

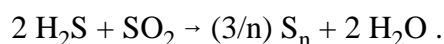
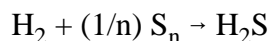
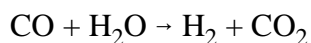
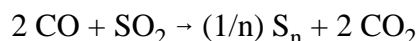
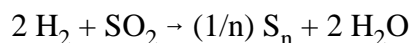
# Bench-Scale Demonstration of Hot-Gas Desulfurization Technology

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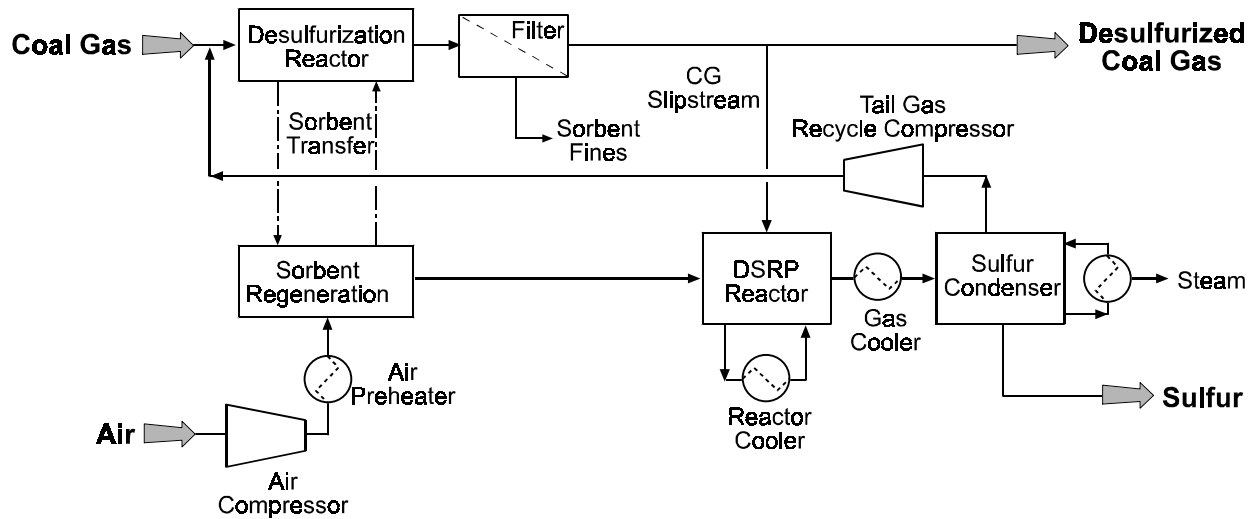
## Introduction

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 (SO<sub>2</sub>)-containing off-gas at HTHP conditions. Over the past 10 years, the U.S. Department of Energy/Federal Energy Technology Center (DOE/FETC) has sponsored a number of approaches for ultimate disposal of this off-gas. The patented Direct Sulfur Recovery Process (DSRP) being developed by Research Triangle Institute (RTI) is a highly attractive option for recovery of sulfur from this regeneration off-gas. Using a slipstream of coal gas as a reducing agent, it efficiently converts the SO<sub>2</sub> to elemental sulfur, an essential industrial commodity that is easily stored and transported.

In the DSRP (Dorchak et al., 1991), the SO<sub>2</sub> 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:



Slipstream tests with actual coal gas (Portzer and Gangwal, 1995; Portzer et al., 1996) demonstrated that, with careful control of the stoichiometric ratio of the gas input, sulfur recovery of 96 to 98 percent can be consistently achieved in a single DSRP stage. The single-stage process, integrated with a metal oxide sorbent regenerator, is shown in Figure 1. Since the tail gas from the DSRP can be recycled as shown in this figure, there are no sulfur emissions from the DSRP.



**Figure 1. Hot-gas desulfurization with DSRP.**

## Objectives

Prior to the current project, development of the DSRP was only done in a laboratory setting, using synthetic gas mixtures to simulate the regeneration off-gas and the coal gas feed. The aim 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. The objectives of this project are to:

- Develop and test an integrated, skid-mounted, bench-scale ZTFBD/DSRP reactor system with a slipstream of actual coal gas
- Test the bench-scale 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)
- Expose the DSRP catalyst to actual coal gas for extended periods and then test its activity in a laboratory reactor to quantify the degradation in performance, if any, caused by static exposure to the trace contaminants in coal gas
- Design and fabricate a six-fold larger-scale DSRP reactor system for future slipstream testing
- Further develop the fluidized-bed DSRP to handle high concentrations (up to 14 percent) of SO<sub>2</sub> that are likely to be encountered when pure air is used for regeneration of desulfurization sorbents

- Conduct extended field testing of the 6X DSRP reactor with actual coal gas and high concentrations of SO<sub>2</sub>.

The accomplishment of the first four objectives—testing the DSRP with actual coal gas, integration with hot-gas desulfurization, catalyst exposure testing, and fabrication of the 6X DSRP—was described previously (Portzer and Gangwal, 1994, 1995; Portzer et al., 1996; Portzer and Gangwal, 1997).

This paper reports the results of further development of the fluidized-bed DSRP, describes the current activities, and presents plans to accomplish the remaining objective—the extended field testing of the 6X DSRP unit.

### **Fluidized-Bed DSRP Background**

The early development work and scaleup of the DSRP focused on treating a regeneration off-gas stream that would have a relatively low concentration of sulfur dioxide, say 1 to 3 vol%. With the desulfurization sorbents and regenerator reactor designs being considered at the time, dilute air regeneration was required and resulted in low SO<sub>2</sub> concentrations. Subsequently, improvements in the sorbents, and the introduction of other regenerator reactor designs (notably the Kellogg transport reactor as implemented in the Sierra Pacific Power Company's Piñon Pine plant) have suggested that "neat air" is a preferred commercial embodiment for hot gas desulfurization. Thus, there is a need for the DSRP to be able to treat high-SO<sub>2</sub> concentration regeneration off-gas.

The DSRP reactions are highly exothermic, and for optimum conversion need to be conducted at a fairly high temperature (550 to 600 °C). Although a fixed-bed reactor design is possible, alternative designs, such as a bubbling fluidized-bed or transport reactor, are likely to be more feasible for dealing with the high exothermicity of the high SO<sub>2</sub> concentration feed streams. The idea of using a fluidized-bed reactor for DSRP had been explored in previous work, but because the catalyst that was used then was simply a crushed material, and had not been optimized for fluidized-bed operation, the single-stage conversion (94 percent) was relatively low and the catalyst was prone to attrition. These preliminary findings suggested the need for the additional catalyst development and testing that was conducted in this task.

### **Task Objectives**

The specific objectives of this task were defined as follows:

- Obtaining and characterizing a suitable fluidizable catalyst for fluid-bed DSRP
- Preparing the catalyst for use in the fluidized-bed reactor
- Conducting shake-down runs with typical SO<sub>2</sub> concentrations to establish operating conditions.

- Conducting an experiment design set looking at the effects of SO<sub>2</sub> concentration, fluidization velocity (space time), oxygen contamination of the regeneration off-gas, reactor pressure, and catalyst bed temperature on SO<sub>2</sub> conversion efficiency.

### Approach /Project Description

The approach taken was to use a multipurpose bench-scale test apparatus at the RTI laboratory with a nominal 4-in. diameter HTHP reactor. The regeneration off-gas feed was simulated by evaporating liquid SO<sub>2</sub> into a preheated nitrogen stream. The reducing coal gas was simulated using a synthetic gas mixture. A 3-in. diameter stainless steel cage with an alumina frit was fitted inside the reactor to hold the fluidized bed of catalyst.

Two different alumina-based fluidized-bed catalysts—a proprietary catalyst, and a nonalumina catalyst—were tested. Because the exact formulations contain proprietary information, the candidate catalysts are identified by letters in this report. Table 1 shows the key physical characteristics of the fresh materials.

In Table 1, Catalysts A and B, with moderate attrition resistance, were selected as candidates for a bubbling fluidized-bed reactor. Catalyst C was identified as a candidate for a transport or riser-type fluidized-bed reactor. Catalyst D was selected as an intentional choice of a poor DSRP catalyst to be a “blank” run.

The tests were conducted with a synthetic gas mixture simulating the composition of a coal gas from an air-blown gasifier. The coal gas produced by the 10-in. pilot gasifier at FETC-Morgantown was used as the basis, as shown in Table 2. It should be noted that a simplification in the experiment protocol introduces a complication in data analysis and interpretation. Because the coal gas feed to the DSRP reactor and the simulated regeneration off-gas (ROG) contain nitrogen, a single nitrogen feed line was used for both, and the synthetic coal gas mixture that was actually fed to the reactor did not contain any nitrogen. The SO<sub>2</sub> was mixed with this nitrogen stream that represents both the ROG nitrogen and the coal gas nitrogen so that the

**Table 1. Catalyst Physical Characteristics**

	Catalyst A	Catalyst B	Catalyst C	Catalyst D
Base material	Alumina	Alumina	Proprietary	Nonalumina
BET surface area (m <sup>2</sup> /g)	227	212	103	10
Attrition loss per RTI 20-h test (%)	7.2	7.2 (est'd)	1.0 (est'd)	
Hg porosimetry pore volume (mL/g)	0.62	0.41	0.32	
Particle size, weighted average diameter (μm)	168	168 (est'd)	100 (approx.)	
Bulk Density (g/mL)	0.81	0.94	0.90	0.85

experimentally measured concentration is not the same as the nominal SO<sub>2</sub> concentration that is being simulated with the experiment. Table 3, based on material balance calculations, relates the two values, and for interest shows the approximate rotameter setting for the supply of liquid SO<sub>2</sub> to the preheater.

A typical test run was conducted in one day, with the reactor heated with a low-pressure nitrogen purge overnight. Following calibration of the analyzers, the unit was pressurized with nitrogen, and a stable flow was established. The coal gas flow and the liquid SO<sub>2</sub> (LSO<sub>2</sub>) flows were started essentially simultaneously at given flow rates that were established from material balance calculations. The LSO<sub>2</sub> flow was controlled with a needle valve and a rotameter to get the desired SO<sub>2</sub> concentration in the reactor feed to simulate the ROG composition. The coal gas flow rate, controlled by a mass flow controller (MFC), was fine-tuned from observation of the tail gas analyzer output. A shortage of coal gas results in a high outlet SO<sub>2</sub> concentration; conversely, an excess of coal gas results in high outlet H<sub>2</sub>S concentration.

Once stable outlet concentrations had been achieved, the unit was allowed to run for 20 min or more so that several gas chromatograph (GC) data points could be collected. The reactor temperatures, pressure, flow rates, and analyzer outputs were logged using a personal computer-based data logger. Two or three different operating conditions could be set and lined-out conditions obtained in a good day's run.

For two of the runs, air was introduced into the DSRP reactor along with the simulated ROG and the coal gas. This was done to represent the situation in commercial practice when oxygen "slip" occurs in the regenerator. That is, if the air-blown regenerator is not in perfect control, it would be possible for excess air to be fed to that unit, so that some unconsumed oxygen would be discharged along with the SO<sub>2</sub>/N<sub>2</sub> stream. The experiments were run to see what the effect would be of having oxygen in the SO<sub>2</sub> stream that goes to the DSRP reactor.

**Table 2. Coal Gas Composition**

Component	Volume %
CO	14.4%
CO <sub>2</sub>	13.0%
H <sub>2</sub> O	10.0%
H <sub>2</sub>	17.5%
H <sub>2</sub> S	1,400 ppm
N <sub>2</sub>	45.0%

**Table 3. Simulated ROG Concentrations**

SO <sub>2</sub> content of simulated ROG (%)	SO <sub>2</sub> content of actual feed to bench-scale reactor (%)	Calculated LSO <sub>2</sub> flow rate (cc/min)
7.2	6	3.2
14	10	5.8
18	12	6.9

At the end of each day's run, molten sulfur was withdrawn from the pot downstream of the steam-heated sulfur condenser. Due to the variety of operating conditions that was used, no attempt was made to verify a sulfur material balance.

## Results

A single number is used to report the results of each run: the "percent reduction of sulfur compounds," by gas analysis. By material balance, all gaseous sulfur compounds that disappear must have been converted to elemental sulfur, so therefore this number represents the percent conversion. The laboratory bench-scale DSRP unit is equipped with a continuous gas analyzer to measure  $\text{H}_2\text{S}$  and  $\text{SO}_2$  in the tail gas. By a simple calculation, the output of this analyzer gives an instantaneous measure of the degree of conversion. However, the analyzer does not correctly account for the presence of COS in the tail gas. A GC equipped with a thermal conductivity detector (TCD) samples the outlet gas approximately every 8 min, and the results of that analysis, which include COS concentration, are used in this report to calculate the percent reduction value. Furthermore, the calculation takes into account the fact that  $\text{H}_2\text{S}$  is introduced in the coal gas (in addition to the  $\text{SO}_2$  of the regeneration off-gas) as a sulfur compound that must be converted to elemental sulfur.

Figure 2 summarizes the results of all the test runs, reporting conversion as a function of catalyst type. Catalyst D clearly has unacceptably low conversion, as expected, and Catalyst B showed the best performance, although it was only slightly better than Catalyst A.

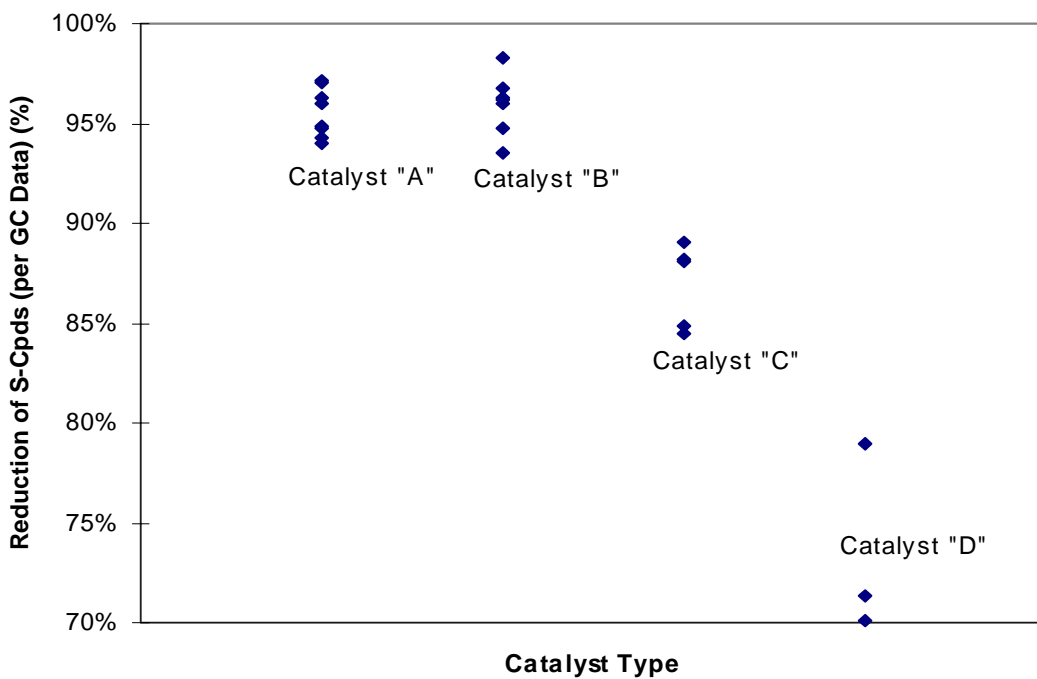


Figure 2. Effect of catalyst type.

Most of the runs were conducted at either of two pressure levels. The higher pressure—250 psig—represents a typical operating pressure that would expect to be encountered in a commercial embodiment of the DSRP. The lower pressure—150 psig—was chosen because that may be the coal gas pressure at the Power Systems Development Facility (PSDF) at Wilsonville, Alabama, during the slipstream testing under certain operating scenarios. Figure 3 shows a slightly favorable trend with increased pressure, as has also been shown in previous work.

The operating conditions selected for the test series intentionally span only a narrow range of temperature. The test protocol called for adjustment of the furnace temperature to attempt to maintain the same catalyst bed temperature for all runs. Nonetheless, there was some variation in actual bed temperature. As Figure 4 shows, a higher catalyst temperature results in greater conversion to elemental sulfur. This result is consistent with previous experience.

Figure 5 shows the effect of inlet concentration of SO<sub>2</sub> on the conversion; the runs made with the higher SO<sub>2</sub> concentrations have higher conversions. This particular response is well known in Claus technology and Selectox technology. Figure 6 plots the actual measured concentration of sulfur compounds in the outlet as a function of inlet concentration. From those data it appears that outlet concentration is independent of inlet concentration. Thus, by material balance considerations, higher apparent reduction efficiencies are achieved when the inlet concentration is higher, as Figure 5 shows.

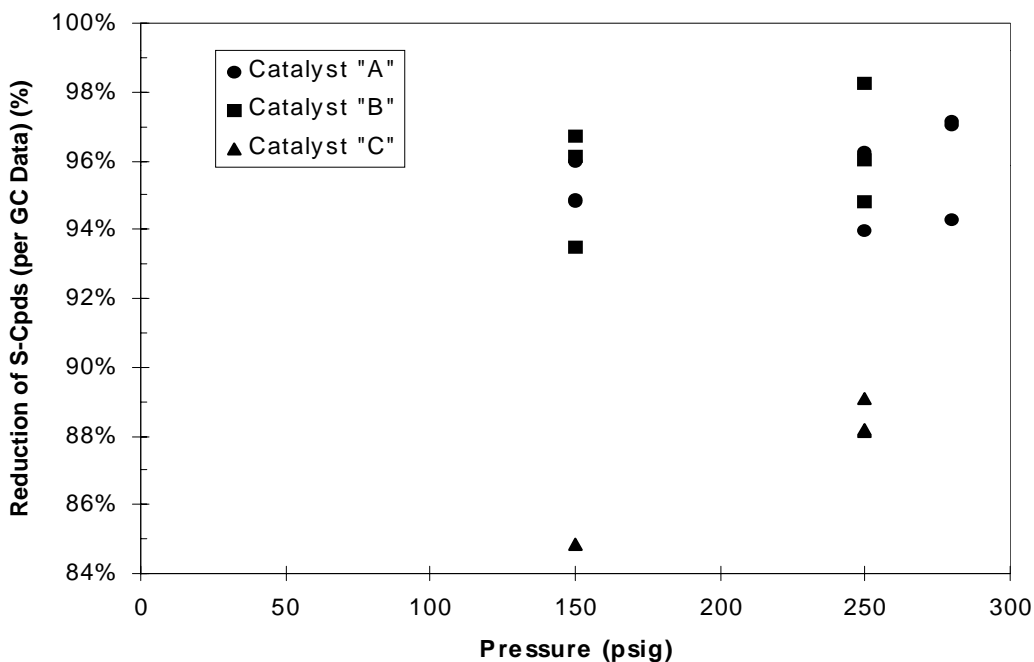


Figure 3. Effect of pressure.

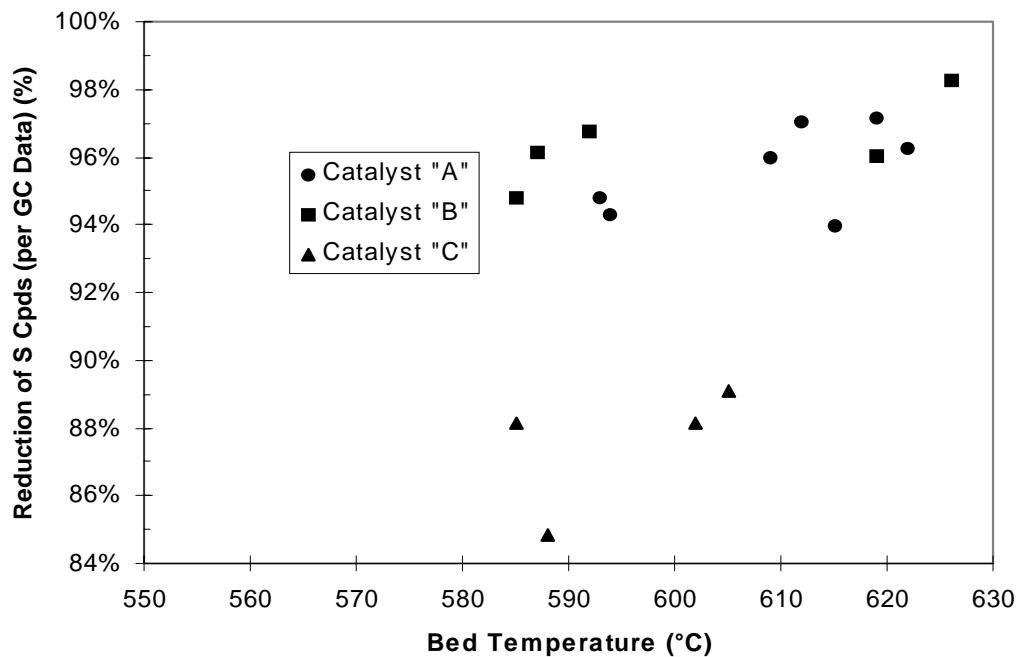


Figure 4. Effect of bed temperature.

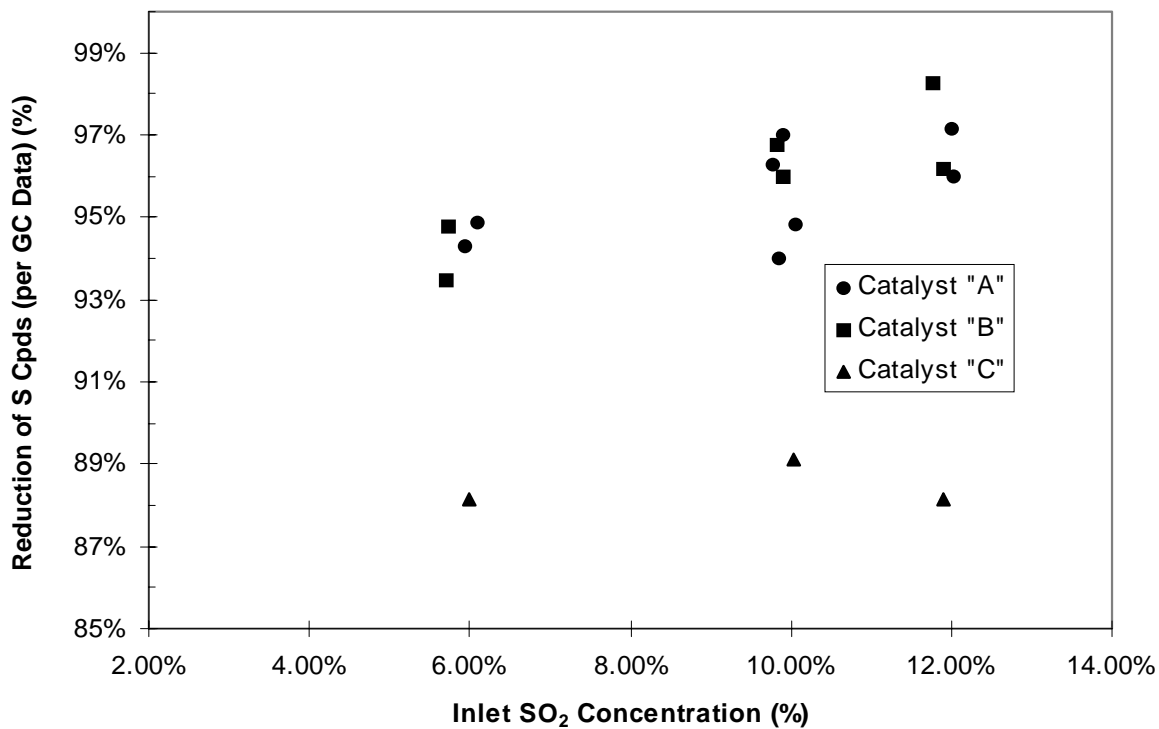
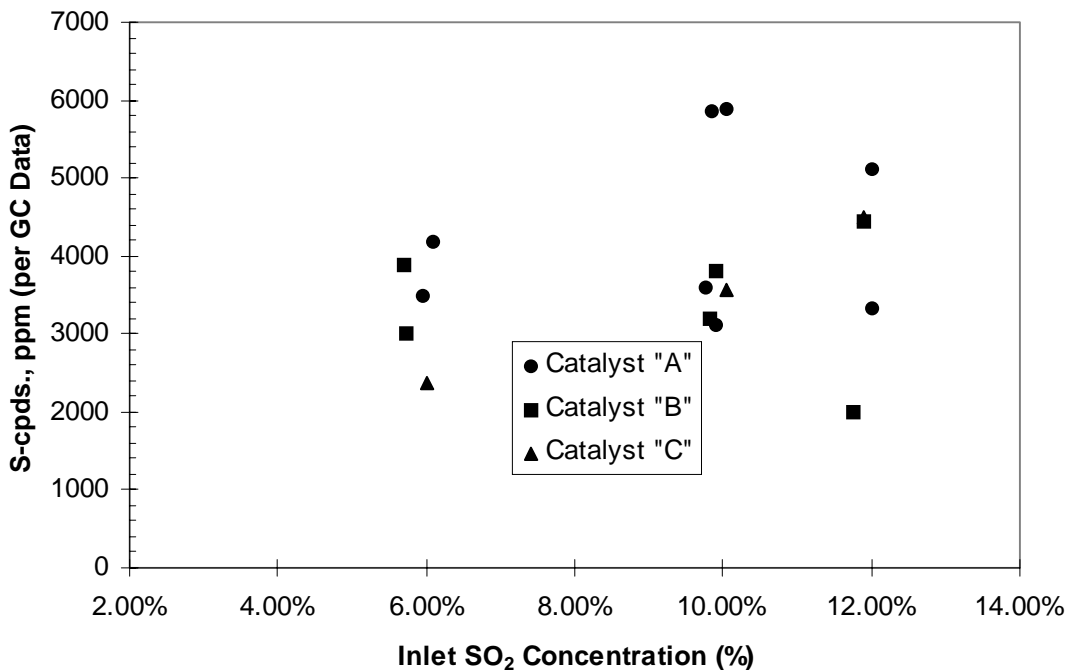


Figure 5. Effect of inlet concentration.





**Figure 6. Outlet concentration of sulfur compounds.**

The introduction of approximately 1 percent oxygen along with the ROG into the DSRP reactor did not seem to have any deleterious effects. Without any adjustment of the coal gas flow, the outlet concentrations of sulfur compounds increased dramatically, as was expected. Increasing the coal gas flow rate to correct for consumption by oxygen returned the outlet sulfur compound concentrations to their previous values. Similarly, with shutdown of the oxygen flow (after 3 h of operation in one case), and subsequent reduction in coal gas flow, the outlet sulfur concentrations returned to original values, indicating no change in the performance of the catalyst.

### **Applications/Benefits**

To address the need for the DSRP to process sorbent regeneration off-gases containing high concentrations of SO<sub>2</sub> (up to 14 vol%), the commercial embodiment of the process is likely to be based on some type of fluidized-bed reactor that incorporates a heat exchanger to remove the high heat of reaction. A bubbling bed reactor, a fast fluidized-bed reactor, and a transport (entrained bed) reactor have all been considered. Figure 7 is a schematic representation of a fast fluidized-bed reactor incorporating a solids cooler that has been conceptualized for DSRP.

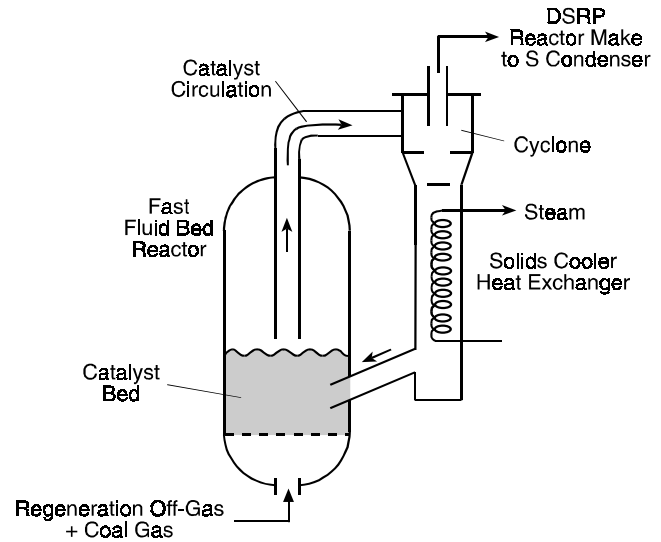
From the experimental work described in this paper, a good bubbling bed catalyst—designated “B”—has been developed, using a commercially available alumina. Conversions were 98 percent in a single stage, based on GC data. Attrition is low with this material, but probably not low enough for this catalyst to be affordable for commercial-scale transport reactor use, especially considering that the alumina material is fairly expensive. To address the need for a lower cost, highly attrition-resistant material for transport reactor use, catalyst C was developed and tested. Although the activity was disappointing—single-stage conversion was 90 to 92 percent—it has

low enough attrition for use in a transport reactor, and it is much less costly than Catalyst B or A.

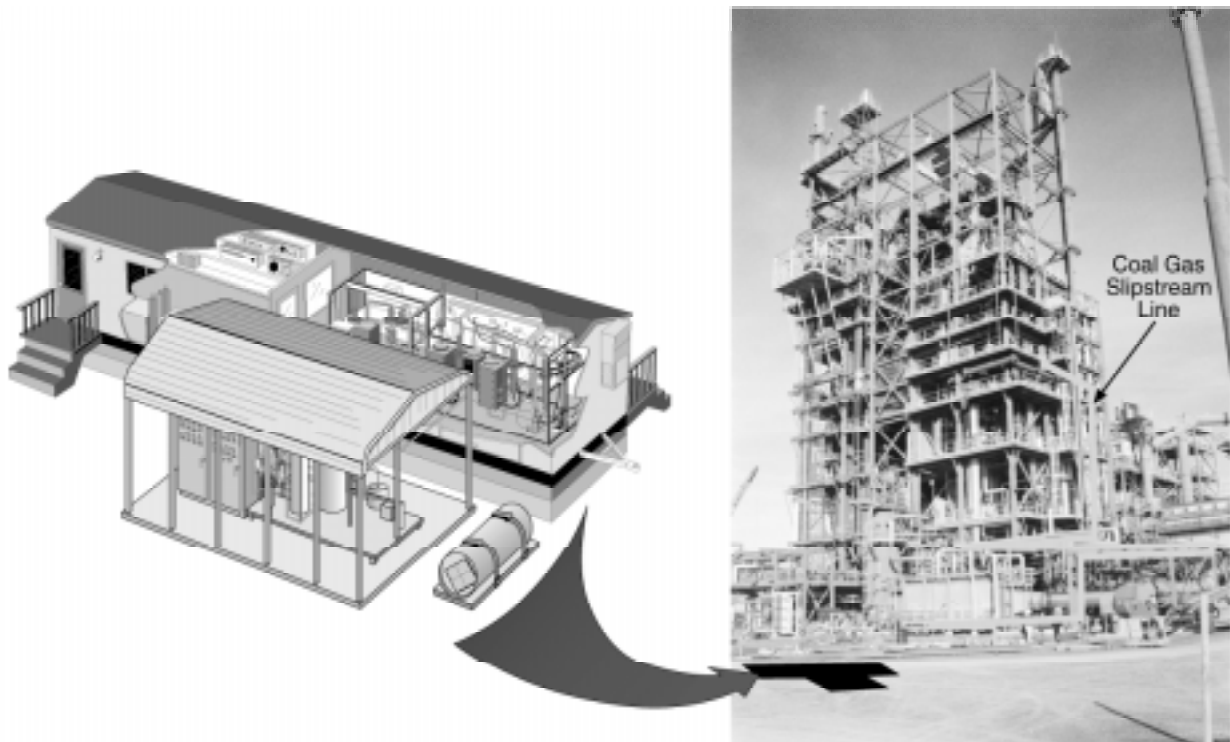
Even as the technology for the sorbent-based gas desulfurization develops, and the characteristics of the resulting regeneration off-gas change, the DSRP continues to look favorable as a feasible commercial process for the production of elemental sulfur.

### Future Activities

The planning is nearly complete, and construction/fabrication activities are underway for the future field test of the DSRP with actual coal gas at FETC's PSDF field test using the skid-mounted six-fold larger (6X) DSRP with a slipstream of actual coal gas at PSDF. Modification of the 6X unit will be completed, consistent with specific site requirements. The mobile laboratory will be refitted at RTI as a control room for the 6X unit and will be moved along with the skid-mounted 6X unit to Wilsonville, Alabama, for the testing to be conducted in FY 1999-2000. Figure 8 shows an



**Figure 7. Conceptualized fast fluidized-bed reactor.**



**Figure 8. Artist's conception of equipment arrangement for PSDF field test.**

artist's conception of how the mobile laboratory will be used in conjunction with the 6X unit at that field test site. The proposed route of the coal gas slipstream line is overlaid on the photograph.

## Acknowledgments

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