Development of a Hot-Gas Desulfurization System for IGCC Applications

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ABSTRACT

Integrated gasification combined cycle (IGCC) power plants are being advanced worldwide to produce electricity from coal because of their superior environmental performance, economics, and efficiency in comparison to conventional coal-based power plants. One key component of an advanced IGCC power plant is a hot-gas desulfurization system employing regenerable sorbents. To carry out hot-gas desulfurization in a fluidized-bed reactor, it is necessary that the sorbents have high attrition resistance, while still maintaining high chemical reactivity and sulfur absorption capacity. Also, efficient processes are needed for the treatment of SO$_2$-containing regeneration off-gas to produce environmentally benign waste or useful byproducts.

A series of durable zinc titanate sorbents were formulated and tested in a bench-scale fluidized-bed reactor system. Reactive sorbents were developed with attrition resistance comparable to fluid-bed cracking (FCC) catalysts used in petroleum refineries. In addition, progress continues on the development of the Direct Sulfur Recovery Process (DSRP) for converting SO$_2$ in the regeneration off-gas to elemental sulfur. Plans are under way to test these bench-scale systems at gasifier sites with coal gas. This paper describes the status and future plans for the demonstration of these technologies.

INTRODUCTION

IGCC power plants are being advanced worldwide to produce electricity from coal due to their potential for superior environmental performance, economics, and efficiency in comparison to conventional coal-based power plants. Conventional power plants rely on the thermally inefficient Rankine steam cycle and operate at near ambient pressure resulting in large flue-gas flow rates; treatment of these large flue gas volumes is relatively expensive. In contrast, in an IGCC system, coal is gasified at elevated pressure, typically 20 to 30 atmospheres (atm), to produce a relatively low volume fuel gas which is desulfurized prior to burning in a combustion turbine to produce electricity. In the first generation Cool Water IGCC plant demonstrated at Dagget, California, the fuel gas was cooled and sulfur was removed using a commercially available liquid-phase scrubbing process.$^{1,2}$ Although this plant was a success in terms of emissions, its thermal efficiency of 32 percent was similar to conventional power plants due in large measure to the energy penalty imposed by cooling the gas.$^3$

Advanced IGCC plants (Figure 1) are being developed with a projected efficiency, high heating value basis to electricity, as high as 47 percent. A key component of these plants is a hot-gas desulfurization system employing efficient regenerable mixed-metal oxide sorbents. Leading sorbent candidates include zinc ferrite and zinc titanate. These sorbents can remove hydrogen sulfide (H$_2$S) in the fuel gas down to very low levels [typically less than 20 parts per million by volume (ppmv)] at 500 to 750 °C and can be easily regenerated for multicycle operation using air.$^{4,5}$ The desulfurization and regeneration reactions can be carried out using fixed-, moving-, or fluidized-bed reactors. Fluidized-bed reactors are perhaps most suited for hot-gas desulfurization due to their ability to control the temperature during the highly exothermic regeneration that is typically carried out using an air-diluent (typically nitrogen or steam) mixture. The sorbent regeneration results in a dilute sulfur dioxide (SO$_2$)-containing off-gas which must be treated in an environmentally acceptable manner. Options for treating this gas include conversion to elemental sulfur or sulfuric acid or recycle to the gasifier in which an in-bed disposable sorbent such as limestone or dolomite is employed. Elemental sulfur recovery from the off-gas is believed
Figure 1. Schematic of a simplified IGCC system.

to be the most desirable option because sulfur can be easily stored or sold—a preferable choice by most utilities.

Research Triangle Institute (RTI) with the U.S. Department of Energy/Morgantown Energy Technology Center (DOE/METC) sponsorship is developing highly efficient, attrition-resistant, zinc titanate sorbents for fluidized-bed reactors and the DSRP for catalytically reducing the SO$_2$-containing off-gas using a small slip stream of coal gas to elemental sulfur. A conceptual hot-gas desulfurization system employing fluid-bed desulfurization coupled with the DSRP is shown in Figure 2. This paper describes the current status and future plans for demonstration of the fluid-bed zinc titanate sorbent and DSRP technologies.

DEVELOPMENT OF FLUIDIZABLE ZINC TITANATE SORBENTS

Background

Recent developments in hot-gas desulfurization processes have focused on regenerable, solid mixed-metal oxide sorbents, such as zinc ferrite and zinc titanate to remove reduced sulfur species from the fuel gas. Both zinc ferrite and zinc titanate have high sulfur capacity and both can reduce the H$_2$S level of fuel gas below 10 ppmv. They can be easily regenerated with diluted air for multicycle operation.

Fluidized-bed reactors offer several potential advantages provided that durable reactive sorbents can be developed. These advantages include excellent gas-solid contact, ability to
Figure 2. A conceptual hot-gas desulfurization system coupled with the DSRP process.
continuously add or remove sorbent, excellent temperature control of the highly exothermic regeneration, use of small particles leading to faster overall kinetics, and continuous steady-state operation. However, highly attrition-resistant sorbents with good sulfur capacity which are capable of withstanding stresses induced by rapid temperature swings, chemical transformations, and fluidization and transport are required before fluidized beds can be employed successfully.

A number of techniques were investigated to prepare zinc ferrite sorbents in 50 to 400 µm particle size range with enhanced long-term durability and chemical reactivity. The techniques included spray drying, impregnation over alumina, crushing of durable pellets and screening, and granulation. Of all the techniques investigated, the granulation technique proved to be highly successful. Zinc ferrite formulations prepared using the granulation technique exhibited superior performance in terms of attrition resistance and long-term chemical reactivity over those prepared using the other techniques mentioned earlier. Despite superior performance of formulations prepared by granulation, zinc ferrite was found to be limited to a maximum temperature of about 550 °C and to moderately reducing coal-gas (e.g., a low Btu gas containing at least 15 percent steam), beyond which it tended to lose mechanical strength primarily due to excessive reduction and iron carbide formation, particularly under highly reducing conditions. To find an alternative to zinc ferrite that would be suitable to high severity reducing gases and/or higher temperatures (up to 760 °C), earlier studies conducted at RTI in high-temperature, high-pressure (HTHP) fixed-bed and thermogravimetric reactors had culminated into a zinc titanate sorbent.

Desulfurization Chemistry

Zinc titanate is formed by a solid-state reaction of zinc oxide and titanium dioxide at temperatures ranging between 750 to 900 °C. Predominant zinc titanate phases as observed by X-ray diffraction (XRD) are Zn$_2$TiO$_4$ and ZnTiO$_3$ which contain ZnO and TiO$_2$ in molar ratios of 2 and 1, respectively. Other zinc titanate forms may also be present. Unlike zinc ferrite, only zinc oxide present in zinc titanate participates in the desulfurization while TiO$_2$ provides the stability of ZnO against reduction by CO and/or H$_2$ present in the fuel gas. Overall chemical reactions during desulfurization and regeneration of the zinc titanate sorbent are the following:

**Sulfidation:**

\[
\begin{align*}
\text{Sulfidation:} & \quad \text{Zn}_2\text{TiO}_4 + 2\text{H}_2\text{S} \rightarrow 2\text{ZnS} + \text{TiO}_2 + 2\text{H}_2\text{O} \\
& \quad \text{ZnTiO}_3 + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{TiO}_2 + \text{H}_2\text{O}
\end{align*}
\]

**Regeneration:**

\[
\begin{align*}
\text{Regeneration:} & \quad 2\text{ZnS} + \text{TiO}_2 + 3\text{O}_2 \rightarrow \text{Zn}_2\text{TiO}_4 + 2\text{SO}_2
\end{align*}
\]

Sorbent Preparation and Characterization

A series of zinc titanate sorbent formulations were prepared using the granulation technique (which had been successfully used previously for zinc ferrite as earlier discussed) by varying ZnO to TiO$_2$ molar ratio, various binders and binder levels, calcination conditions, and with and without the addition of a number of additives. These sorbents were characterized for screening purposes before testing in RTI's HTHP fluidized-bed reactor (shown in Figure 3), details of which are given elsewhere. The sorbent characterization included chemical reactivity in a thermogravimetric analyzer (TGA), pore size distribution, BET surface area, attrition resistance, and bulk density. A description of all these sorbent characterization techniques is given
elsewhere. Efforts to produce fluidizable zinc titanate sorbents by spray drying were unsuccessful as evidenced by their overall poor performance both in terms of attrition resistance and chemical reactivity.

**Bench-Scale Testing**

Based on the characterization data, a number of sorbents were selected for bench-scale testing. The particle size range of all the sorbent formulation tested was 100 to 300 μm. Ten 10-cycle runs were conducted in an HTHP skid-mounted bench-scale fluidized-bed reactor system (Figure 3) which is capable of operation at up to 870 °C at 20 atm. The bench-scale testing variable included sorbent type, temperature (550 to 750 °C), fuel gas type (KRW or Texaco gasifier gas), steam content of fuel gas, and fluidizing gas velocity (6 to 15 cm/s). In all the 10 multicycle tests, the sulfur absorption capacity for zinc titanate sorbents at breakthrough remained fairly constant over 10 cycles at about 40 to 60 percent of the theoretical capacity. This was in contrast to zinc ferrite sorbents where the sulfur capture capacity of the sorbent decreased drastically with cycling. Furthermore, zinc titanate sorbents consistently reduced the H₂S level of coal-gas to below 20 ppmv. The details of these bench-scale test results are given elsewhere.⁹⁻¹¹

Out of a series of zinc titanate formulations tested in our bench unit, Formulation ZT-4 was found to have the best overall performance. Its attrition resistance was comparable to an equilibrium FCC catalyst used in petroleum refineries. Also, no measurable zinc loss was observed when ZT-4 was subjected to bench-scale testing at temperatures as high as 750 °C and superficial fluidizing velocities up to 15 cm/s (U/Ur > 8) in the presence of Texaco gasifier gas.

**Sorbent Regeneration**

The sulfided sorbent was regenerated using 1 to 5 percent oxygen in nitrogen. Sulfate formation was not found to occur at 760 °C and 15 atm. Also, regeneration of the sulfided zinc titanate sorbent led to stoichiometric amount of SO₂ in the regeneration off-gas with potentially no oxygen according to the reaction: ZnS + 1.5 O₂ → ZnO + SO₂. A quasi-steady-state generation of SO₂-containing off-gas was demonstrated indicating that a nearly constant steady-state SO₂ content in the regeneration off-gas of a commercial fluidized-bed system can be obtained. The constancy of SO₂ concentration is believed to be essential for economical processing downstream to elemental sulfur or sulfuric acid as discussed later in this paper.

**Temperature Dependence of Sulfidation Reaction**

The sulfidation reaction was found to be controlled by intrinsic chemical reaction rather than external or pore diffusion. The apparent activation energy for the sulfidation reaction ranged from 15 to 20 kcal/mol depending on the sorbent composition. This indicates that significant reduction in size of the desulfurization system can be achieved by increasing the operating temperature. A simple mathematical model that assumed well-mixed solid phase and plug flow of gas made a reasonable prediction of the breakthrough behavior in the batch HTHP reactor using a rate constant based on TGA measurements.
Figure 3. Bench-scale fluid-bed sorbent test facility.
Effect of Hydrochloric Acid and Ammonia

Injection of hydrochloric acid (HCl) and ammonia (NH₃) into a fluidized bed of zinc titanate at up to 750 °C did not have any deleterious effect on the performance of the sorbent. At a superficial contact time of 0.63 s, at 1 atm and 744 °C, about 50 percent of the inlet NH₃ was decomposed by a molybdenum-doped zinc titanate (ZT-13). This translates into a first-order rate constant for NH₃ decomposition of 1.1 per s. Furthermore, the presence of HCl in the coal-gas significantly enhanced the desulfurization reactivity of zinc titanate. Some HCl was permanently retained by the sorbent.¹²

Long-term Test with ZT-4

Following the superior performance of ZT-4 sorbent during bench tests as discussed earlier, a 100-cycle test is currently being performed to determine its long-term chemical reactivity and attrition resistance. Table 1 shows the test conditions. So far, 80 cycles of sulfidation-regeneration have been successfully completed. Pertinent results obtained during the initial 50 cycles of testing are reported here. Bench-scale test data for Cycles 51 to 80 are currently being analyzed.

<table>
<thead>
<tr>
<th>Table 1. Test Conditions Used in 100-Cycle Test</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sulfidation</strong></td>
</tr>
<tr>
<td>Sorbent : ZT-4 (Zn/Ti = 1.5 atomic)</td>
</tr>
<tr>
<td>Temperature : 750 °C (nominal)</td>
</tr>
<tr>
<td>Pressure : 15 atm (220 psia)</td>
</tr>
<tr>
<td>Particle size : 100 to 300 μm (d₅₀ = 175 μm)</td>
</tr>
<tr>
<td>Sorbent charge : 500 g</td>
</tr>
<tr>
<td>Total gas flow rate : 76 slpm (161.5 scfh)</td>
</tr>
<tr>
<td>Superficial gas velocity : 0.5 ft/s (U/Uₘ &gt; 8)</td>
</tr>
<tr>
<td>Coal gas : Simulated Texaco gas</td>
</tr>
<tr>
<td>H₂S content of coal gas : 11,400 ppmv (1.14%)</td>
</tr>
<tr>
<td><strong>Regeneration</strong></td>
</tr>
<tr>
<td>Temperature : 760 to 785 °C</td>
</tr>
<tr>
<td>Pressure : 15 atm (220 psia)</td>
</tr>
<tr>
<td>Total gas flow rate : 76 slpm</td>
</tr>
<tr>
<td>O₂ content of regeneration gas : 2.3 to 2.5%</td>
</tr>
<tr>
<td>Diluent : Nitrogen</td>
</tr>
</tbody>
</table>

Figure 4 shows the H₂S concentration profiles as a function of time for Cycles 1, 10, 20, 30, 40, and 50. As can be seen, the prebreakthrough H₂S level in all the cycles was consistently below 20 ppmv even at 750 °C and 18 percent steam in coal-gas. We, however, observe some
Figure 4. Breakthrough curves for selected cycles (100-cycle test).

decline in the breakthrough time needed to reach an H₂S concentration of 500 ppmv with cycling. The inlet H₂S concentration was 11,400 ppmv as shown in Table 1.

Figure 5 shows the sulfur absorption capacity of the sorbent at breakthrough for Cycles 1 to 50. During the first 18 cycles, the sulfur capacity remained at 13.42 g S/100 g of fresh sorbent, indicating about 60 percent capacity utilization. The theoretical saturation sulfur absorption capacity of ZT-4 is about 22.5 g S/100 g of fresh sorbent. During the 50th cycle, the sulfur capacity of the sorbent was 8.95 g S/100 g of fresh sorbent. This indicates a 33 percent drop from the first cycle. It may be noted here that the measured sulfur capacity is directly proportional to the breakthrough time.

Examination of the structural properties of the sorbent revealed that this loss in the sulfur capture capacity is due to the drop in the surface area and median pore diameter. Loss in surface area is primarily due to the prolonged exposure of sorbent at high temperature (~800 °C).

The total physical loss of sorbent from the reactor during the entire 50 cycles of testing was only 0.5 percent. In a previous 100-cycle test with zinc ferrite, 21 percent of the sorbent was lost from the reactor in 50 cycles at 625 °C in a significantly less reducing KRW gas containing 20 percent steam.® This indicates superiority of zinc titanate over zinc ferrite for operation at more severe conditions.

Another major concern in this test was zinc vaporization at 750 °C. Sorbent samples after 10, 18, 26, 34, 42, and 50 cycles were extracted for Zn and Ti analyses. The average Zn content of the fresh sample was 44.7 wt%, while it was 43 wt% for the 50-cycle regenerated material, indicating a 3.80 percent zinc loss. This small amount of zinc loss may not be significant, but no definite conclusions can be made about zinc loss until further tests are made.
500 ppm is defined as Breakthrough

Figure 5. S-capacity at breakthrough (100-cycle test; 750 °C, 15 cm/s, Texaco gas).

The next important variable in this testing was the attrition resistance. Therefore, attrition resistance measurements were made in a three-hole attrition tester on fresh, 10-cycle regenerated and 50-cycle regenerated sorbent samples. The details of the attrition tester and the test procedure are given elsewhere.9 11 Figure 6 shows the 5-h and 20-h weight loss data. Also included in this figure is the attrition resistance of the US260 equilibrium FCC catalyst for comparison purposes. The sorbent loss due to attrition decreased from 39.66 percent in fresh state to 1.10 percent for the 50-cycle regenerated material, indicating at least an order-of-magnitude increase in the attrition resistance. This encouraging finding is critically important in the design of a commercial fluidized-bed hot-gas desulfurization system. This test is ongoing and should be completed by the end of this year.

DIRECT SULFUR RECOVERY PROCESS

Background

As shown in Figure 1, the regeneration of sulfided zinc titanate sorbent produces an off-gas stream typically containing 1 to 3 percent sulfur dioxide (SO₂). This gas stream must be treated in an environmentally acceptable manner. Options for treating this gas include conversion to elemental sulfur or sulfuric acid or recycle to the gasifier in which an in-bed disposable sorbent such as limestone or dolomite is employed. Production of elemental sulfur is perhaps the most desirable option as sulfur can be easily stored and transported and is an essential industrial commodity.
In the DSRP, which has been under development since 1988, a near stoichiometric mixture of off-gas and raw coal-gas (2 to 1 mol ratio of reducing gases to $\text{SO}_2$) is reacted in the presence of a selective catalyst to produce elemental sulfur directly:\textsuperscript{13,14}

$$2\text{H}_2 + \text{SO}_2 \rightarrow (1/n)\text{S}_n + 2\text{H}_2\text{O}$$
$$2\text{CO} + \text{SO}_2 \rightarrow (1/n)\text{S}_n + 2\text{CO}_2$$
$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2.$$

Initial work on the DSRP was directed at screening a number of catalysts. Tests were carried out in a 1-in. diameter, fixed-bed reactor containing 25 to 50 cc of catalyst. The best catalysts to date have shown that sulfur recoveries as high as 96 percent can be obtained in a single catalytic stage at 450 to 700 °C, 20 atm, and space velocities of 1000 to 7500 standard cubic centimeter per cubic centimeter of catalyst per hour (scc/(cc-h)).\textsuperscript{13,14} Furthermore, experiments simulating two reactors in series with an intermediate sulfur condensation step have demonstrated that over 99 percent overall sulfur recovery is feasible.\textsuperscript{13,14}

A schematic block-diagram of the DSRP is shown in Figure 7. This process consists of two fixed-bed catalytic reactors, each followed by a sulfur condenser. Hot regenerator off-gas is mixed with a hot coal-gas slip stream and fed to the first DSRP reactor. Approximately 96 percent of the sulfur gas in the inlet stream of the first reactor is converted to elemental sulfur. The outlet gas of the first DSRP reactor is cooled to condense out the sulfur. The gas could be
recycled after the Stage I condenser. Alternatively, adjusting the stoichiometric ratio of coal gas to regenerator off-gas to 2 at the inlet of the first reactor also controls the effluent stoichiometry of the first reactor since any \( \text{H}_2\text{S} \) and COS produced by reactions: \( 3\text{H}_2 + \text{SO}_2 \rightarrow \text{H}_2\text{S} + 2\text{H}_2\text{O} \), and \( 3\text{CO} + \text{SO}_2 \rightarrow \text{COS} + 2\text{CO}_2 \) yields an \((\text{H}_2\text{S} + \text{COS})\) to \( \text{SO}_2 \) ratio of 2 to 1. The cooled gas stream is then passed to the second DSRP reactor at 250 to 350 °C where 80 to 90 percent of the remaining sulfur species are converted to elemental sulfur via the modified Claus reaction \([2\text{H}_2\text{S} + \text{SO}_2 \rightarrow (3/n)\text{S}_n + 2\text{H}_2\text{O}]\) at high pressure. The total efficiency of the two reactors for the conversion of sulfur species to elemental sulfur is projected to be about 99.5 percent.

A preliminary economic study, in which the two-stage DSRP was compared to conventional processes indicated that the DSRP can produce a ton of elemental sulfur at costs much less than those for the conventional processes and at significantly lower capital investment. Further cost savings might be realized for IGCC system applications by designing a proper recycle system for the gas leaving the first stage DSRP condenser and eliminating the second stage equipment.

**Bench-Scale Testing**

Based on encouraging results, the laboratory scale DSRP system was scaled up by a factor of 40. A skid-mounted integrated two-stage DSRP unit was constructed. The DSRP bench-scale unit hardware has been described in detail previously. The unit consists of a simulated off-gas and coal gas delivery system connected to two high-pressure reactors and condensers in the configuration shown conceptually in Figure 7. The system is rated to 400 pounds per square inch gauge (psig) and the reactors, capable of operation at up to 400 psig at 750 °C, hold up to 1 L of catalyst each. Thirty-five parametric DSRP tests have been conducted in the bench-scale unit at a range of pressures (1.7 to 25 atm), space velocity (1000 to 7500 scc/(cc-h)), coal-gas type (KRW, GE, Texaco), reducing gas to \( \text{SO}_2 \) ratio (1.6 to 2.2) and off-gas...
SO₂ concentration (2 to 12.4 vol %). The Stage I temperature typically ranges from 500 to 700 °C, whereas the Stage II temperature ranges from 250 to 350 °C.

**Stage I Results**

Sulfur conversion after Stage I as a function of experimental parameters is shown in Table 2. As found in the previous laboratory-scale experiments, the conversions were insensitive to temperature and space velocity but were a strong function of pressure and reducing gas/SO₂ ratio. As seen from Table 2, pressure has a rather dramatic effect from 1.7 to about 10 atm. Between 10 and 21.4 atm, conversion increases slowly and as high as 96 percent conversion is achieved. Increase in space velocity from 1,250 to 7,500 scc/(cc-h) does not appear to reduce conversion. It may be possible that throughput and sulfur production can be increased significantly by operating at higher space velocities. The optimal reducing gas to SO₂ ratio is about 2 as anticipated. Conversions are lower both at a higher ratio of 2.17 as well as lower ratios of 1.79 to 1.84 as can be seen from Table 2. However, the conversions are relatively insensitive to the temperature between 524 and 660 °C. All of the results obtained in this bench-scale testing corroborate the data previously obtained in the laboratory-scale reactor.

**Table 2. Parametric Study of Conversion to Elemental Sulfur in Stage I**

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>Temperature (°C)</th>
<th>Space Velocity [scc/(cc-h)]</th>
<th>Stoichiometric Ratio</th>
<th>Conversion to Elemental Sₓ</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.4</td>
<td>627</td>
<td>3,750</td>
<td>2.00</td>
<td>95.8</td>
</tr>
<tr>
<td>21.4</td>
<td>552</td>
<td>7,500</td>
<td>2.00</td>
<td>94.9</td>
</tr>
<tr>
<td>21.4</td>
<td>524</td>
<td>3,750</td>
<td>2.00</td>
<td>94.5</td>
</tr>
<tr>
<td>21.4</td>
<td>608</td>
<td>2,500</td>
<td>1.84</td>
<td>92.1</td>
</tr>
<tr>
<td>21.4</td>
<td>660</td>
<td>1,250</td>
<td>2.17</td>
<td>91.1</td>
</tr>
<tr>
<td>21.4</td>
<td>660</td>
<td>1,250</td>
<td>1.79</td>
<td>89.6</td>
</tr>
<tr>
<td>14.6</td>
<td>610</td>
<td>2,500</td>
<td>1.84</td>
<td>89.3</td>
</tr>
<tr>
<td>14.6</td>
<td>656</td>
<td>1,250</td>
<td>1.79</td>
<td>88.5</td>
</tr>
<tr>
<td>9.8</td>
<td>662</td>
<td>1,250</td>
<td>1.79</td>
<td>86.4</td>
</tr>
<tr>
<td>9.8</td>
<td>610</td>
<td>2,500</td>
<td>1.84</td>
<td>84.1</td>
</tr>
<tr>
<td>1.7</td>
<td>659</td>
<td>1,250</td>
<td>1.90</td>
<td>18.1</td>
</tr>
</tbody>
</table>

Efforts were also directed at demonstrating the DSRP with higher concentration, up to 12 percent, of SO₂, typically obtained in the regeneration off-gas from the GE moving-bed regenerator. A series of experiments were carried out with gases containing 0.5 to 12.4 percent SO₂ using a dry GE/Lurgi coal-gas as the reductant. Runs were made at two pressures and varying hourly gas space velocity. The Stage II reactor was not operated in this series of
experiments. In the GE moving-bed/DSRP concept, the Stage I effluent, after sulfur condensation, can be recycled back to the regenerator and/or the gas turbine depending on emission regulations.

The conversion data taken with the high \( \text{SO}_2 \) concentration in the regeneration off-gas are shown in Figure 8. As can be seen, the conversions are clearly limited by stoichiometry, i.e., the molar ratio of \( \text{H}_2\text{S} \) to \( \text{SO}_2 \). Problems with the liquid \( \text{SO}_2 \) pump led to problems in controlling the high \( \text{SO}_2 \) concentrations, making it difficult to control the stoichiometry. As presented in the figure, at each pressure level, the conversion correlates well with the stoichiometry. As expected, conversions are somewhat higher at 14.6 atm than at 9.8 atm. Extrapolating up to a stoichiometry of 2 results in conversions of over 95 percent at 14.6 atm. At 9.8 atm and an hourly gas space velocity of 5,000, conversion is still over 90 percent. Somewhat surprising, at the lower pressure, increasing space velocity results in higher conversion. This may be indicative of kinetic effects that limit the effect of Claus-type reactions that inhibit Stage II conversion as discussed next.

**Stage II Results**

During the bench-scale testing, the Stage II reactor was operated in an integrated manner at temperatures from 244 to 337 °C. The results, however, show that the overall conversions to elemental sulfur after Stage II were lower than after Stage I as indicated by two sets of data in Table 3. Since sulfur condensation was not complete between the reactors, Claus reactions apparently produce \( \text{H}_2\text{S} \) and \( \text{SO}_2 \) from sulfur and \( \text{H}_2\text{O} \). As a result, overall conversion from the integrated two-stage operation is lower.

![Conversion Limit](image)

**Figure 8.** DSRP sulfur recovery from off-gases containing 7.5 to 12.4 percent \( \text{SO}_2 \).
Table 3. Conversion to Elemental Sulfur After Stages I and II

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>Space Velocity [scc/(cc·h)]</th>
<th>Reducing Gas to SO₂ Ratio</th>
<th>Conversion to Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Stage I</td>
</tr>
<tr>
<td>21.4</td>
<td>3,750</td>
<td>2.00</td>
<td>95.8</td>
</tr>
<tr>
<td>21.4</td>
<td>3,750</td>
<td>2.00</td>
<td>94.5</td>
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</tbody>
</table>

Discussions with experts in sulfur recovery processes have indicated that the scale of equipment has a major impact on sulfur removal by condensation. As the scale increases to commercial, it becomes relatively easier to efficiently remove the sulfur using an interstage condenser as practiced commercially in the Claus process. For bench-scale equipment of the size used in this study, it is very difficult to design a highly efficient sulfur condenser. However, we have made improvements to the sulfur condenser design. The improved design consists of a steam-jacketed condenser with a turbulent-flow coil for condensing and coalescing the sulfur on the coil wall. Using this new design, a number of two-stage tests were again conducted and the results are shown in Table 4.

Table 4. Bench-Scale Test Results with Improved Sulfur Condensers

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Temperature (°C)</th>
<th>Reducing Gas to SO₂ Ratio</th>
<th>Overall SO₂ Conversion to Sulfur (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reactor 1</td>
<td>Reactor 2</td>
<td>Reactor 1</td>
</tr>
<tr>
<td>SS1ᵇ</td>
<td>525</td>
<td>300</td>
<td>2.14</td>
</tr>
<tr>
<td>SS2</td>
<td>633</td>
<td>306</td>
<td>1.93</td>
</tr>
<tr>
<td>SS3</td>
<td>641</td>
<td>298</td>
<td>2.00</td>
</tr>
<tr>
<td>SS4</td>
<td>620</td>
<td>288</td>
<td>2.00</td>
</tr>
<tr>
<td>SS5</td>
<td>623</td>
<td>286</td>
<td>2.00</td>
</tr>
<tr>
<td>SS6</td>
<td>623</td>
<td>260</td>
<td>2.00</td>
</tr>
<tr>
<td>SS7ᵈ</td>
<td>623</td>
<td>286</td>
<td>2.00</td>
</tr>
<tr>
<td>SS8</td>
<td>623</td>
<td>300</td>
<td>2.00</td>
</tr>
<tr>
<td>SS9ᵉ</td>
<td>623</td>
<td>300</td>
<td>2.00</td>
</tr>
</tbody>
</table>

ᵃ21.4 atm, 2000 scc/cc·h, 3.2% SO₂ off-gas, Texaco coal gas, 10% steam in gas mixture.
ᵇSpace velocity was 4000 scc/cc·h.
ᶜNA = Not available due to experimental problems.
ᵈPressure was 350 psig; test was run for 16 h.
ᵉWater removed interstage, 350 psig, test was run for 8 h.
As shown in Table 4, additional conversion was obtained in the second reactor when low conversions were achieved in the first reactor presumably due to a less active catalyst. However, additional conversion in the second reactor was not achieved when conversions in the first reactor were high—around 95 to 96 percent. Note also that Test SS7 was a 16-h test which demonstrated a long-term plug- and leak-free operation at a pressure of 350 psig. This relatively long duration test, in addition to proving operability and reliability, also confirmed the high efficiency of the sulfur condensers.

Prior to Test SS8, the Stage II reactor was opened to replace the catalyst. It was found that the catalyst was agglomerated due to the deposition of sulfur in the bed allowing gas channeling. This may be the reason why no additional Stage II conversion (in either direction) was obtained in Tests SS6 and SS7. In Test SS8, a fresh batch of the catalyst was used. It was seen that the reverse Claus reaction slightly decreased the overall conversion after Stage II for this test. However, this decrease was nowhere near the decrease obtained in the Stage II reactor with the condensers previously used (Table 3). The results therefore indicate that even more efficient condensation will be required to achieve sufficient sulfur removal and allow additional conversion in Stage II. One important reaction that occurred in Stage II was COS conversion. COS formed in the first reactor was completely reacted in the second reactor.

Finally, Test SS9, in which the water was removed using an interstage cooler, was conducted to see if most of the sulfur could be removed with the water. This test showed that conversion in the second reactor could be increased to achieve an overall 98.5 percent conversion. Examination of the sulfur removed in the condensers after each reactor indicated that even after removing the water at interstage level, only about 80 percent of the sulfur produced in the first stage could be removed and about 20 percent still carried over to the second stage.

Thus, to increase the conversion further, i.e., beyond 99 percent, it appears that even more efficient interstage sulfur removal is necessary. However, as stated earlier, condensation should improve with increase in scale of equipment.

FIELD TESTING

Plans have been initiated for testing the zinc titanate sorbent and DSRP with process gases in the field. The zinc titanate will be tested at the pilot-scale at the Allison Gas Turbines Division of the General Motors Corporation. Allison is developing a direct coal-fired, two-stage combustor-turbine system in a field test at an operating coal gasifier site (site selection will be finalized shortly), zinc titanate sorbent and DSRP will be tested in an integrated manner using a slip stream of coal-gas. This second test will be conducted in late 1993. It will involve transporting the skid-mounted units at RTI to the gasifier site. The field tests will demonstrate the operation of both processes in a rigorous manner and evaluate any degradation of sorbent or DSRP catalyst, if any.

CONCLUSIONS

The development of fluid-bed zinc titanate and DSRP technologies is proceeding to the point where plans are underway for testing these technologies in the field with coal-derived gases. Zinc titanate produced by RTI’s granulation technique exhibits excellent sulfur capacity, regenerability, and attrition resistance up to 750 °C in simulated gas environments. The attrition resistance of the sorbent consistently increases with cycling. A very promising ZT-4 zinc titanate
sorbent formulation has shown attrition resistance comparable to a commercial "equilibrium" FCC catalyst after 50 cycles (~120 h of sulfidation and regeneration in a bubbling fluid bed). The zinc titanate sorbent manufacturing process can be used to produce commercial quantities of the sorbent with equipment currently available.

Experimental results in a bench-scale unit demonstrate the effectiveness of the DSRP in obtaining near 96 percent conversion in one stage of reaction. Thermal degradation of the catalyst was not observed in the liter-size adiabatic reactors. Laboratory results reported earlier, which were largely restricted to gases containing 2 percent SO$_2$, were confirmed in the relatively large bench unit. In another series of tests, the potential of the DSRP was demonstrated on gases containing up to 12.4 percent SO$_2$. Conversions were up to 96 percent of the theoretical limit in a single stage of reaction at relatively high gas space velocity. The effect of kinetic limitations on conversion is becoming more apparent. At times, increased space velocity yielded higher conversions. Reversal of conversion can occur in the second stage of reaction if sulfur is not effectively removed in the interstage condensers. By removing additional sulfur with the water at the interstage level, sulfur conversion did increase to 98.5 percent. Further improvement in interstage sulfur condensation and its subsequent removal will be required to achieve 99 percent or higher conversion. DOE/METC and RTI are vigorously pursuing technology transfer activities. The goal of these activities is to find industrial partners who would be willing to participate in the continued development of the sorbent and DSRP technologies toward a commercial process.

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REFERENCES


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