

**APPENDIX F** Advances in Hot Gas Desulfurization with Elemental Sulfur  
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## **Advances in Hot Gas Desulfurization with Elemental Sulfur Recovery**

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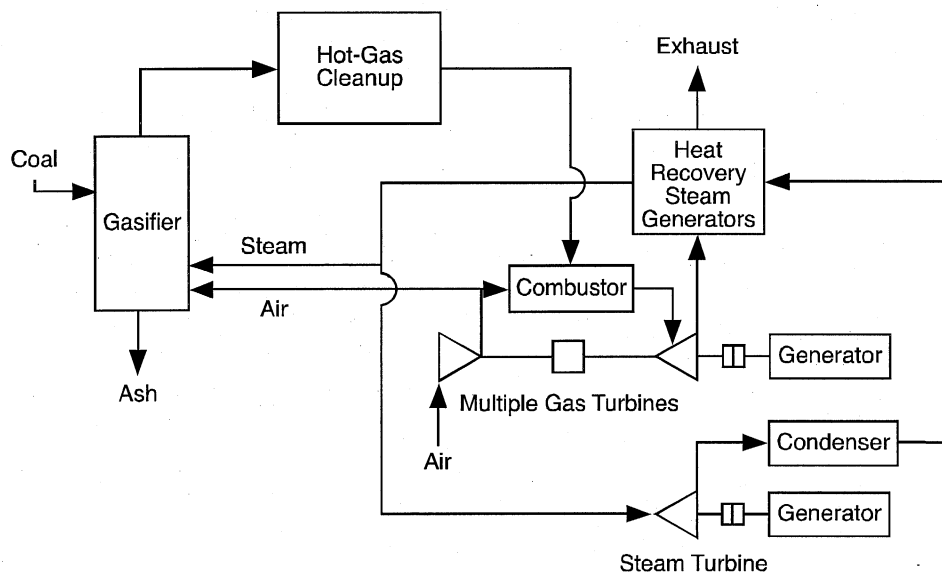
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### **INTRODUCTION**

Hot-gas desulfurization (HGD) of coal gas in integrated gasification combined cycle (IGCC) power systems has received a great deal of attention over the past two decades due to the potential for high thermal efficiency (up to 47%) and low environmental impact of these advanced power systems. In an advanced IGCC system, coal is gasified at elevated pressures, typically 20 to 30 atm, to produce a low-volume fuel gas that is desulfurized prior to burning in a combustion turbine to produce electricity. Higher efficiency and lower cost are achieved by efficient air and steam integration, and modular designs of the gasification, hot-gas cleanup, and turbine subsystems (Figure 1). Hot gas cleanup primarily involves removal of particulates and sulfur—mostly hydrogen sulfide ( $H_2S$ ) and some carbonyl sulfide (COS).  $H_2S$  and COS can be efficiently removed to less than 20 ppmv at 350 to 650 °C using zinc-based metal oxide sorbents that can be regenerated for multicycle operation.

Air regeneration of these sorbents results in a dilute sulfur dioxide ( $SO_2$ )-containing tail gas that needs to be disposed. Options include conversion of the  $SO_2$  to calcium sulfate using lime (or limestone) for landfilling or conversion to saleable products such as sulfuric acid or elemental sulfur. Elemental sulfur, an essential industrial commodity, is an attractive option because it is the lowest volume product and can be readily stored, disposed, transported, and/or sold.

Research Triangle Institute (RTI), with U.S. Department of Energy (DOE) sponsorship, is pursuing the development of two processes for elemental sulfur production in conjunction with hot-gas desulfurization. The first process, called the Direct Sulfur Recovery Process (DSRP), involves the selective catalytic reduction of the  $SO_2$  tail gas to sulfur using a small slipstream of the coal gas. DSRP is a highly efficient process that can recover up to 99% of  $SO_2$  as elemental



**Figure 1. Advanced IGCC system.**

sulfur in a single catalytic reactor. However, for every mole of sulfur produced two moles of hydrogen ( $H_2$ ) and/or carbon monoxide (CO) are consumed in DSRP and this represents an energy penalty for the IGCC plant. DSRP is currently in an advanced state of development.

A second-generation process being pursued by RTI involves the use of a modified zinc-based sorbent (containing zinc and iron). This sorbent can be regenerated using  $SO_2$  and  $O_2$  to directly produce sulfur. This process, called the Advanced Hot-Gas Process (AHGP), is expected to use much less coal gas than DSRP. DSRP is currently at the pilot-plant scale development stage, whereas AHGP has been demonstrated at small bench-scale. Both DSRP and AHGP are scheduled for slipstream testing at DOE's Power Systems Development Facility (PSDF), Wilsonville, Alabama, in 1999.

This paper summarizes the results of DSRP field testing and the recent laboratory development efforts for the DSRP and the AHGP. In addition, this paper presents the results of a preliminary engineering and economic evaluation of the two processes used in conjunction with an IGCC power plant employing HGD. The computer process simulations used to develop the mass and energy balances, and economic evaluations were carried out by RTI's subcontractor, North Carolina State University (NCSU).

## BACKGROUND

### Sorbent Development

Research on HGD methods for coal gas in IGCC systems has concentrated on the use of regenerable metal oxide sorbents (Gangwal, 1991, 1996; Gangwal et al., 1993, 1995; Harrison, 1995; Jalan, 1985; Thambimuthu, 1993). This research and development effort has been spearheaded by DOE's Federal Energy Technology Center (FETC) and its predecessor agencies since 1975.

The HGD process using a regenerable metal oxide (MO) sorbent is typically carried out in a two-reactor system consisting of a desulfurizer and an air regenerator



The main requirement of the metal oxide sorbent is that it should selectively react with  $\text{H}_2\text{S}$  and  $\text{COS}$  in a reducing fuel gas at desired conditions (2 to 3 Mpa, 350 to 750 °C). The thermodynamics of the reaction should be favorable enough to achieve the desired level of  $\text{H}_2\text{S}$  and  $\text{COS}$  removal (as much as 99% or more). The metal oxide should be stable in the reducing gas environment, i.e., reduction of MO to M should be slow or thermodynamically unfavorable since it leads to loss of valuable fuel gas and could also lead to volatile metal evaporation and decrepitation of sorbent structure.

The principle requirement during air regeneration is that the sorbent should predominantly revert back to its oxide rather than to sulfate ( $\text{MO} + \text{SO}_2 + 1/2 \text{O}_2 \rightarrow \text{MSO}_4$ ). Air regeneration is highly exothermic and requires tight temperature control using large quantities of diluent ( $\text{N}_2$ ) or other means to prevent sorbent sintering and sulfate formation.

The bulk of research on regenerable sorbents has been on zinc-based sorbents because sorbents based on zinc oxide appear to have the fewest technical problems among all sorbents. Zinc oxide ( $\text{ZnO}$ ) has highly attractive thermodynamics for  $\text{H}_2\text{S}$  adsorption and can reduce the  $\text{H}_2\text{S}$  to parts-per-million levels over a very wide temperature range. Iron oxide appears to be the most popular sorbent for use at around 400 °C.

A combined  $\text{ZnO}$ -iron oxide ( $\text{Fe}_2\text{O}_3$ ) sorbent, namely, zinc ferrite ( $\text{ZnFe}_2\text{O}_4$ ) was developed by Grindley and Steinfeld (1981) to combine the advantages of  $\text{ZnO}$  and  $\text{Fe}_2\text{O}_3$ . A temperature range of 550 to 750 °C received the major research emphasis in the United States during the 1980s and early 1990s. Because of zinc oxide's potential for reduction ( $\text{ZnO} + \text{H}_2 \rightarrow \text{Zn} + \text{H}_2\text{O}$ ) at >600 °C followed by evaporation, a zinc oxide-titanium oxide sorbent, namely zinc titanate sorbent, was developed and tested at high temperature and high pressure (HTHP) (Gangwal et al., 1988). Zinc titanate is currently one of the leading sorbents.

During recent years, research emphasis has shifted toward lower temperatures (350 to 550 °C) based on a study in the Netherlands (NOVEM, 1991). According to this study, the thermal efficiency of an 800-MWe IGCC plant increased from 42.75% using cold-gas cleanup to 45.14% using HGD at 350 °C and to 45.46% using HGD at 600 °C. The small efficiency increase from 350 to 600 °C suggested that temperature severity of HGD could be significantly reduced without much loss of efficiency.

## Reactor and Systems

A two-reactor configuration is necessary for HGD due to its cyclic nature. Early developments emphasized fixed beds. The highly exothermic regeneration led to a move away from fixed beds toward moving beds (Ayala et al., 1995; Cook et al., 1992) and fluidized beds (Gupta and Gangwal, 1992). Two DOE Clean Coal Technology IGCC demonstration plants, namely Tampa Electric and Sierra-Pacific, employing General Electric's (GE's) moving-bed HGD reactor system and M.W. Kellogg's transport reactor HGD system, respectively, are scheduled to begin operation this year. Fluidized-bed HGD systems are receiving a lot of emphasis due to several potential advantages over fixed- and moving-bed reactors, including excellent gas-solid contact, fast kinetics, pneumatic transport, ability to handle particles in gas, and ability to control the highly exothermic regeneration process. However, an attrition-resistant sorbent that can withstand stresses induced by fluidization, transport, chemical transformation, and rapid temperature swings must be developed.

Development of an iron-oxide sorbent-based fluidized-bed HGD reactor system has been carried out in Japan over the past several years (Sugitani, 1989). The process is now up to 200 tons of coal per day. The sorbent is prepared by crushing raw Australian iron oxide which is inexpensive, but attrition is a big problem with this sorbent. Durable zinc titanate and other zinc-based sorbent development is ongoing for application at the Sierra-Pacific plant for Kellogg's transport reactor (Gupta et al., 1996, 1997; Jothimurugesan et al., 1997; Khare et al., 1996).

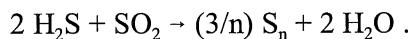
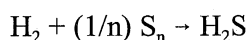
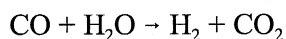
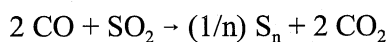
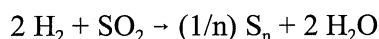
A schematic of Kellogg's transport reactor system at Sierra-Pacific is shown in Figure 2. This technology represents a significant development in HGD because it allows regeneration with neat air. Neat air regeneration produces a more concentrated SO<sub>2</sub> tail-gas stream containing around 14 vol% SO<sub>2</sub>.

The initial sorbent tested at Sierra-Pacific was Phillips Z-Sorb III. Its attrition resistance was not acceptable. Phillips is continuing efforts to improve their sorbent. Recently RTI and Intercat have provided a much more attrition-resistant zinc titanate sorbent, EX-SO3, to Sierra-Pacific for testing after qualifying it through a series of bench- and process development unit (PDU)-scale tests (Gupta et al., 1997). This sorbent has been circulated in the system and has demonstrated satisfactory attrition resistance. Chemical reactivity tests with the sorbent are to be conducted shortly after the Sierra coal gasifier is fully commissioned and begins smooth operation.

## SULFUR RECOVERY PROCESSES AND RECENT DEVELOPMENT

### Direct Sulfur Recovery Process

The patented DSRP being developed by RTI is a highly attractive option for recovery of sulfur from regeneration tail gas. Using a slipstream of coal gas as a reducing agent, it efficiently converts the  $\text{SO}_2$  to elemental sulfur, an essential industrial commodity that is easily stored and transported. In the DSRP (Dorchak et al., 1991), the  $\text{SO}_2$  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:



RTI constructed and commissioned a mobile laboratory for DSRP demonstration with actual coal gas from the DOE-Morgantown coal gasifier. Slipstream testing using a 1-L fixed-bed of DSRP catalyst 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% can be consistently achieved in a single DSRP stage. The single-stage process, as it is proposed to be integrated with a metal oxide sorbent regenerator, is shown in Figure 3. With the tail-gas recycle stream shown in the figure, there are no sulfur emissions from the DSRP.

RTI also demonstrated the ruggedness of the DSRP catalyst by exposing it to

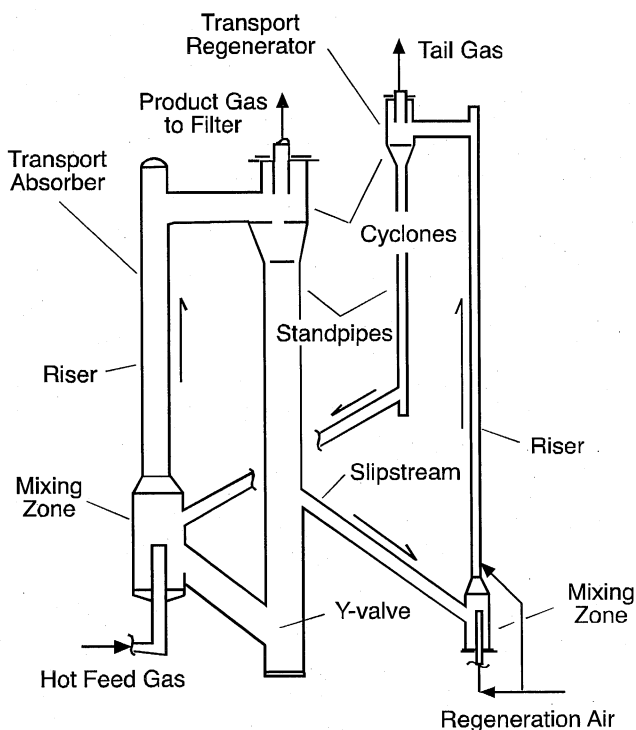


Figure 2. Schematic of Sierra hot-gas desulfurization system.

coal gas for over 250 hours in a canister test. The results 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<sub>2</sub> in a simulated regeneration tail gas to elemental sulfur. This demonstration of a rugged, single-stage catalytic process resulted in additional online 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 tail gas.

Canisters of fixed-bed DSRP catalyst have been prepared for another exposure test with actual coal gas, this time at FETC's Power Systems Development Facility (PSDF) at Wilsonville, Alabama. Exposure is expected to take place in the 1999-2000 time frame.

Additional development and testing of a fluidized-bed process is planned, capable of producing elemental sulfur from 14 vol% SO<sub>2</sub> at HTHP. These tests intend to demonstrate the use of DSRP in conjunction with the Kellogg transport regenerator that produces 14 vol% SO<sub>2</sub>. Due to the exothermic nature of the DSRP reactions, a fluidized-bed reactor is a preferred configuration at these high SO<sub>2</sub> concentrations. Two candidate attrition-resistant fluidizable DSRP catalysts have been prepared in cooperation with a catalyst manufacturer. A series of tests was conducted using these catalysts with up to 14 vol% SO<sub>2</sub> tail gas, at pressures from 1.0 to 2.0 Mpa, temperatures from 500 to 600 °C, and space velocities from 3,000 to 6,000 std cm<sup>3</sup>/cm<sup>3</sup>. Sulfur recoveries up to 98.5% were achieved during steady-state operation, and no attrition of the catalyst occurred in the fluidized-bed tests.

Planning is underway to conduct a long-duration field test using a skid-mounted six-fold larger (based on reactor volume) (6X) DSRP unit with a slipstream of actual coal gas at PSDF. The

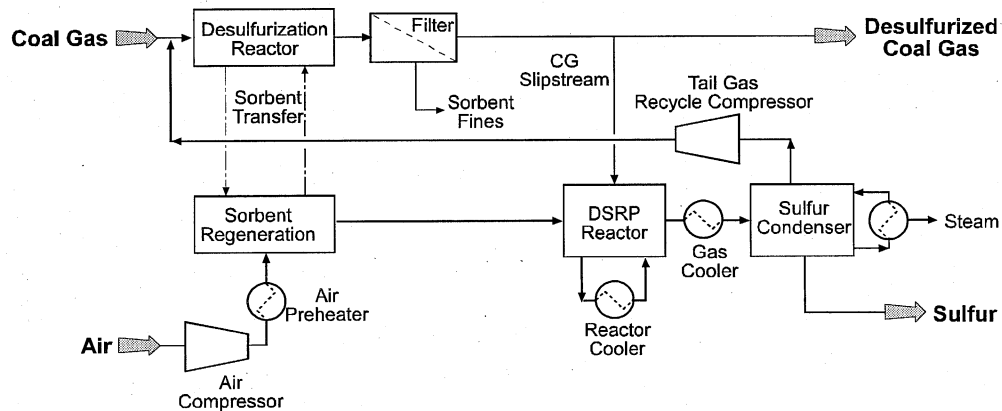
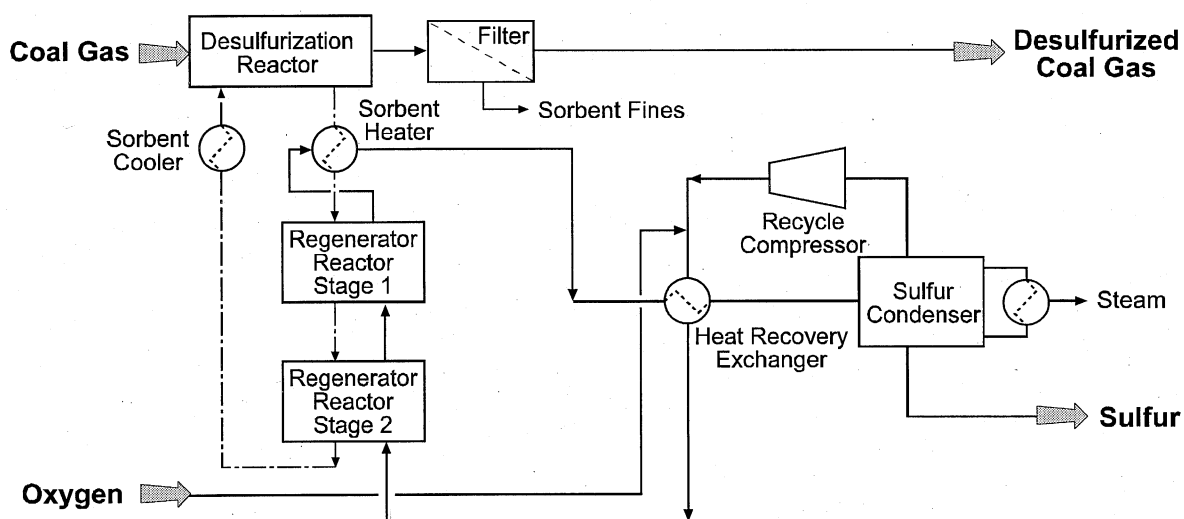


Figure 3. Hot-gas desulfurization with DSRP.

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 the 1999-2000 time frame. This larger unit will utilize a fluidized-bed reactor and will be designed for production of up to 22 times more sulfur than the 7.5-cm I.D. bench-scale unit used in the previous slipstream tests.

### Advanced Hot-Gas Process

In the DSRP, for every mole of  $\text{SO}_2$ , 2 mol of reducing components are used, leading to a small but noticeable consumption of coal gas. Novel regeneration processes that could lead to elemental sulfur without use of coal gas or with limited use of coal gas are being developed (Gangwal et al., 1996; Harrison et al. 1996). KEMA's hot-gas cleanup process (Meijer et al., 1996) uses a proprietary fluidized-bed sorbent that can remove  $\text{H}_2\text{S}$  to below 20 ppmv and that can be regenerated using  $\text{SO}_2$ - $\text{O}_2$  mixtures to produce elemental sulfur directly. Along similar lines, a second-generation process, known as the Advanced Hot-Gas Process (AHGP), is being developed by RTI to regenerate the desulfurization sorbent directly to elemental sulfur with minimal consumption of coal gas. In this process (Figure 4), a zinc-iron sorbent is used and the regeneration is carried out in two stages with  $\text{SO}_2$  and  $\text{O}_2$ , respectively. The iron sulfide is regenerated by  $\text{SO}_2$  in one stage to elemental sulfur. In the other stage, zinc sulfide and any remaining iron sulfide are regenerated by  $\text{O}_2$  to provide the required  $\text{SO}_2$ . The sorbent is then returned to the desulfurizer.

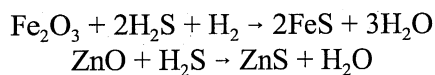


**Figure 4. Advanced hot-gas process.**

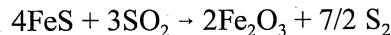
The key chemical reactions of interest are as follows:

1. Sulfidation

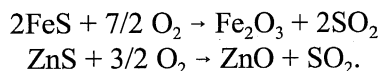




2. SO<sub>2</sub> regeneration



3. O<sub>2</sub> regeneration



The feasibility of SO<sub>2</sub> regeneration of combined zinc-iron sorbents was demonstrated using a thermogravimetric analyzer and high-pressure microreactor. Zinc sulfide shows essentially no SO<sub>2</sub> regeneration at temperatures of interest (500 to 600 °C), but zinc is needed to act as a polishing agent in the desulfurizer. A number of sorbents were prepared and tested at the bench scale over multiple cycles. Based on these tests, a highly attrition-resistant sorbent (R-5-58) was prepared and the process was demonstrated over 50 cycles in a 7.5-cm I.D. bench-scale reactor.

The results showed that R-5-58 removed H<sub>2</sub>S down to 50 to 100 ppm levels with stable desulfurization activity over the duration. The surface area and pore volume of the sorbent did not change appreciably and the attrition index before and after the test was 3.6% and 1.2%, respectively. Sulfur balances were adequate and the SO<sub>2</sub> regeneration step accounted for up to 70% of the total regeneration of the sorbent. This compares to a theoretical limit of approximately 80%, assuming complete regeneration by SO<sub>2</sub> of the iron component.

The sorbent is being optimized further to increase its desulfurization efficiency. The goal is to develop a sorbent that can remove H<sub>2</sub>S below 20 ppmv. Plans call for demonstrating the process at PSDF with a slipstream of actual coal gas in FY 1999 in conjunction with the DSRP field test at PDSF.

## ENGINEERING EVALUATION/COMPARISON

### Approach

An engineering and economic evaluation of the DSRP (Figure 3) and AHGP (Figure 4) for large-scale IGCC plants was conducted by NCSU using ASPEN PLUS<sup>®</sup> computer process simulation software and published generalized cost estimating methods (Gangwal, *et al*, 1998). For both processes the scope of the equipment and process steps included in the simulations were the same: coal gas desulfurization (but not the high temperature particulate removal), regeneration of the desulfurizing sorbent, and production, isolation, and short term storage of elemental sulfur. The recovered sulfur was assumed to have a market value, and thus generate a cost credit. Coal gas consumed in the process was evaluated at a cost based on the potential power generation that was lost. High pressure steam generated in the process was assumed to provide a cost credit based on the power that could be recovered from it.

Base case simulations of both processes assumed 0.85 mol% H<sub>2</sub>S in the coal-gas feed. Such an H<sub>2</sub>S concentration in the coal gas would be produced by an oxygen-blown Texaco gasification using a roughly 3.6 wt% sulfur-containing coal. Both base cases generate 260 MWe from the clean coal gas. Simulations that deviate from the base cases use suffixes to denote the changes. Table 1 displays the significance of the suffixes. In all cases a coal-gas feed pressure and temperature of 275 psia and 482 °C, respectively, was used. However, H<sub>2</sub>S concentration was varied from 0.25 to 2.5 mol% and power produced was varied from 110 to 540 MWe. Table 2 shows the composition and flow rate of the raw coal gas feed to the base case HGD processes. The requirement of a higher amount of coal gas to produce the same 260 MW power by DSRP versus the AHGP is noteworthy. The DSRP was assumed to use the standard Sierra-Pacific dual transport reactor configuration shown in Figure 2 for HGD. The DSRP reactor used for the 14% SO<sub>2</sub> tail gas was a fast fluidized bed with an alumina-based catalyst.

The AHGP reactor configuration on the other hand used a transport sulfider and a bubbling multistage fluidized-bed regenerator as shown in Figure 5. This vessel combines two stages of regeneration with one stage of heat transfer (to recover a portion of the heat of reaction as preheat for the sorbent). The large cross-sectional area bubbling reactor was required to provide a greater residence time for the slow SO<sub>2</sub> regeneration stage.

## Results

The preliminary process and economic evaluations conducted using ASPEN PLUS are

**Table E-1. Simulation Cases Considered**

Simulations	H <sub>2</sub> S feed concentration (mol%)	MW produced
DSRP, AHGP (base cases)	0.85	260
DSRP-b, AHGP-b	2.50	260
DSRP-c, AHGP-c	0.25	260
DSRP-100, AHGP-100	0.85	110
DSRP-500, AHGP-500	0.85	540

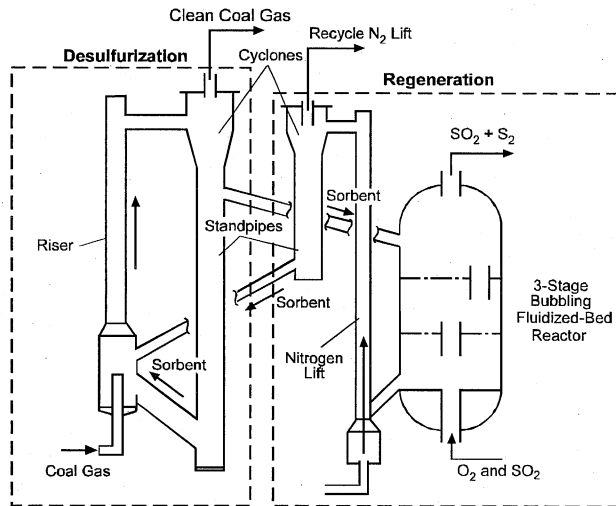
**Table E-2. Raw Gas Feed to Base Case Simulations**

Component	DSRP (lb/h)	AHGP (lb/h)
H <sub>2</sub> S	6,300	6,100
H <sub>2</sub> O	70,500	69,000
H <sub>2</sub>	11,800	11,500
CO	218,200	213,400
CO <sub>2</sub>	117,400	114,800
N <sub>2</sub>	36,300	35,500
Total	460,500	450,300

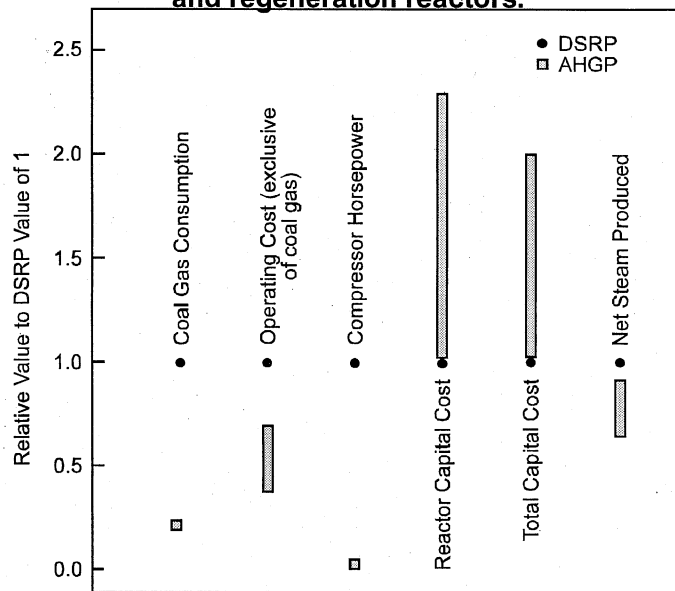
summarized. Figure 6 compares key elements using a simple method in which each parameter for the DSRP-based process is arbitrarily assigned the value of 1.0. A range of values is produced for AHGP to cover the various cases being considered. The big advantage of the AHGP is clearly the reduced parasitic consumption of coal gas. The other operating cost elements are also lower for AHGP, because that process has a considerably lower compression power requirement. A desulfurization process based on the DSRP requires a large flow of compressed air to provide the oxygen necessary to regenerate the sulfided sorbent, and thus has a large compressor horsepower duty. By comparison, the AHGP uses oxygen only for a smaller, polishing regeneration and, by using pure oxygen, the compression duty is lowered further. The AHGP also has the SO<sub>2</sub> loop recycle compressor, but its duty is quite small compared to the DSRP air compressor.

The value of "capital cost of all equipment" for the AHGP is higher than for the DSRP-based process, as Figure 5 shows. The higher equipment cost is primarily due to the higher cost of the AHGP reactor vessel(s). Although there are three separate reactor steps required with the DSRP-based process, the single AHGP multistage reactor vessel(s) is larger. The larger size is primarily due to the longer residence time required for the SO<sub>2</sub> regeneration.

Another advantage of the DSRP is that it is the easier, more understood, process to operate. This is because balancing the SO<sub>2</sub> production and consumption in the AHGP may be difficult.



**Figure 5. Schematic of AHGP desulfurization and regeneration reactors.**



**Figure 6. Comparison of key elements of DSRP and AHGP.**

Presumably a simpler process would have lower operating labor costs.

Although the AHGP has a higher initial cost, indicated by its larger capital requirements, it has a significantly lower annual operating cost than DSRP. As Figure 7 shows, the operating cost advantage of the AHGP increases as the sulfur to be recovered increases. The negative annual costs of AHGP at higher sulfur feed result from the sulfur credit with less consumption of coal gas. The operating cost difference is large enough to offset the installation cost of AHGP. As Figure 8 shows, AHGP has a lower cumulative HGD investment after only 2 years of operation. Both Figures 7 and 8 are presented to illustrate only cost comparison of the two processes. Emphasis should not be placed on the accuracy of the absolute cost numbers presented in these figures.

### CONCLUSIONS

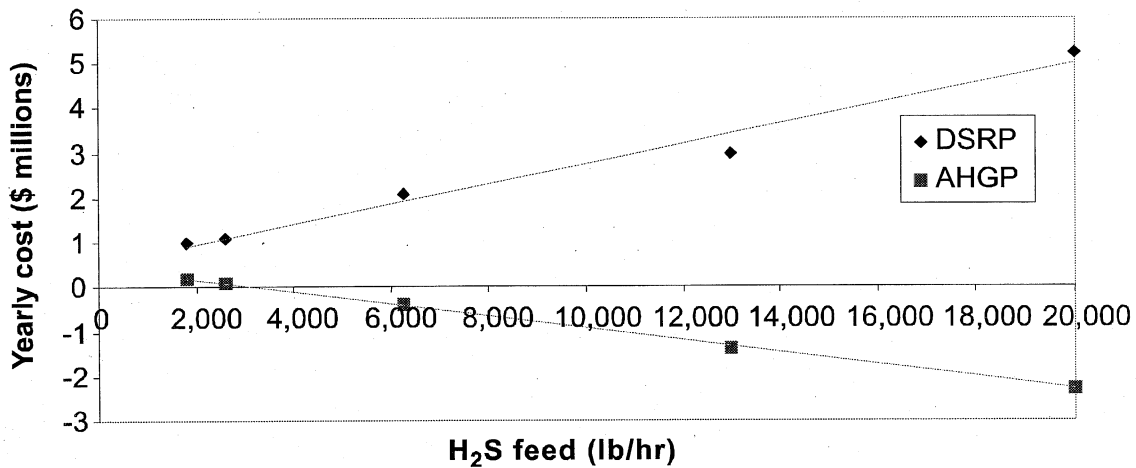


Figure 7. Annual costs as a function of sulfur feed.

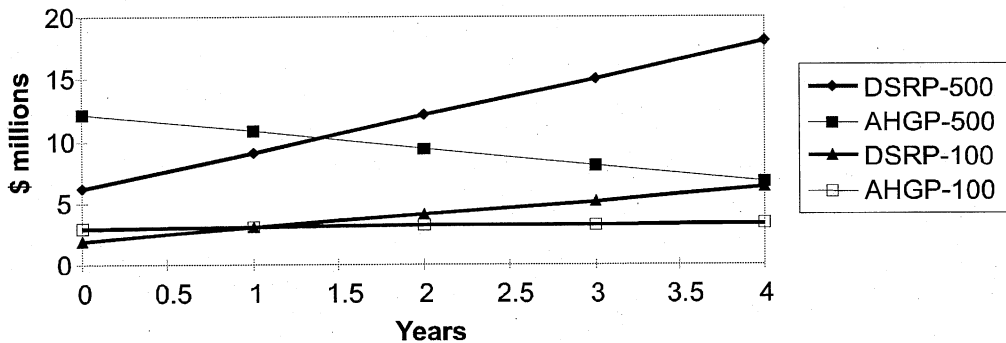


Figure 8. Cumulative HGD investment.

ASPEN simulations of DSRP and AHGP revealed the complexity of both HGD processes. The AHGP appears to be the more difficult process to operate and may require more employees than the DSRP. Capital costs for the AHGP are higher than those for the DSRP—development of DSRP is also much closer to commercialization than AHGP. However, annual operating costs for the AHGP appear to be considerably less than those of the DSRP. Preliminary economic comparison shows that the total cost (capital plus cumulative operating cost) of implementing AHGP will be less than that of implementing DSRP after as little as 2 years of operation. Thus, despite its greater complexity, the potential savings with the AHGP encourage further development and scaleup of this advanced process.

## REFERENCES

- Ayala, R.E., A.S. Feitelberg, and A.H. Furman. 1995. "Development of a High-Temperature Moving-Bed Coal Gas Desulfurization System." In *Proceedings of 12th Ann. Int. Pittsburgh Coal Conf.*, p. 1053, September 11-15, Pittsburgh.
- Cook, C.S., et al. 1992. "Integrated Operation of a Pressurized Fixed Bed Gasifier and Hot Gas Desulfurization System." In *Proceedings of 12th Annual Gasif. Gas Stream Cleanup Systems Contractor's Review Meeting*, Volume 1, DE93000228, p. 84.
- Dorchak, T.P., S.K. Gangwal, and W.J. McMichael. 1991. The Direct Sulfur Recovery Process. *Environmental Progress* 19(2):68.
- Gangwal, S.K. 1991. "Hot-Gas Desulfurization Sorbent Development for IGCC Systems." IChemE Symposium Series No. 123. Sheffield, UK, pp. 159-170.
- Gangwal, S.K. 1996. "Sulfur Removal from Gas Streams at High Temperature," 3rd International Symposium on Gas Cleaning at High Temperature. University of Karlsruhe, Karlsruhe, Germany, September.
- Gangwal, S.K., et al. 1988. "Bench-Scale Testing of Novel High-Temperature Desulfurization Sorbents." Report No. DOE/MC/23126-2662 (DE89000935).
- Gangwal, S.K., R. Gupta, and W.J. McMichael. 1993. "Sulfur Control Options for IGCC Systems." In *Proceedings of 17th Biennial Low-Rank Fuels Symposium*, University of North Dakota, Energy and Environmental Research Center, St. Louis, MO, May 10-13.
- Gangwal, S.K., R. Gupta, and W.J. McMichael. 1995. "Hot-Gas Cleanup-Sulfur Recovery-Technical, Environmental, and Economic Issues," *Heat Recovery Systems and CHP*. Vol. 15, No. 2, p. 205-214, Elsevier Science Limited.
- Gangwal, S.K., J.W. Portzer, G.W. Roberts, and S.C. Kozup. 1998. "Engineering Evaluation of Hot-Gas Desulfurization with Sulfur Recovery." Topical Report. DOE Contract No. DE-

- AC21-94MC31258. Research Triangle Institute. Research Triangle Park, NC.
- Grindley, T., and G. Steinfeld. 1981. "Development and Testing of Regenerable Hot Coal-Gas Desulfurization Sorbents." DOE/MC/16545-1125.
- Gupta, R., and S.K. Gangwal. 1992. "Enhanced Durability of Desulfurization Sorbents for Fluidized Bed Applications—Development and Testing of Zinc Titanate Sorbents." DOE/MC/25006-3271.
- Gupta, R., B.S. Turk, and S.K. Gangwal. 1996. "Bench-Scale Development of Fluid-Bed Spray Dried Sorbents." In *Proceedings of Advanced Coal-Fired Power Systems '96 Review Meeting*, Morgantown Energy Technology Center, Morgantown, WV, July.
- Gupta, R., B.S. Turk, and Albert A. Vierheilig. 1997. "Desulfurization Sorbents for Transport-Bed Applications." In *Proceedings of 1997 FETC Power Systems and Environmental Control Contractor's Meeting*, Pittsburgh, PA, July.
- Harrison, D.P. 1995. "Control of Gaseous Contaminants in IGCC Processes, An Overview," In *Proceedings of 12th Ann. Int. Pittsburgh Coal Conference*, p. 1047, September 11-15, Pittsburgh.
- Harrison, D.P., F.R. Groves, J.D. White, W. Huang, and A. Lopez-Ortiz. 1996. "Advanced Sulfur Control Processing." In *Proceedings of Advanced Coal-Fired Power Systems '96 Review Meeting*, Morgantown Energy Technology Center, Morgantown, WV, July.
- Jalan, V. 1985. "High-Temperature Desulfurization of Coal Gases." In *Acid and Sour Gas Treating Processes*, Gulf Publishing Co., Houston, TX, Nov. 7.
- Jothimurugesan, K., S.K. Gangwal, R. Gupta, and B.S. Turk. 1997. "Advanced Hot-Gas Desulfurization Sorbents." In *Proceedings of 1997 FETC Power Systems and Environmental Control Contractor's Meeting*, Pittsburgh, PA, July.
- Khare, G.P., G.A. Delzer, G.J. Greenwood, and D.H. Kunbicek. 1996. "Phillips Sorbent Development for Tampa Electric and Sierra Pacific." In *Proceedings of Advanced Coal-Fired Power Systems '96 Review Meeting*, Morgantown Energy Technology Center, Morgantown, WV, July.
- Meijer, R., F.J.J.G. Janssen, G.L. Faring, and J.W. H. Hellendoorn. 1996. "KEMA's Hot Gas Cleanup Process." In *Proceedings of 3rd International Symposium on Gas Cleaning at High Temperature*. University of Karlsruhe, Karlsruhe, Germany, September.
- NOVEM. 1991. "System Study High Temperature Gas Cleaning at IGCC Systems." Netherlands Agency for Energy and the Environment.

- Portzer, J.W., and S.K. Gangwal. 1995. "Slipstream Testing of Hot Gas Desulfurization with Sulfur Recovery." In *Proceedings of the Advanced Coal-Fired Power Systems '95 Review Meeting*, pp. 220-228. DOE/METC-95/1018, Vol. 1, NTIS/DE 95009732. Springfield, VA: National Technical Information Service.
- Portzer, J.W., B.S. Turk, and S.K. Gangwal. 1996. "Durability Testing of the Direct Sulfur Recovery Process." In *Proceedings of the Advanced Coal-Fired Power Systems Review Meeting July 16 B18, 1996*. (CD-ROM). U.S. Department of Energy. Morgantown, WV.
- Sugitani, T. 1989. Development of Hot-Gas Desulfurization Process. *Journal of the Fuel Society of Japan* 68(9):787.
- Thambimuthu, K.V. 1993. Gas Cleaning for Advanced Coal-Based Power Generation. Report by IEA Coal Research, IEACR/53, London, UK.

**APPENDIX G** Candidate Processes and Materials for the Direct Oxidation of H<sub>2</sub>S  
in Coal Gas: A Literature Review



# CANDIDATE PROCESSES AND MATERIALS FOR THE DIRECT OXIDATION OF H<sub>2</sub>S IN COAL GAS

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## Task 1: Literature Review

**Scope:** This review focuses on homogeneous and heterogeneous catalytic processes and liquid phase processes to oxidize H<sub>2</sub>S in coal gas to elemental sulfur at temperatures below 200°C and pressures near 20 atm. Although the exact inlet gas composition will depend on the type of gasifier, Table 1 shows the general range of compositions considered in this review.

SO<sub>2</sub>, obtained by burning the required portion of elemental sulfur, is used as the oxidant. The ultimate goal is to recover elemental sulfur from coal gasification in a process such as that shown in Figure 1.

In this process, coal gas containing H<sub>2</sub>S is brought into contact with a catalyst or absorber in which H<sub>2</sub>S is removed and converted to elemental sulfur. Variations of this general process are discussed below in considering the three options for sulfur removal and recovery:

- Heterogeneous catalysts
- Liquid phase absorption/reaction
- Supported liquid phase catalysts

The scope of this literature review is to identify candidate materials and processes that can be tested experimentally for H<sub>2</sub>S oxidation to elemental sulfur at the conditions shown in Figure 1.

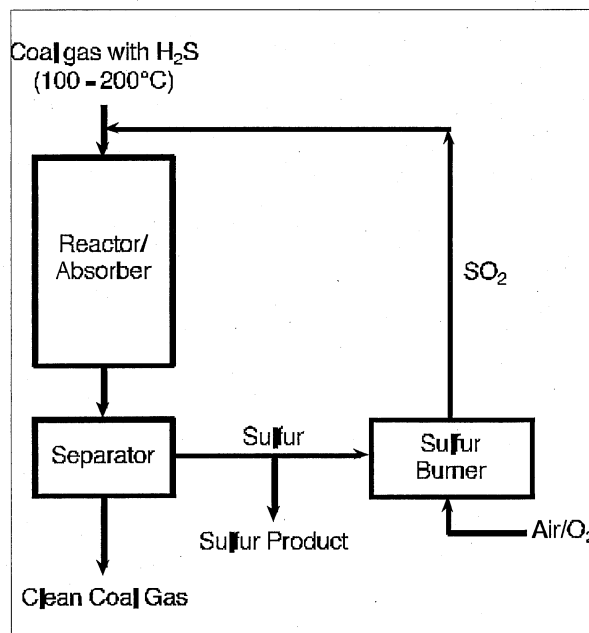
## Summary of the Literature

Three types of catalysts and processes were examined: heterogeneous catalysts, liquid phase absorption/reaction, and supported liquid catalysts.

**Table 1. Composition of Coal Gas\***

Component	Concentration range
CO	30-50%
H <sub>2</sub>	20-40%
CO <sub>2</sub>	2-3%
H <sub>2</sub> O	10-15%
H <sub>2</sub> S	1,000-4,000 ppm

\* Does not include trace compounds (NH<sub>3</sub>, alkali metals, etc.)

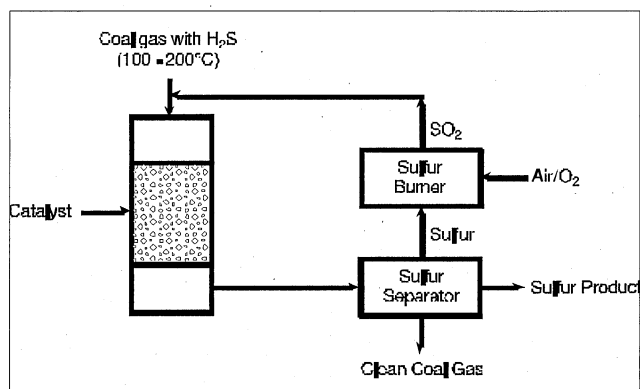


**Figure 1. Schematic of the sulfur recovery process.**

## Section 1—Heterogeneous Catalysts

When using heterogeneous catalysts, the solid catalyst promotes the gas phase reaction of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  to produce elemental sulfur, which is recovered as a liquid. The reaction would be carried out in a fixed bed, as shown in Figure 2.

**Overall Process.** The coal gas containing  $\text{H}_2\text{S}$  is contacted with a reactor in which gaseous  $\text{SO}_2$  is also introduced from a recycle burner. A portion of the sulfur produced is passed through a burner to form  $\text{SO}_2$ , which is recycled to the top of the reactor.



**Figure 2. Heterogeneous catalyst for the Claus reaction.**

Despite the possibility that the liquid sulfur could plug the pores of the catalyst, the process is similar in principle to Fischer Tropsch (FT) synthesis, in which waxes are produced from gaseous reactants. In FT synthesis, the catalyst in this process continues to promote the gas phase reaction for long periods of time while the liquid product is collected downstream. This suggests the possibility of a continuous process in which liquid sulfur is formed and collected downstream of the catalyst bed, just as waxes are collected in FT synthesis. However, if the catalyst loses activity rapidly, parallel beds would be needed to enable periodic regeneration and recovery of the sulfur. This would be both cumbersome and costly. Thus, a key challenge would be to find a catalyst with long life in the presence of molten sulfur.

**Catalysts.** Although the Claus reaction is carried out industrially at temperatures between 200°C and 280°C, the inlet gas to the catalytic reactor in that process does not contain CO and  $\text{H}_2$ . This is a key difference between the commercial Claus process and conditions shown in Figure 2. These reducing gases may cause undesirable reactions, such as the formation of COS, and may affect the modified alumina catalysts used industrially for the Claus reaction. In addition, reactions between CO/ $\text{H}_2$  and any of the reactants or products of the Claus reaction must be avoided in order to minimize the consumption of these valuable fuel gases. The challenge is thus to selectively promote the Claus reaction when the  $\text{H}_2\text{S}$  and  $\text{SO}_2$  reactants are in dilute concentrations in the presence of large concentrations of CO and  $\text{H}_2$ .

**Table 2. Inlet Gas Composition Studied by Pearson (1975)\***

Component	Concentration, %
CO	1.2
$\text{H}_2$	2.4
$\text{CO}_2$	6
$\text{H}_2\text{O}$	33.8
$\text{H}_2\text{S}$	0.75
$\text{SO}_2$	0.375
$\text{N}_2$	55

\* Catalysts were tested at a GHSV of 550  $\text{h}^{-1}$ .

A review of the literature did not identify any directly related studies in which the Claus reaction was carried out in the presence of large concentrations of CO and  $\text{H}_2$ . However, closely related studies suggest that alumina catalysts related to those used for commercial Claus catalysis should be tested, after modifications that avoid deactivation due to sulfur deposition in catalyst pores over sulfate formation. Pearson (1975) studied the Claus reaction at temperatures between 135°C and 175°C using a gas composition corresponding to a Claus tail gas, which contained low levels of CO and  $\text{H}_2$  (Table 2).

The catalyst tested most extensively was described only as an “active” alumina, with a surface area of 300 m<sup>2</sup>/g. In all tests, conversion of H<sub>2</sub>S/SO<sub>2</sub> was about 96 to 98 percent and remained at this level until the catalyst reached 60 to 70 wt% sulfur loading, after which the conversion declined rapidly. With a sulfur loading of about 92 wt%, the conversion was only 31 percent, and calculations showed that this corresponded to completely full pores. Tests comparing the sulfate tolerance of these materials showed that the promoted alumina, described only as “S-501,” was most tolerant to sulfate formation.

One further study of the low-temperature Claus reaction in the presence of reducing gases showed that iron-based materials are active, though it is doubtful that iron catalysts can be used in the presence of the high levels of CO and H<sub>2</sub> that are of interest here. Smith et al. (1978) studied “commercial hematite ore pellets” to form sulfur from the off-gas produced in a metallurgical cupola. When the cupola was operated at reducing conditions, the off-gas contained the components shown in Table 3.

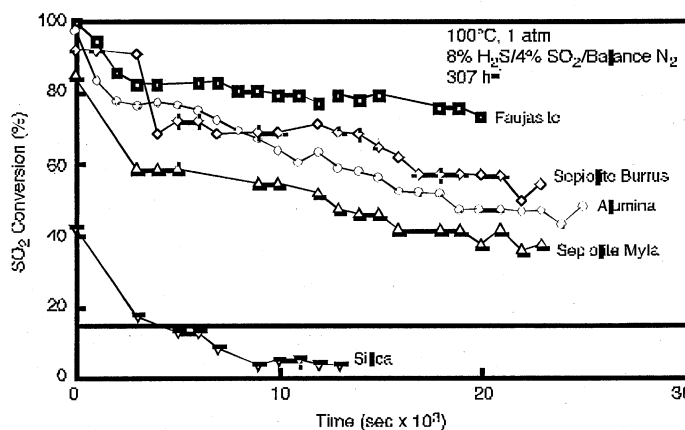
**Table 3. Cupola Off-Gas Composition—  
Inlet Gas for Claus Reactor (Smith et al.,  
1978)**

Component	Concentration, %
CO	0.9-1.9 %
H <sub>2</sub>	(not measured)
CO <sub>2</sub>	1.1-1.5 %
H <sub>2</sub> O	0.47-2.26 %
H <sub>2</sub> S	128-227 ppm
SO <sub>2</sub>	77-339 ppm
N <sub>2</sub>	(not measured)

The values reported in Table 3 span the range of concentrations reported for a series of six tests. The oxygen content was not reported, though presumably it was negligible when the cupola was operated at reducing conditions.

Interestingly, separate lab tests on the iron pellets showed that the pellets alone had no Claus activity, which means that the active catalyst was not the iron. Further analysis showed that traces of “silicates and halides of Mg, Al, Mn, Fe, Ca, and Na” had deposited on the pellets during the tests, which changed the pellets’ composition and catalytic activity. Unfortunately, the exact composition of these apparently effective Claus catalysts is not further described, making it impossible to duplicate them. However, these results suggest that “silicates and halides” of these metals may be active low-temperature Claus catalysts. Unfortunately, no further information is given that would enable candidate catalysts to be suggested.

Finally, a series of papers show that sepiolite, a naturally occurring magnesium silicate (Si<sub>12</sub>Mg<sub>8</sub>O<sub>30</sub> (OH)<sub>4</sub> • 8H<sub>2</sub>O), and faujasite are active low temperature Claus catalysts, but no studies were carried out in the presence of CO or H<sub>2</sub> (Alvarez et al., 1996; Guijarro et al., 1995; Alvarez et al., 1993). Only one test of faujasite is reported, but in a direct comparison to two sepiolites and -alumina, it maintained a slightly higher level of conversion (see Figure 3).



**Figure 3. SO<sub>2</sub> conversion in the Claus reactions  
as a function of time for various heterogeneous  
catalysts (Alvarez et al., 1993)**

Much more extensive tests on sepiolites were carried out using 0.4 to 8 percent H<sub>2</sub>S and near-stoichiometric amounts of SO<sub>2</sub> (in nitrogen) at temperatures between 70°C and 200°C, which spans the ~120°C melting point of sulfur. Deactivation tests at 100°C show that sulfur accumulates primarily in the micropores of the catalyst, as expected, leading to steady deactivation. However, the authors show that the deactivation is less rapid than would be expected because of the loss of surface area to deposited sulfur, leading them to conclude that the "...sulfur formed ...is solely responsible for the catalysis [of the Claus reaction]." Even if this conclusion is questionable, this experimental result is significant, because it suggests that a heterogeneous catalyst can remain relatively active despite the inevitable accumulation of sulfur. This could be even more important at temperatures above the melting point of sulfur, because liquid sulfur may be more catalytically active than solid sulfur. Finally, despite the uncertain effect of CO and H<sub>2</sub> on conventional alumina catalysts used for the Claus process, these materials with some modifications should be considered candidates for further study.

These modifications include the addition of metals that have been shown to be active for the selective oxidation of H<sub>2</sub>S to elemental sulfur in the presence of syngas or hydrocarbons. Although it is uncertain whether these catalysts would also promote the Claus reaction in the presence of these compounds, the milder oxidation potential of SO<sub>2</sub> (versus oxygen) suggests that they be evaluated.

Several studies show that vanadium may be such a candidate [Haas, 1979; Li and Shyn, 1997]. Using a gas containing 6,600 to 12,000 ppm sulfur in various mixtures of hydrogen (up to 12 percent), CO (<1 percent), and methane (up to 80 percent), Haas (1979) showed that a 10 percent V<sub>2</sub>O<sub>5</sub>/alumina catalyst selectively oxidized H<sub>2</sub>S to sulfur at temperatures between 315°C and 482°C. Although these are higher temperatures than those of interest here, the selective formation of sulfur in the presence of high levels of hydrogen suggests that these catalysts be tested. Tests on a vanadium/mordenite catalyst showed similar results to those on vanadium/alumina, but with slightly higher H<sub>2</sub>S conversion at temperatures near 260°C, and more tolerance of HN<sub>3</sub>, which may be important in coal gas applications. [Though not carried out in the presence of CO, H<sub>2</sub>, or hydrocarbons, Li and Shyn (1997) show that bulk vanadium/antimony catalysts are active for H<sub>2</sub>S oxidation to sulfur at 250°C, approximately the temperatures of interest here.]

***Supported Liquid Phase Catalysts.*** In addition to the conventional heterogeneous catalysts considered above, a more exploratory class of catalysts can be envisioned. These are catalysts in which the active component from homogeneous Claus catalysts is supported on a solid material. Despite extensive study on the general concept of supporting homogeneous catalysts on solid supports, few reports are available in which a commercially practical catalyst of this type has been developed. We are aware of no reports in which a Claus catalyst has been prepared and tested at conditions of interest here.

The general problem in supporting homogeneous catalysts has been that the catalysts are easily leached from the support, lose their high activity or selectivity when supported on solid carriers, or decompose at the higher temperatures needed to operate at industrially practical reaction rates. Nevertheless, Rossarie and Maurie (1978a) show that various salts of weak acids are active homogeneous Claus catalysts (e.g., potassium and sodium benzoate). We suggest preparing and testing two exploratory solid catalysts composed of these two salts on non-acidic alumina supports that are comparable to those used for commercial Claus catalysis but do not contain added alkalis (other than those in the salt).

**Summary.** Five heterogeneous catalysts, including a commercial alumina as baseline catalyst, are recommended for study of the low-temperature Claus reaction, as shown in Table 4.

However, specific materials and preparation procedures need to be further defined. For the first three catalysts shown in Table 4, preference will be given to testing existing commercial materials that have known properties and that can be readily obtained for any scale-up that may be needed.

**Section 2—Liquid Phase Absorption/Reaction**

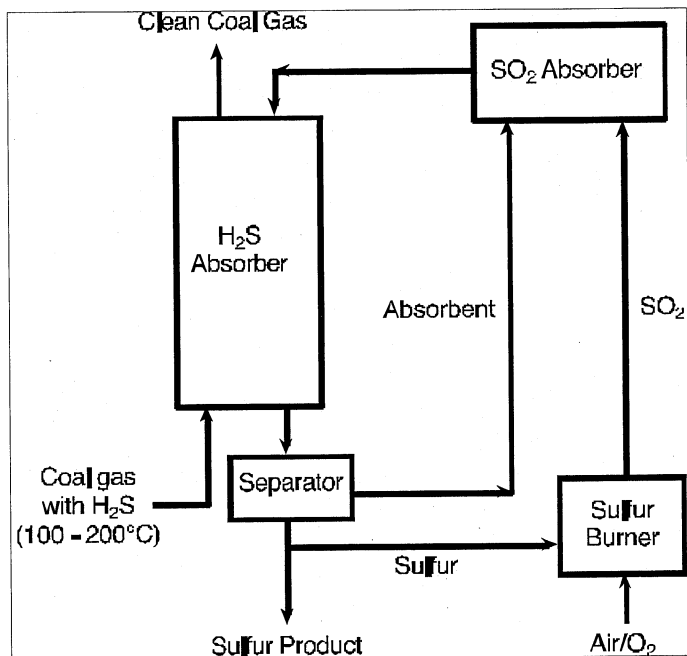
Despite the desirability of a gas phase catalytic process, the low concentrations of H<sub>2</sub>S and SO<sub>2</sub> in the coal gas, coupled with the need for high conversions to meet environmental requirements, suggest that these reactants may have to be separated from the coal gas as absorbed liquids and reacted in a separate step. Several reports show the feasibility of such processes, which are especially applicable to the low temperatures of interest here, because the absorbent can be easily maintained as a liquid.

There are many variations on these processes in the literature, but we have focused on two processes that exemplify the two principle approaches to the liquid phase route of interest here: homogeneous catalysis of the Claus reaction and liquid phase stoichiometric reaction of H<sub>2</sub>S and SO<sub>2</sub> to produce sulfur. Both processes can be represented as shown in Figure 4.

In both processes, H<sub>2</sub>S is contacted with a liquid absorbent that contains SO<sub>2</sub>, which appears in most cases to enhance the absorption of H<sub>2</sub>S. Sulfur is formed in the liquid phase and separated from the absorbent, with a portion of it being recovered as product and a portion being sent to a burner to produce SO<sub>2</sub>.

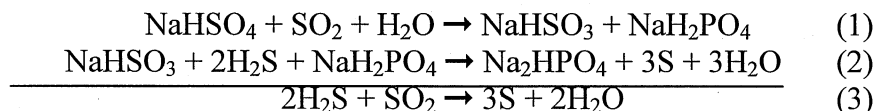
**Table 4. Heterogeneous Catalysts Recommended for Low-Temperature Claus Reaction**

Catalyst	Rationale
Sepiolite	has low temperature Claus activity, but the effect of CO and H <sub>2</sub> at the levels of interest here is not known.
Faujasite	has slightly higher reported activity than sepiolite and is not likely to be affected by CO and H <sub>2</sub> .
commercial alumina Claus catalysts	active for the reaction, but like the sepiolite, the effect of CO and H <sub>2</sub> at the levels of interest here is not known.
sodium and potassium benzoate on alumina	active low-temperature homogeneous Claus catalysts, and alumina supports are tolerant of the required reaction conditions
vanadium/alumina	vanadium selectivity oxidizes H <sub>2</sub> S to sulfur in the presence of CO and H <sub>2</sub> , and aluminas are active for the Claus reaction



**Figure 4. Liquid phase processes for sulfur recovery.**

The liquid absorbent is recycled to an absorber in which SO<sub>2</sub> is recovered. In the homogeneous catalytic process, this liquid also contains a catalyst. In the case of a stoichiometric reaction, the liquid reacts with the two gases in a self-regenerating cycle, such as the following (Sherif et al., 1975):



In a number of references, the distinction between processes that are in fact catalytic and those that involve a stoichiometric reaction is unclear. This is because in some cases the catalyst is not identified. The situation is further complicated by the fact that the water produced in the reaction can serve as the catalyst (German Patent 2,001,284). In summarizing the literature below, we have focused on those studies in which sufficient information is given to provide guidance on candidate processes, as well as catalysts and absorbent liquids, that are applicable to the conditions of interest here—especially the presence of CO and H<sub>2</sub>.

**Homogeneous Catalysis of the Claus Reaction.** Rossarie and Maurie (1978a) describe such a process in which H<sub>2</sub>S is absorbed from a gas stream containing 65 percent H<sub>2</sub>, 31 percent CO<sub>2</sub>, 3.4 percent CO, and 0.7 percent H<sub>2</sub>S into a solution containing SO<sub>2</sub> flowing countercurrently. The reaction was carried out at 55 atm and 115°C. The liquid is “diethylene glycol monomethyl ether or monomethyl ether” and 0.5 percent potassium benzoate and is used as the homogeneous catalyst. Sulfur yield was 99+ percent in the two examples given. Other homogeneous catalysts that are claimed include “...salts of weak acids such as sodium benzoate, or nitrogen compounds such as amines.” This example provides an absorbent/catalyst system that functions in the presence of significant concentrations of CO and H<sub>2</sub>, though these compounds were not present at concentrations typical of coal gas.

**Liquid Phase Stoichiometric Reaction.** Sherif et al. (1975) describe a process involving the absorption of H<sub>2</sub>S from the coal gas into a liquid, forming sulfur in the liquid phase, and recovering sulfur from the resulting mixture. SO<sub>2</sub> is absorbed in an aqueous alkali metal phosphate. An example of the reaction sequence is shown in Reactions (1) through (3). The process is claimed to operate best around 66°C to 77°C and is designed primarily for flue gas desulfurization. Optimum concentrations of SO<sub>2</sub> are below 15 percent.

**Candidate Liquid Absorbents.** Many of the studies for both the catalytic process and the liquid phase stoichiometric process use liquids that are similar or identical to those used in conventional acid gas removal processes, for example, the “amines” claimed by Rossarie and Maurie (1978). This has led us to review the potential use of various liquids as candidates for the absorbent needed by both processes considered here.

There are a wide range of alkanolamines and other absorbents for removal of H<sub>2</sub>S from a range of gas streams, primarily natural gas. The most widely used absorbents are monoethanol amine, diethanol amine, and mixtures of various glycols (Kohl and Nielsen, 1997a). Although we did not identify literature discussing the specific effects of high levels of CO and H<sub>2</sub> on the absorption of H<sub>2</sub>S in these amines, we would expect that H<sub>2</sub>S absorption would not be significantly affected. These amines would be expected to absorb SO<sub>2</sub>, but no literature was identified showing this, although closely related aromatic amines are used to remove dilute levels of SO<sub>2</sub>

(Kohl and Nielsen, 1997b). Additional selective absorbents for SO<sub>2</sub> include various glycol ethers (Kohl and Nielsen, 1997c). Additional absorbents reported for H<sub>2</sub>S include alkali phosphates and carbonates (German Patent 2,001,284; U.S. Patent 2,368,595) and aluminum sulfate/sulfuric acid (U.S. Patent 2,563,437).

For the purpose of this review, the candidate absorbents include those shown in Table 5, which have been reported for absorption of H<sub>2</sub>S, SO<sub>2</sub>, or both. For those that have been reported only for H<sub>2</sub>S or SO<sub>2</sub> absorption, a cursory examination of their chemical properties does not appear to preclude their being used in the process of Figure 4.

**Table 5. Candidate Liquid Absorbents**

Absorbents for H <sub>2</sub> S		Absorbents for SO <sub>2</sub>		Absorbents for H <sub>2</sub> S and SO <sub>2</sub>	
Absorbent	Reference	Absorbent	Reference	Absorbent	Reference
alkanolamines (MEA, DEA, etc.)	Kohl and Nielsen, 1997a	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> / sulfuric acid	U.S. Patent 2,563,437	“aqueous citrate”	George et al., 1969
alkali carbonates (K <sub>2</sub> CO <sub>3</sub> )	German Patent 2,001,284	tetraethylene glycol dimethyl ether	Kohl and Nielsen, 1997c	K <sub>3</sub> PO <sub>4</sub>	German Patent 2,001,284; U.S. Patent 2,368,595
		monobasic phosphates and sodium citrate	U.S. Patent 2,031,802; U.S. Patent 2,729,543		

### Section 3—Liquid Phase Claus Catalyst Supported on a Solid

A third class of materials considered here are solids composed of a microporous material in which a liquid phase catalyst or liquid absorbent/reactant is retained (as a liquid) in the micropores. This has the advantage of concentrating the H<sub>2</sub>S and SO<sub>2</sub> reactants from the gas phase. The overall process would be carried out as shown in Figure 2. As in Figure 2, the sulfur may, in principle, be collected as a liquid downstream of the reactor. However, it is also possible that as sulfur accumulates in the pores, the activity will decrease and periodic regeneration would be needed.

In this type of catalyst, the support does not need to be catalytically active, but should have a high microporosity and be tolerant of sulfur, H<sub>2</sub>S, SO<sub>2</sub>, and coal gas components at the temperatures of interest. All else being equal, the smaller the pores, the lower the vapor pressure of the liquid (due to the Kelvin effect), and the less the loss of liquid due to the inevitable process of vaporization.

Candidate support materials include activated carbon, high surface area silica, and perhaps alumina (though its inherent acidity may limit the rates of reaction or cause it to react with H<sub>2</sub>S or SO<sub>2</sub>). Liquids include those discussed above in Section 2—both homogeneous liquid phase catalysts and liquid phase absorbent/reactants (see Table 6).

**Table 6. Candidate Supported Liquids for the Claus Reaction\***

Liquid	Rationale	Support	Rationale
“diethylene glycol monomethyl ether or monomethyl ether” and 0.5% potassium benzoate	reported homogeneous Claus catalyst (Rossarie and Maurie, 1978a)	activated carbon	high microporosity and tolerance to sulfur and coal gas
aqueous alkali metal phosphate	reported liquid phase absorbent/reactant (Sherif et al., 1975)	high surface area silica	

\* Note that either of the candidate liquids could be used with either of the supports, making a total of four candidate materials

## References

- Alvarez, E., S Mendioroz, V. Munoz, J.M. Palacios, Appl. Catal.B, 9, 1996, 179-199.
- Alvarez, E., S Mendioroz, J.M. Palacios, Appl. Catal. A, 93, 1993, 231-244.
- George,....., et al., presented at the Mining Society, AIME Fall Meeting, Salt Lake City, UT, Sept. 17-19, 1969.
- German Patent 2,001,284
- Guijarro, M.I., S. Mendioroz, V. Munoz, Appl. Catal. A, 132, 1995, 335-351.
- Haas, R.H., U.S. Patent 4,171,347, Oct. 16, 1979.
- Kohl, A.L. and R. Nielsen, Gas Purification, Gulf Publishing, Houston, TX, 1997, (a) p. 40-186, (b) p.590-593, (c) p. 602.
- Li and Shyn.
- Pearson, M.J., Energy Processing/Canada, July-August 1976, 38-42.
- Rossarie, J. and J. Maurin, US Patent 4,107,269, Aug. 15, 1978, (a) Example 2, (b) Example 1.
- Sherif, F.G., J.S. Hayford, J.E. Blanch, US Patent 3,911,093, Oct. 7, 1975.
- Smith, J.W., C. Knight, W.H. Powlesland, P.H.I. Harper, “Dry Desulfurization of Industrial Process Gases by Low Temperature Catalytic Oxidation”, in Treatment of Coke Oven Gas, Dept. of Metallurgy and Material Science, McMaster University, Ontario, Canada, 1978, 14-1 to 14-16.
- U.S. Patent 2,563,437
- U.S. Patent 2,368,595