

Advanced Sulfur Control Processing

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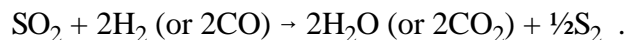
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Introduction

Advanced integrated gasification combined cycle (IGCC) power plants call for hot particulate removal and hot-gas desulfurization (HGD) following gasification in order to achieve high thermal efficiency. The Morgantown Energy Technology Center's (METC's) HGD research program has focused on the development of regenerable metal oxide sorbents to remove hydrogen sulfide (H₂S) from coal gas. Leading sorbents such as zinc titanate can reduce the H₂S in coal gas to low parts-per-million levels and can be regenerated using air for multicycle operation. The sulfidation-regeneration cycle for a generic metal oxide (MO) is as follows:



Because the regeneration reaction is highly exothermic, temperature control is required to prevent overheating and sorbent sintering. One way to control the temperature is to use a highly dilute air stream, typically containing up to 3 vol% oxygen. This would result in a tail gas containing up to 2 vol% sulfur dioxide (SO₂). More elegant methods to control exothermicity of air regeneration that could potentially produce up to 14 vol% SO₂ are being developed (Cook et al., 1992; Campbell et al. 1995). In any event, a problematic tail gas containing 2 to 14 vol% SO₂ is produced that must be disposed of. The most desirable treatment option for the tail gas is to convert the SO₂ to elemental sulfur. METC is sponsoring the development of the Direct Sulfur Recovery Process (DSRP) (Gangwal and Portzer, 1995) that uses the reducing components (H₂, CO) of coal gas to directly and efficiently reduce the SO₂ to elemental sulfur in the presence of a catalyst in one step:



In the DSRP, for every mole of SO₂, 2 mol of reducing components are used. DSRP is a leading first generation technology and is undergoing field testing at gasifier sites. This study seeks to develop more advanced HGD approaches leading to elemental sulfur recovery in IGCC systems.

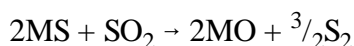
Objectives

The objective of this study is to develop a second generation HGD process that produces elemental sulfur without or with minimal use of coal gas and has better overall economics than DSRP when integrated with the overall IGCC system.

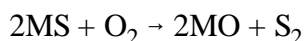
Approach

Direct production of elemental sulfur during sorbent regeneration was chosen as the approach for development of the required second generation HGD process. Concepts that were evaluated to produce elemental sulfur from sulfided sorbent included:

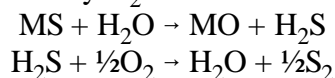
1. SO₂ regeneration



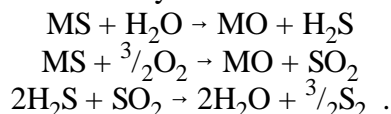
2. Substoichiometric oxidation



3. Steam regeneration followed by H₂S oxidation



4. Steam-air regeneration followed by Claus reaction



Preliminary assessment of these concepts indicated that Concept 1, SO₂ regeneration faced the fewest technical and economic problems among the four options (Gangwal et al., 1995). Elemental sulfur is the only likely product of SO₂ regeneration and the SO₂ required for the regeneration can be obtained by burning a portion of the sulfur produced. With SO₂ regeneration, sulfate formation, a major cause of sorbent decrepitation, does not occur. This should result in longer sorbent life. At high pressure, dry SO₂ is also simpler to separate from elemental sulfur than steam. Thus, recycle of unused SO₂ to the regenerator would be possible and this would be much less energy intensive than the use of steam. Efforts have thus concentrated on SO₂ regeneration.

Based on a theoretical evaluation of a number of potential sorbent candidates, iron- and zinc-based regenerable sorbents were chosen for experimental evaluation in this study (Gangwal et al., 1995). The selection criteria included desulfurization efficiency, SO₂ regenerability, cost, and knowledge base. Iron was considered to be the most promising candidate among numerous metals based on the above selection criteria. Also zinc remained a candidate for consideration (primarily in combination with iron) due to its excellent desulfurization efficiency, its extensive knowledge base, and its low cost, even though ZnS showed essentially no SO₂ regenerability at temperatures of interest. In combination with iron, zinc can act as a polishing agent to remove

H₂S down to very low levels and can be regenerated using air to produce SO₂ needed for regeneration of the iron sulfide. Thermogravimetric analyzer (TGA) and lab-scale reactor testing of a number of iron-zinc sorbents demonstrated the feasibility of direct regeneration of these sorbents using SO₂ to produce elemental sulfur (Gangwal et al., 1995). This year the experimental work has progressed to the bench-scale. A number of sorbents were prepared and tested at the bench-scale over multiple cycles. Work on development and multicycle testing of attrition-resistant zinc and iron sorbents is continuing. Based on results of bench-scale testing of promising sorbents, an economic evaluation for a 300 MWe plant is to be conducted next year.

Project Description

Summary of Previous Experiments

Laboratory experiments to test the SO₂ regeneration concept were carried out using a high-pressure TGA and a high-pressure lab-scale reactor (Gangwal et al., 1995). The reactor was made of a ½-in. stainless steel tube capable of operation at 750 °C and 200 psig. Provision was made for sulfiding up to 10 g of sorbent with simulated coal gas and regenerating the sulfided sorbent with up to 15 vol% SO₂. The gas exiting the reactor passed through heated tubing into a 130 °C convective oven where a 0.1-μm filter was used to collect sulfur. The gas finally vented through a back pressure regulator.

A number of proprietary sorbents based on iron and zinc oxides were prepared and tested for SO₂ regeneration. The benchmark zinc titanate and zinc ferrite sorbents were ZT-4 and L-7. These sorbents have been developed for fluidized-bed desulfurization incorporating air regeneration under a previous DOE contract. The sulfided ZT-4 sorbent which was based purely on ZnO as the active sorbent showed essentially no regeneration with 3.3 percent SO₂ in N₂ at up to 800 °C and 10 atm. However, sulfided iron- and zinc-iron-based sorbents showed good regeneration with SO₂. TGA rates of SO₂ regeneration ranged from 2.2×10^{-4} to 5.8×10^{-4} g sulfur/g sorbent/min with 3.3 vol% SO₂ at 700 °C and 10 atm.

A zinc-iron sorbent designated R-5 showed promising results and was tested further using the high-pressure lab-scale reactor. About 5 g of the sorbent was loaded in the reactor and fully sulfided using simulated coal gas. SO₂ regeneration was then started at 7.8 atm and 700 °C with 15 vol% SO₂ in N₂. Samples were withdrawn after 5.5 h and 10 h of regeneration for TGA analysis. As expected, the TGA analysis showed that the zinc portion of the sorbent was not regenerated but the iron portion of the sorbent regenerated at a rate of 2.1×10^{-4} g sulfur/g sorbent/min. This result is similar to rates with the high-pressure TGA. At the end of 10-h, sulfur plugging occurred and solid yellow sulfur was recovered downstream of the reactor.

The R-5 sorbent was also tested for SO₂ regeneration as a function of SO₂ concentration and for air regeneration. The SO₂ regeneration rate, as measured by the high pressure TGA, increased from 2.2×10^{-5} to 3.7×10^{-4} g sulfur/g sorbent/min at 650 °C and 10 atm when SO₂ concentration was increased from 3.3 to 15 vol%. The air regeneration rate at 10 atm and 700 °C was around 5×10^{-4} g sulfur/g sorbent/min with 2 vol% O₂ in N₂.

Process Concept

Based on the results presented above, the concept of SO₂ regeneration with iron- and zinc-based sorbents showed significant promise for development as an effective HGD system resulting in sulfur recovery with limited use of coal gas. A number of HGD processes could be conceptualized using alternative combinations of SO₂ and air regeneration. The similarity of air and SO₂ regeneration rates and the significant increase in SO₂ regeneration rate with SO₂ concentration were highly encouraging. It suggested that, with further increase in SO₂ concentration to 90 to 100 vol%, rates could be increased sufficiently to allow the use of even lower regeneration temperatures around 600 °C. This temperature is closer to the expected sulfidation temperature of iron sorbents which is around 450 °C. A conceptual three-reactor process based on sulfidation of iron-zinc sorbents followed by SO₂ regeneration followed by air regeneration is shown in Figure 1. The SO₂ regeneration produces sulfur from the iron portion of the sorbent and the air regeneration regenerates the zinc portion of the sorbent.

In this process concept, the sorbent from the sulfider at around 450 °C would have to be heated to around 600 °C for SO₂ regeneration. The required heat could be obtained using indirect heat exchange with coal gas which is being cooled to 450 °C, by injecting a small amount of O₂ along with SO₂ in the SO₂ regenerator, by indirect heat exchange with the sorbent being returned from the air regenerator to the sulfider, or using a convenient combination of these approaches. An alternative process concept with partial air (or O₂) regeneration of the sorbent to effect the required temperature increase and some zinc regeneration prior to SO₂ regeneration can also be visualized. A number of other process combinations are also possible but are not presented here in the interest of space.

Bench-Scale Testing

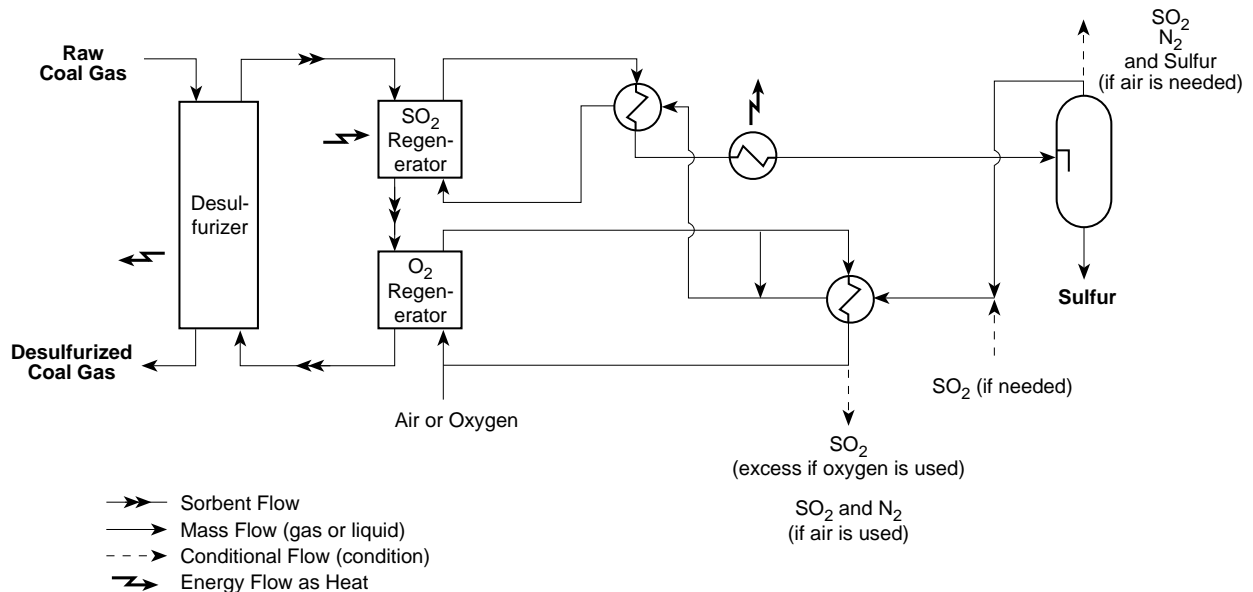


Figure 1. Three-Reactor System for SO₂ Regeneration Followed by O₂ Regeneration

Efforts this year have concentrated on scale-up of the R-5 sorbent preparation to

attrition-resistant fluidizable form, construction and commissioning of a high-temperature, high-pressure (HTHP) bench-scale unit and multicycle HTHP testing of the iron-zinc sorbents simulating the conceptualized three-reactor process of Figure 1.

The bench-scale reactor system which was built by modifying an existing unit is shown in Figure 2. The system has the capability of simulating a complex coal gas mixture using a set of mass flow controllers for gaseous components and a positive displacement pump for water to generate steam. The reactor can operate either as a fluidized-bed or as a fixed-bed with up to a 3-in. inside diameter sorbent cage. The pressure and temperature rating of the reactor is 400 psig at 750 °C and it is Alon-processed to reduce corrosion of the stainless steel. Reactor throughput up to 400 slpm of gas can be processed and sorbent up to 1.0 liter can be tested.

For SO₂ regeneration, pure SO₂ or SO₂ mixed with N₂ can be fed to the reactor by displacement of liquid SO₂ from a tank using a head pressure of nitrogen. Air regeneration (air line not shown in the figure) can also be carried out. Two separate reactor exits and downstream vent systems are utilized. SO₂ regeneration is conducted through a hot exit line with a sulfur condenser, catch pot, and a hot pressure control valve. This line is maintained hot to prevent sulfur plugging. Sulfidation and air regeneration are conducted through the other exit line. Gas samples are analyzed continuously for H₂S during sulfidation and SO₂ during air regeneration using Ametek continuous analyzers. Oxygen during air regeneration is measured continuously using a fuel cell-based analyzer and H₂S, COS, and SO₂ are measured intermittently during

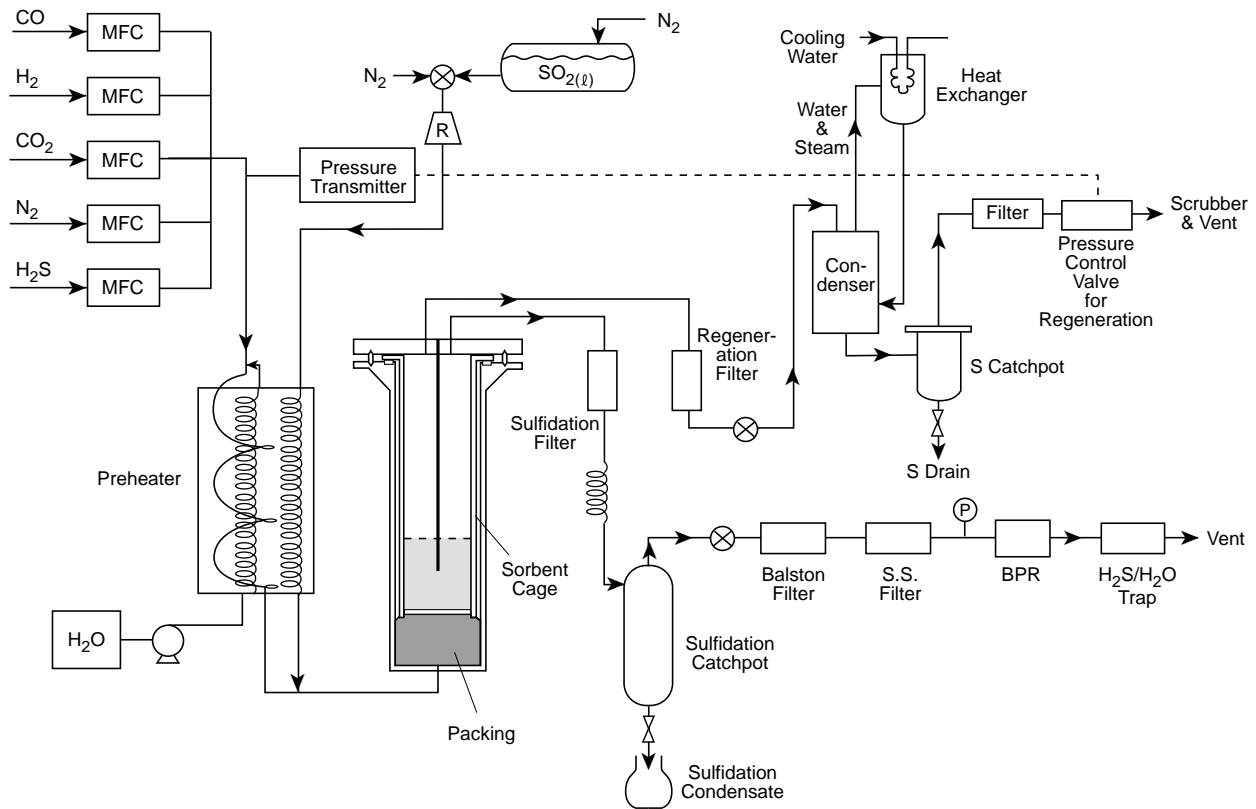


Figure 2. Bench-Scale Reactor System

sulfidation using a gas chromatograph with a flame photometric detector.

Results

Iron- and zinc-based sorbents were tested at HTHP conditions for multiple cycles. The sorbent preparation is proprietary and a patent application is pending, thus any information that could result in revealing the chemical composition and structure of the sorbents such as breakthrough curves and physical properties will not be presented. The R-5 sorbent recipe was scaled up to kilogram quantities of fluidizable attrition-resistant form with the help of a catalyst manufacturer. Two separate scale-up procedures were attempted. Using the first procedure, sorbents R-5-AWB, R-5-B, and R-5-C were produced in kilogram quantities. Using the second procedure, sorbents R-5-52, R-5-57, and R-5-58 were prepared in kilogram quantities.

R-5-B had poor attrition resistance and was immediately rejected. R-5-AWB, R-5-C, R-5-52, and R-5-58 were tested over multicycles simulating the three-reactor process of Figure 1 (R-5-57 is yet to be tested). The nominal test conditions for these multicycle tests are shown in Table 1.

The cycles typically consisted of sulfidation until breakthrough, followed by two types of regeneration. The first type of regeneration was a full air regeneration (up to 60 min) whereas the second type consisted of SO₂ regeneration (for 30 to 120 min followed by air regeneration for up to 60 min. Since a procedure for directly measuring elemental sulfur in a gas stream containing large amounts of SO₂ is yet to be developed, the amount of elemental sulfur produced during SO₂ regeneration was determined by actual measurement of the elemental sulfur that was collected or by the difference between the SO₂ produced by the two types of regeneration.

A total of 40 cycles have been run. The number of cycles completed with the various sorbents is shown in Table 2.

Table 1. Bench-Scale Test Conditions

Pressure:	275 psig	Coal gas composition (vol%)	
Flow rate:	18-75 slpm	CO:	15
Sorbent amount:	270-350 g	H ₂ :	10
Temperature (°C)		N ₂ :	Balance
Sulfidation:	420-460	CO ₂ :	10
SO ₂ regeneration:	625	H ₂ O:	10-15
Dilute air regeneration:	600-650	H ₂ S:	0.3
SO ₂ gas (vol%)		Oxidizing gas (vol%)	
SO ₂ :	50-65	O ₂ :	1-2
N ₂ :	Balance	N ₂ :	Balance

Because of the proprietary nature of the sorbents, the results presented here are of a general nature while patent protection is being sought. Generally each of the sorbents was able to reduce the H₂S to below 100 ppmv and was regenerable over multiple cycles. Also, measurable (several grams) quantities of elemental sulfur were produced during SO₂ regeneration of each of the sorbents. As much as 60 to 80 percent of the sulfur adsorbed by the sorbents has been recovered as elemental sulfur. However, the sorbents produced by the first procedure, namely R-5-AWB and R-5-C, underwent excessive loss in reactivity with cycles. In addition, they underwent significant attrition, as measured by a three-hole attrition tester, following cyclic testing. On the other hand, the sorbents prepared by the second procedure, namely R-5-52 and R-5-58, showed no loss in reactivity over the cyclic operation and also very low attrition, comparable to FCC catalysts, as measured both before and after cyclic testing by the three-hole attrition tester. In fact, the reactivity of both R-5-52 and R-5-58 improved with cycling.

Table 2. No. of Cycles Completed

Sorbent	Active metal	No. of cycles
R-5-AWB	Zn, Fe	5
R-5-C	Zn, Fe	17
R-5-52	Fe	10
R-5-58	Zn, Fe	8

Applications

As briefly discussed, the HGD process envisioned in Figure 1 or other similar processes that could result in direct production of elemental sulfur during regeneration have potential advantages over existing process options if they can be economically integrated with IGCC. The other options are production of undesirable calcium waste, production of sulfuric acid, or production of elemental sulfur using DSRP. Production of sulfuric acid is attractive if a market is readily available nearby. It may be difficult to find several such sites for IGCC plants. Elemental sulfur is the preferred option and DSRP is a highly efficient process but, as discussed earlier, requires the use of a small portion of the coal gas that results in an energy penalty to the power plant. Application of reactive and attrition-resistant sorbent such as R-5-58 to an IGCC with the capability to undergo direct SO₂ regeneration to elemental sulfur, where the SO₂ can be obtained by burning a portion of the elemental sulfur product, is a process option that needs to be developed further.

Future Activities

Approximately 15 cycles will be completed with sorbents R-5-58 and R-5-57 each. Then one of these sorbents will be tested for up to 50 cycles to demonstrate sorbent and process durability. Based on the results of testing, an economic evaluation for a 300 MWe plant will be conducted.

Acknowledgments

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References

- Cook, C.S., et al. 1992. Integrated Operation of a Pressurized Fixed-Bed Gasifier and Hot Gas Desulfurization System. In *Proceedings of the 12th Annual Gasification and Gas Stream Cleanup System Contractors' Review Meeting*. Vol. 1, DE93000228, p. 84.
- Campbell, W.M. et al. 1995. Hot-Gas Desulfurization Using Transplant Reactors. In *12th International Pittsburgh Coal Conference Proceedings*, pp. 1059-1064. September
- Gangwal, S.K., and J.W. Portzer. 1995. Slipstream Testing of Hot-Gas Desulfurization with Sulfur Recovery. In *Proceedings Advanced Coal-Fired Power Systems' 95 Review Meeting*, pp. 220-228, DOE/METC-95/1018 Vol. 1. NTIS/DE 95009732. Springfield, VA.
- Gangwal, S.K., B.S. Turk, and R. Gupta. 1995. Advanced Sulfur Control Concepts. In *Proceedings Advance Coal-Fired Systems' 95 Review Meeting*, pp. 622-630, DOE/METC-95/1018, Vol. 2, NTIS/DE 95009733. Springfield, VA.