used for the followup testing of the exposed catalyst (1996 testing) in the RTI laboratory. The conditions are very similar, with the exception that less catalyst was available for the lab tests (due to a limitation of canister volume, as described). However, the gas flow rate was reduced to maintain the same space velocity.

	1995 Field Test	1996 Lab Test
Temperature (°C)	590-630	575-640
Pressure (psig)	210-265	275
Space velocity (std cm ³ /cm ³ -h)	5,100	2,700-8,200
Reactor diameter (in.)	3.0	3.0
Catalyst volume (cm ³)	1,000	600
Inlet SO ₂ (%)	2.4-4.9%	2.1-5.4%

Table 3 presents some of the results of the 1995 slipstream testing. Single-stage conversion to elemental sulfur of 98% was achieved at the beginning of the run and at the end. Thus, there was no detrimental effect of 160 h of exposure of the catalyst to coal gas. These calculations are based on measurements of the inlet and outlet gas compositions by continuous analyzers and by gas chromatograph (GC), and they include the H₂S in the coal gas feed. The “percent conversion to elemental sulfur” is the difference of the molar flow rates of sulfur compounds in the reactor inlet and outlet, divided by the molar flow rate of the inlet sulfur compounds. The SO₂ conversion to elemental sulfur and other sulfur compounds is essentially 100 percent (as evidenced by low concentrations of SO₂ in the DSRP tail gas). Some of the elemental sulfur produced is apparently further reduced, however, as Table 3 shows. The “percent conversion [of SO₂] to H₂S and COS” is the difference in the molar flow rates of the outlet and inlet reduced sulfur compounds, divided by the inlet SO₂ molar flow. Thus, even though total conversion of the SO₂ in the ROG was achieved, the ultimate value of total overall conversion to elemental sulfur was limited by the presence of reduced sulfur compounds (in the outlet) to less than 100 percent.

Table 3. One Stage DSRP Results During Lined-out Operation (1995)

Run Time (min)	SO₂ Conversion (%)	SO₂ Conversion to H₂S and COS	SO₂ Conversion to Sulfur (%)
Run No. 1 (0-4 h exposure time)			
200	100.0	5.8	93.2
220	100.0	1.1	98.0
240	9.6	0.2	98.6
260	96.4	-2.1	96.4
Run No. 9 (155 h exposure time)			
91	100.0	0.7	97.8
117	100.0	1.0	97.7
134	100.0	0.8	98.1
151	99.7	0.8	97.9

Following 200 h additional coal gas exposure in early 1996, the catalyst charge was tested in the RTI laboratory DSRP bench unit using simulated ROG and simulated coal gas. Table 2 summarizes the operating conditions; Table 4 summarizes the results of the best runs. Several test runs were made, with a total operating time (with SO₂ feed) of 22 h. Known optimum conditions, as well as less-than-optimum conditions were used. Only 86 percent conversion was obtained initially; by the end of the series the conversion was up to 96 percent, with the runs that Table 4 reports. This value compares to the 98 percent that was achieved using the same catalyst during the July 1995 METC campaign. Examining the data, it was difficult to determine the effect of any of the process variables because of the overwhelming effect of an uncontrolled variable: operating time.

Table 4. Performance of Exposed Catalyst (1995 + 1996 exposure)

Run No.	Space velocity	SO₂ (%)	Conversion to elemental sulfur (%)
5B	4,000	3.5	94.5
6A	2,800	5.4	94.9
6B	2,700	5.4	95.9

Figure 3 shows that, as the trials proceeded, the conversion gradually improved. This suggests that some sort of “induction period,” not previously observed with the DSRP, was involved with the doubly exposed DSRP catalyst. 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 (a possible experimental artifact that is also related to the specifics of the fixed-bed gasifier used at GE). It is possible that the tar has had an effect on conversion, as noted below.

Table 5 reports the results of carbon analysis of the DSRP catalyst. Normally, carbon is not a factor with the DSRP process, as the fresh catalyst and that used at METC are both essentially carbon free. However, the catalyst exposed at METC had over 30 wt% carbon clinging to the pellets, and even after testing in the reactor in the RTI lab it still had nearly 6 percent carbon. The carbon presence is believed to be the reason for the conversion shortfall experienced by the doubly exposed catalyst. It is interesting to note that even with 5.7 percent carbon contamination, the DSRP performance is nearly as good as that obtained with fresh catalyst.

A major goal of the long duration testing of the DSRP is to determine if the presence of trace contaminants (principally volatile heavy metals) affects performance over time. Table 6 reports the results of sampling of the METC coal gas for trace metals. It is apparent that the heavy metals of concern — As, Hg, Pb and Se — are present, although at low levels, in the coal gas

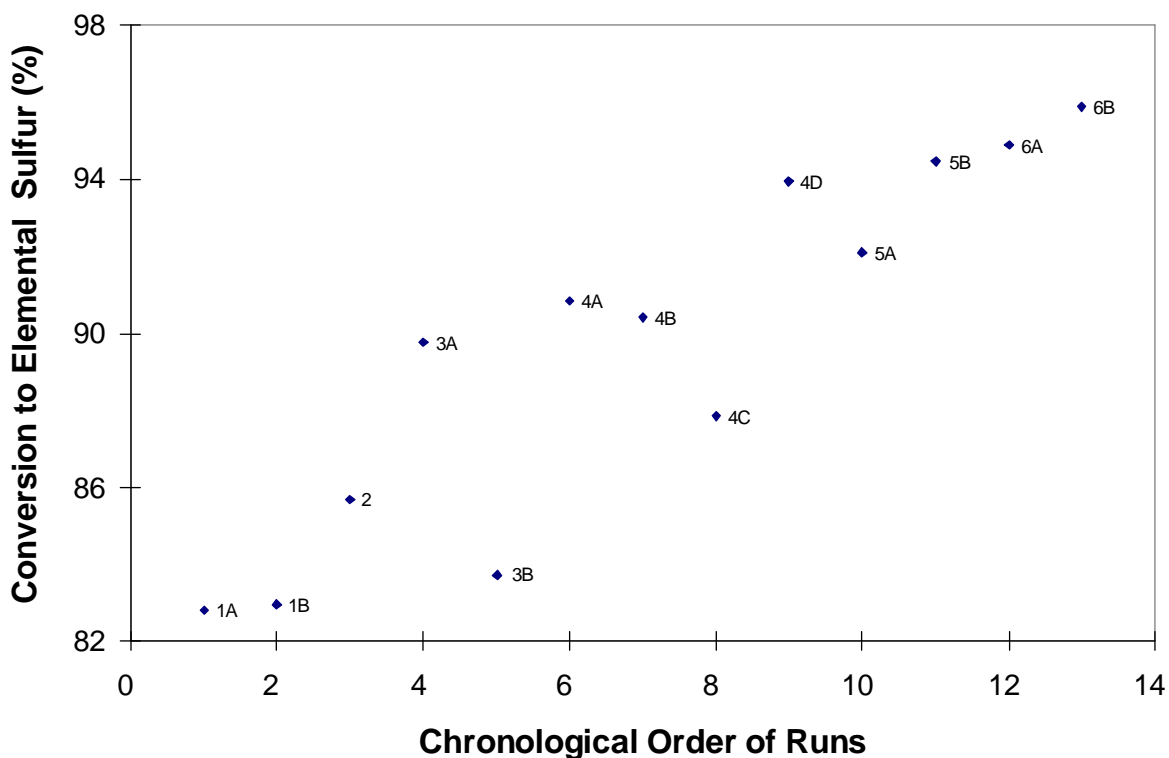


Figure 3. Conversion Improvement with Operating Time.

Table 5. Results of Carbon Testing

	Percent
Fresh DSRP catalyst	0.036
After 160+ h at METC	0.037
After 200 additional h at GE	31.32
After testing in RTI bench unit	5.70

Table 6. Trace Metal Content of METC Coal Gas (1995 Test)

Trace Metal	Concentration ($\mu\text{g/L}$)
As	0.0015
Hg	0.0075
Pb	0.0075
Se	0.0015

being fed to the DSRP. The fact that performance of the process did not seem to deteriorate with 160 h of exposure at METC suggests that trace metals are not a factor. However, some additional analysis was undertaken to determine if the DSRP catalysts act to sequester trace contaminants.

Table 7 reports the results of the analysis of the DSRP catalyst; this analysis is ongoing. No sequestering of mercury was detected. The arsenic and selenium analyses were confounded by the background signals from the matrix of the catalyst components — and require additional analytical work. Lead was not found after exposure at METC, but an appreciable amount was found after the GE exposure.

Applications/Benefits

The results of the development work conducted on this project show that, after a significant exposure time to actual coal gas, the DSRP catalyst continues to function in a highly efficient manner to convert SO_2 in a simulated regeneration off-gas to elemental sulfur. This

Table 7. Results of Trace Metal Testing

	Concentration on Catalyst ($\mu\text{g/g}$)			
	Fresh	After 160 h @ METC	After 200 h additional @ GE	After testing in DSRP
As	Additional analysis required			
Hg	<0.005	<0.005	<0.005	<0.005
Pb	2.5	3.0	167	144
Se	Additional testing required			

demonstration of a rugged, single-stage catalytic process resulted in additional on-line experience and the assembling of more process engineering data. The development of the DSRP continues to look favorable as a feasible commercial process for the production of elemental sulfur from hot gas desulfurizer regeneration off-gas.

Future Activities

The future work on this project will consist of completion of the third objective, design and fabrication of a six-fold larger DSRP test unit, to make it available for slipstream testing on a larger pilot gasifier or commercialized desulfurizer. Discussions about such a future test are under way.

Acknowledgments

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