

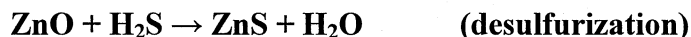
# 1. INTRODUCTION

## 1.1. Background

Gasification of heavy feedstock (e.g. coal, petcoke, resid, biomass, and others) produces a raw syngas that must be cleaned before it can be used to produce electricity in an IGCC power plant and/or synthetic liquid fuel using Fischer-Tropsch synthesis. The commercially proven process for gas cleaning involves quenching the gas to remove particulates and trace contaminants. Then a complex multi-step highly equipment intensive amine-based process consisting of an amine scrubber, regenerator, Claus plant and tail gas treatment plant to remove H<sub>2</sub>S and recover elemental sulfur follows. Also conventional amine systems cannot effectively remove COS which needs to be hydrolyzed first in a separate reactor.

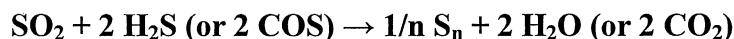
To reduce the cost of electricity and increase efficiency of IGCC systems, research has been conducted on solid sorbent-based desulfurization systems for the past two decades (*Cicero et al., 1999; Gangwal et al., 1997; Thambimuthu, 1993*). This research and development effort has been spear headed by the Department of Energy's (DOE) National Energy Technology Laboratory (NETL) and its predecessor agencies since 1980.

Sorbent-based desulfurization typically use a zinc-oxide-based sorbent and is carried out in a two-reactor system consisting of a desulfurizer and an air-regenerator:



Early developments emphasized fixed-bed reactors. The highly exothermic regeneration led to a move away from fixed beds toward moving beds (*Ayala et al., 1995*) and fluidized-beds (*Gupta and Gangwal, 1992*) fluidized-bed reactors, in particular transport reactors, are currently receiving the maximum emphasis (*Gangwal et al., 2002<sup>a</sup>*) due to several potential advantages including smaller foot print (lower cost), ability to continuously add and remove sorbent and ability to control the highly exothermic regeneration. However an attrition-resistant sorbent that can withstand stresses induced by fluidization, transport, chemical transformation, and rapid temperature swings must be developed.

Air regeneration leads to a problematic dilute SO<sub>2</sub> tail gas that must be disposed. Converting to a salable product- sulfuric acid or elemental sulfur- is an attractive option. Elemental sulfur is particularly attractive because it is the smallest volume sulfur product and because it can be stored easily, transported over long distances, readily disposed, or sold. Direct Sulfur Recovery Process (DSRP), a promising process, is currently in an advanced development stage to treat the SO<sub>2</sub> tail gas (*Gangwal and Portzer, 2002*). In this process, the SO<sub>2</sub> is catalytically reduced to elemental sulfur at the pressure and temperature condition of the tail gas using a small slipstream of the syngas:



The combined sorbent/DSRP process is slated to begin undergoing field-testing this year under a separate DOE contract with RTI (DE-AC26-99FT 40675). In this contract, a promising zinc-oxide sorbent called RTI-3 (*Gangwal et al., 2002<sup>a</sup>*) will be tested using a KBR transport reactor system at the ChevronTexaco Montebello 3 ton/day gasifier. DSRP will be tested on the full tail gas flow of about 2200 scfh.

## **1.2. Objective**

The original goal of this project was the development of simpler and economically superior processing of known regenerable sorbents used for sulfur control in advanced IGCC systems. The major objective was to produce an elemental-sulfur by product. Through contract modification the goal was broadened to also include a novel approach to produce elemental sulfur. These modifications directed an investigation into direct catalytic oxidation of H<sub>2</sub>S to elemental sulfur in the presence of the raw syngas components including H<sub>2</sub>, CO, H<sub>2</sub>O and CO<sub>2</sub>.

## **1.3. Project Tasks and Chronology**

The original project Tasks were as follows:

**Task 1. Assessment of Concepts**

**Task 2. Evaluation of Selected Concepts**

**Task 3. Laboratory Development**

**Task 4. Feasibility Demonstration**

**Task 5. Process Performance, Evaluation, and Economics**

Work on the first two tasks above led to the Advanced Hot-Gas Process (AHGP) concept, which aimed to avoid the problematic SO<sub>2</sub> tail gas from regeneration. AHGP was developed through laboratory and bench-scale testing in Tasks 3 and 4, and developed to the point of field-testing. A process model was developed and an economic evaluation was conducted in comparison to DSRP in Task 5. Section 2 describes the AHGP and its development in more detail.

As mentioned above, contract modifications directed an investigation into direct catalytic oxidation of H<sub>2</sub>S. This work led to the discovery of a highly promising process called Single-step Sulfur Recovery process (SSRP). This process works at lower temperature following quench of the high-pressure syngas. As the quench removes most of the trace contaminants and complies better with the DOE's Vision 21 plant, DOE's emphasis changed towards lower-temperature operation. As a result, the field test of the high-temperature AHGP was abandoned and project resources were directed toward development of SSRP. The SSRP work was conducted under the following Tasks:

**Task 1. Literature Review**

**Task 2. Lab-Scale Testing**

**Task 3. Bench-Scale Testing**

**Task 4. Preliminary Economic Evaluation**

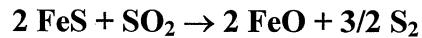
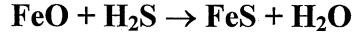
Tasks 1 to 3 of SSRP are described in detail in Section 3. Task 4 is described in Section 4.

## 2. ADVANCED HOT GAS PROCESS (AHGP)

### 2.1. Introduction

As mentioned in Section 1, DSRP results in a problematic dilute SO<sub>2</sub> tail gas that needs to be disposed and results in the energy penalty of consumption of 2 mol of reductants in syngas for every mol of sulfur. AHGP is a second-generation process that regenerates the sulfided sorbent directly to elemental sulfur using SO<sub>2</sub>. Thus a dilute SO<sub>2</sub> tail gas is not produced and potentially the energy penalty is avoided. SO<sub>2</sub> regeneration involves the reaction of nearly pure SO<sub>2</sub> with sulfided sorbent at elevated temperature and pressure. Under these conditions, elemental sulfur is the only product predicted from thermodynamics.

Some H<sub>2</sub>S sorbents based on metal oxides other than zinc oxide—iron oxide, for example—can be regenerated following sulfidation using SO<sub>2</sub> to directly produce the desirable elemental sulfur byproduct according to the following sulfidation and regeneration reactions:

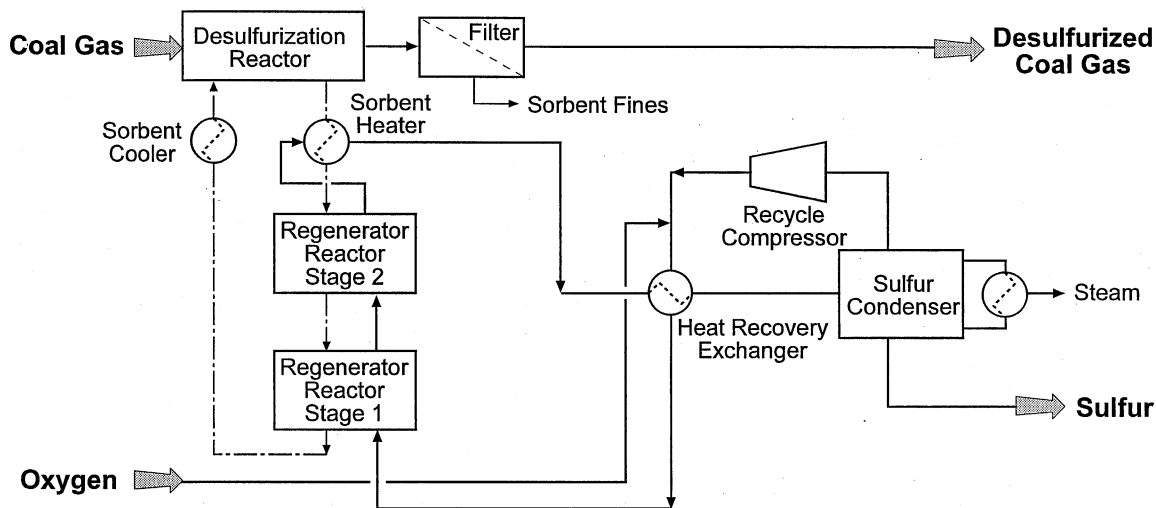


Based on a theoretical evaluation of a number of potential sorbent candidates, iron- and zinc-based regenerable sorbents were chosen for experimental evaluation. Iron oxide was considered the most promising candidate based on a combination of factors—desulfurization efficiency, SO<sub>2</sub> regenerability, cost, and knowledge base. Zinc oxide is a leading candidate due to its excellent desulfurization efficiency, its extensive knowledge base, and its low cost.

Although zinc sulfide (ZnS) shows essentially no SO<sub>2</sub> regenerability at temperatures of interest, zinc oxide can act as a polishing agent when combined with iron oxide to remove H<sub>2</sub>S down to very low levels. Advantageously, the ZnS can be regenerated using air to produce the SO<sub>2</sub> needed for regeneration of the iron sulfide (FeS).

### 2.2. Process Description

Based on a feasibility study, initial laboratory testing, and successful bench-scale testing of several sorbent formulations, AHGP was conceptualized as shown in Figure 2.1. The primary elements of the process are a single desulfurization reaction stage, but two stages of regeneration: an SO<sub>2</sub> regeneration stage, and an oxygen regeneration stage. The sulfided sorbent flows counter-currently to an internally recirculating regeneration gas (high concentration SO<sub>2</sub>). The desulfurization of the coal gas (sulfidation of the sorbent) takes place at about 450°C at the pressure of the coal gas (typically 2.0 MPa) in the desulfurization reactor. This would most likely be a “transport” type fluidized-bed reactor, resulting in a research focus on attrition-resistant sorbents.



**Figure 2.1.** Conceptualized Advanced Hot Gas Process (AHGP)

The sulfided sorbent enters a multistage reaction vessel to be heated to 600°C using waste heat from the regenerated sorbent. This reactor is envisioned to be a bubbling-type fluidized bed. The heated sorbent passes to Stage 2 of the regenerator to contact the re-circulating SO<sub>2</sub> gas stream. The elemental sulfur formed exits in the gaseous state. The partially regenerated sorbent then passes into Stage 1 (the lowest stage) of the regenerator, where oxygen is added to the regeneration gas. In this heat-integrated process, the energy from the exothermic O<sub>2</sub> regeneration is used to drive the endothermic SO<sub>2</sub> regeneration. The regenerated sorbent is then cooled and re-circulated to the desulfurization reactor.

The regeneration off-gas exiting from Stage 2 is cooled to condense out the sulfur, which is removed as a molten product. The exit gas from the sulfur condenser is then compressed slightly (to recover the pressure drop losses from re-circulation) and is reheated by countercurrent exchange with the hot regeneration off-gas. With control of the ratio of iron and zinc in the sorbent, and by balancing the amount of oxygen supplied to Stage 1 with the amount of elemental sulfur that is actually being produced, the SO<sub>2</sub> material balance of the re-circulation loop can be maintained. For startup purposes, an external supply of liquid SO<sub>2</sub> could be used to charge the re-circulation loop.

### 2.3. Development of AHGP

The development of AHGP was carried out under the following Tasks:

- Task 1. Assessment of Concepts**
- Task 2. Evaluation of Selected Concepts**
- Task 3. Laboratory Development**
- Task 4. Feasibility Demonstration**
- Task 5. Process Performance, Evaluation and Economics**

Work under Tasks 1 and 2 is described in detail in Appendix A. Concepts to recover sulfur (as elemental sulfur) from sulfided sorbents without producing the problematic SO<sub>2</sub> tail gas were assessed and evaluated. The following alternative regeneration concepts were evaluated for the sulfided sorbent:

- Partial oxidation.
- Steam regeneration.
- SO<sub>2</sub> regeneration.

Based on this evaluation, all alternative regeneration concepts were eliminated except for SO<sub>2</sub> regeneration. Laboratory development of the SO<sub>2</sub> regeneration concept was conducted under Task 3 using thermogravimetric analysis (TGA) and a high-pressure lab-scale reactor as shown in Appendix A. Zinc and iron sorbents were chosen as the primary candidates for the SO<sub>2</sub> regeneration concept, based on literature information and thermodynamic calculations. Several sorbents were prepared and screened. Laboratory tests of SO<sub>2</sub> regeneration of a promising zinc-iron sorbent (R-5) showed that the iron portion of the sorbent could be completely regenerated with SO<sub>2</sub>. The zinc portion was regenerated using O<sub>2</sub>. This two-step regeneration led to the concept of the AHGP (Figure 2.1).

A high-temperature, high-pressure (HTHP) bench-scale reactor system was commissioned to test the AHGP under Task 4. Numerous test cycles were conducted for candidate sorbents as described in Appendix B. This led to the development of a proprietary R-5-58 sorbent, which was tested for 50 cycles as described in detail in Appendices C and D. The SO<sub>2</sub> regeneration step accounted for 55 to 70% of the total regeneration of the sorbent compared to a theoretical limit of 80% based on complete regeneration of the iron component by SO<sub>2</sub>.

Sorbent improvement studies to further improve both reactivity and attrition-resistance were conducted as detailed in Appendix D. Numerous sorbents were prepared and tested. The total active metal component of R-5-58 was 20 wt% (ZnO + Fe<sub>2</sub>O<sub>3</sub>) on an inert support. Attempts were made to prepare attrition resistant sorbents with higher ZnO and Fe<sub>2</sub>O<sub>3</sub> (closer to 90% total) and a silica-based binder. Cyclic tests of these sorbents showed that although attrition resistance was improved, the reactivity was reduced due to the reaction of the silica with the zinc and iron.

Simultaneous to these studies, an engineering and economic comparison of AHGP with DSRP was conducted under Task 5 as detailed in Appendices E and F. Aspen Plus process simulations of DSRP and AHGP revealed the complexity of both HGD process. The capital cost of AHGP was higher than that of DSRP but operating costs were lower. For high sulfur coal (>3%), a preliminary comparison shows that the total cost of implementing AHGP will be less than that of DSRP after just 2 years of operation. AHGP however is more complex as a process.

Plans were made for a field test of AHGP at the Power System Development Facility (PSDF). At about this time, a more promising process called SSRP was discovered and field test plans for AHGP were abandoned in favor of SSRP. SSRP development is described in detail in the next section. The rest of this report is dedicated to SSRP.