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**Summary and Assessment of METC Zinc
Ferrite Hot Coal Gas Desulfurization
Test Program, Final Report**

Volume I

MASTER

By
V.S. Underkoffler

December 1986

Work Performed Under Contract No.: DE-AC21-84MC21098

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Gilbert/Commonwealth
Reading, Pennsylvania

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P.O. Box 880
Morgantown, West Virginia 26507-0880

By
Gilbert/Commonwealth
P.O. Box 1498
Reading, Pennsylvania 19603

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ABSTRACT

The Morgantown Energy Technology Center (METC) has conducted a test program to develop a zinc ferrite-based high temperature desulfurization process which could be applied to fuel gas entering downstream components such as molten carbonate fuel cells or gas turbines. As a result of prior METC work with iron oxide and zinc oxide sorbents, zinc ferrite evolved as a candidate with the potential for high capacity, low equilibrium levels of H_2S , and structural stability after multiple regenerations. The program consisted of laboratory-scale testing with a two-inch diameter reactor and simulated fixed-bed gasifier gas; bench-scale testing with a six-inch diameter reactor and actual gas from the METC 42-inch fixed bed gasifier; as well as laboratory-scale testing of zinc ferrite with simulated fluidized bed gasifier gas. Optimum operating parameters for zinc ferrite such as temperatures, gas compositions, and space velocities are discussed. From the test results, salient features of zinc ferrite were derived and discussed in regard to system implications, issues raised, and technical requirements.

An assessment of the technical and economic implications of the zinc ferrite process is presented as well as suggested programs for potential commercialization.

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EXECUTIVE SUMMARY

BACKGROUND

The primary objective of the investigation has been the development of a viable process for hot gas desulfurization of coal derived gas to be used by Molten Carbonate Fuel Cells (MCFC). Many studies and reports have indicated that high temperature desulfurization processes have potentially sufficient advantages over low temperature systems to warrant further development. Iron oxide based sorbents have been developed at Morgantown Energy Technology Center (METC) in the past, and concurrently work in this area has been done at Air Products, Institute of Gas Technology (IGT), Giner, Inc., and the University of Kentucky, among others.

In the mid 1970's, work at METC resulted in the development of iron oxide sorbent on fly ash and silica supports having improved strength characteristics and regenerable properties. Tests at METC indicated that iron oxide is capable of removing typically better than 90 percent of the H_2S in a hot gas stream at temperatures between 1000-1500°F. Regeneration with air was carried out up to seventy times with appreciable but generally acceptable loss in activity. The absorbed sulfur was removed from the sorbent mostly in the form of SO_2 .

In light of the knowledge gained during METC'S development program for a regenerable iron oxide sorbent, zinc ferrite evolved as a likely candidate for initial testing as a regenerable sorbent with the capability of lowering sulfur levels to the 1.0 ppm or less required for the MCFC. This compound has the same crystal structure as the magnetite form of iron oxide (i.e., the spinel structure) and is easily made by heating together iron oxide and zinc oxide powders in the correct molar proportions. It was reasoned that this material could have a combination of the absorption efficiency of zinc oxide and the capacity and regenerability that iron oxide is known to have. It is also known from metallurgical practice that zinc ferrite is difficult to reduce, and so it was surmised there would be a lesser probability of elemental zinc volatilization than would be expected in the case of zinc oxide.

This report covers the work that has been performed at METC in developing a zinc ferrite hot gas desulfurization process, beginning with laboratory scale investigations in July 1980 and extending through May 1984. The laboratory scale work summarized herein was conducted on a two-inch diameter test reactor, the initial phase using simulated fixed-bed gasifier gas.

At the completion of the first phase of laboratory scale testing in March 1983, METC proceeded with zinc ferrite testing in a side-stream of gas from the METC fixed bed gasifier. Using a six-inch diameter reactor, tests were conducted through the end of 1983 on various gasified coals. Upon completion of the side-stream tests, METC entered into a program with Kellogg/Rust/Westinghouse (KRW) to design and construct a process development unit for operation with the KRW fluidized-bed gasifier at Waltz Mill, PA. To support this design activity, from March to June 1984, METC conducted a series of tests with the laboratory scale reactor using simulated KRW gas from both oxygen and air-blown modes.

In addition to summarizing the results of these three phases of testing, this report also presents a discussion of the salient features of the zinc ferrite process in regard to the key issues and technical requirements for commercial consideration. Beyond that, an overall engineering assessment of the zinc ferrite process and test program is presented.

DEVELOPMENT AND TESTING OF ZINC FERRITE AT METC

Initially, screening tests were performed with a two-inch diameter reactor using bottled gases to simulate the composition of gas from coal gasification. In these tests it was found that the zinc ferrite sorbent achieved a high level of removal of both H_2S and COS and was regenerable through up to five cycles of absorption and regeneration, considered sufficient to demonstrate regenerability.

The stoichiometry of the following overall absorption reaction indicates that if all of the iron and zinc can be reacted to sulfide, approximately 35 weight percent sulfur loading can be obtained with this sorbent.

The screening tests demonstrated that the zinc ferrite achieved a loading in the range of 15 percent, or less than half of theoretical, but substantially better than the six percent achieved by zinc oxide under the same reactor conditions. Since the tests were at a relatively high space velocity ($1,000 \text{ h}^{-1}$) and atmospheric pressure, higher loadings could be anticipated.

Reasonably optimum parameters for testing zinc ferrite at atmospheric pressure were established early in the lab scale test program which enabled METC to concentrate on various other operating conditions and results.

Operating conditions were:

- Sulfidation Temperature, $1000\text{--}1200^\circ\text{F}$
- Sulfidation Space Velocity, $1000\text{--}2000 \text{ h}^{-1}$
- Regeneration Inlet Temperature, 1000°F
- Regeneration Space Velocity, $500\text{--}600 \text{ h}^{-1}$
- Regeneration Steam/Air Ratio, 50/50 V/V

Subsequently, a larger 6-inch diameter fixed bed absorber/regenerator was constructed and tests were carried out using a slipstream of gas from the 42-inch, pressurized, stirred, fixed-bed gasifier at METC. A fixed-bed design for the absorber was chosen for these tests because use of large-scale fixed-bed reactors is considered to be a commercial possibility. Besides generating data for reactor scale up, the objective was to test absorption with real gas, representative of fixed bed gasifiers such as the Lurgi. Experiments in the test unit were run under conditions of relatively high space velocity with the tests continuing until hydrogen sulfide breakthrough occurred. With an inlet concentration of approximately 2,000 to 3,000 ppm H_2S , outlet concentrations of H_2S of under 10 ppm were usually achieved, corresponding to a capture efficiency of over 99.5 percent.

In anticipation of using the zinc ferrite process in conjunction with the KRW-PDU, another series of lab-scale tests were conducted with simulated KRW coal gas, both air and oxygen-blown, with the revamped two-inch diameter reactor, internally aluminized to minimize H_2S reaction with the reactor

walls. Utilizing a commercial prepared zinc ferrite sorbent, eight absorption tests were conducted, demonstrating that H_2S can be removed to a level of a few ppm before breakthrough.

TECHNICAL ISSUES

Throughout the test program, it became apparent that a number of characteristics of zinc ferrite would become technical issues.

- Ability to achieve the low levels of H_2S .

It was shown that 2000-3000 ppm inlet gas H_2S concentration could be brought down to an exit level near the ZnO equilibrium level, usually less than 10 ppm without difficulty. Though less than 1 ppm is the goal set for MCFC, the 10 ppm level is appropriate for bulk removal. The lower level could be achieved by means of a polishing step with a copper or nickel containing sorbent.

- Reduction in sorbent capacity with repeated regenerations.

Throughout the test program the quantitative effect of multiple regenerations beyond a few cycles was not determined. Indications were observed that the sorbent had reduced porosity after several regenerations which results in a downward trend in absorption capacity.

- Formation of Iron Carbide as a Result of Fuel Gas Composition.

Throughout the laboratory scale testing, the test gas was a simulated Lurgi quenched gas having a high water content. In the side stream tests with actual fuel gas it was observed and confirmed that gases with a high CO/CO_2 ratio and/or low H_2O concentration at high temperatures cause the formation of iron carbide by the reduction of magnetite. Figure ES-1 is a phase diagram on which stable sorbent solid phases are represented in terms of temperature and gas composition. Dry gases produced by the BGC, KRW, and Texaco gasifiers

IRON-CARBON-OXYGEN EQUILIBRIUM DIAGRAM AT ATMOSPHERIC PRESSURE

adapted from Geiger

FIGURE ES-1

lie outside the stable magnetite region and as a result, addition of steam to these gases would be necessary.

- **Formation of Sulfates during Regeneration.**

It was observed that an amount of zinc sulfate is formed during regeneration of zinc ferrite, the reaction being favored by low temperatures and high oxygen concentration. High temperatures to prevent this ($>1,500^{\circ}\text{F}$) result in sintering and loss of reactivity. A consequence of sulfate formation is an evolution of sulfur species at the beginning of the next sulfidation, unless a two stage regeneration (oxidation followed by reduction) is used.

- **Pressure Drop.**

It was observed in the side-stream absorption tests that pressure drop through the zinc ferrite bed is affected by the size of particulates in the fuel gas. Large size particulates result in an unacceptable pressure drop buildup, so that particulate control will be required up-stream of the desulfurization process.

LIMITATIONS OF ZINC FERRITE

The Zinc Ferrite Test Program has served to identify some realistic design parameters that delineate a commercial zinc ferrite desulfurization system. Some identified thus far which would have a significant impact on design and/or operations are as follows:

- **Sulfidation Temperature.**

Optimal absorption at less than 1200°F may require gas/gas heat exchangers and/or partial quenching with water to lower the temperature of raw gas from the gasifier.

- Regeneration Temperature.

To avoid sulfate formation at low temperature or sintering at high temperature the bed requires active temperature control by adjusting the steam/air ratio of the regeneration gas.

- Feed Gas Composition.

Strict operating boundaries of CO/CO₂ ratios, H₂/H₂O ratios, and temperature are necessary to operate in the magnetite stable region of the sorbent. This could create efficiency problems when tailoring fuel gas compositions.

- Regeneration Products.

The product of regeneration is a relatively low concentration stream of SO₂ (2-4 percent) in nitrogen and steam. Recovery of sulfur from this stream requires a secondary clean-up train, e.g., Wellman Lord, and a sulfur recovery process. Sulfur can be recovered as elemental sulfur, converted to H₂SO₄ or landfilled as CaSO₄. Injection of regeneration product to the gasifier with in-situ desulfurization is potentially a much less expensive alternative.

In addition to reviewing the test results, Gilbert/Commonwealth has recently conducted a systems engineering study and conceptual design of a nominal 100 MW power plant using various gasifiers and a zinc ferrite desulfurization system. In doing this study, Gilbert has also concluded that the key systems issue of the zinc ferrite process that can have a major impact on costs is the sorbent capacity and its life over many cycles of absorption and regeneration. Long term testing has been done at lab scale; however additional testing at a larger scale is necessary to be able to project a realistic sorbent life.

There are a number of areas in which additional research and development are necessary in order to reduce costs. These include operation at higher space velocities which reduces capital costs, extending sorbent life which reduces

consumables cost, and finding a more cost effective method of regeneration tail gas treatment. Sulfur recovery can constitute over half the cost of the sulfur treatment process. A KRW PDU test was initiated in late 1986, where regeneration gas is injected into the gasifier and sulfur is removed by dolomite in the fluidized bed gasifier. This has a potential for a large cost reduction. Similar tests are also planned for the METC fixed-bed gasifier.

SUGGESTED PROGRAMS

METC has entered into several programs with contractors to gain further insight into the salient features of the zinc ferrite process. These programs include:

Multicycle Durability	AMAX
Sulfate Formation	SRI International
Solid Phase Boundaries	SRI International
Kinetics and Structural Changes within Sorbent	Louisiana State University
Tail Gas Treatment	R. M. Parsons Co., Arthur D. Little
Tar Effects	Research Triangle Institute
Tar Cracking	Battelle Pacific Northwest Laboratory
Trace Sulfur Removal	Energy Research Corporation

Beyond these studies, which primarily serve to quantify the salient features of the sorbent, empirical activity on the PDU scale is warranted. The current activity that METC is involved in at the KRW gasifier site is a first step toward commercialization. Further testing of zinc ferrite reactors and systems at a commercial scale and with commercial configurations are necessary. This would serve to quantify heat transfer, temperature control, pressure drop, and other operating characteristics. Below is a listing of several research and development needs for the process to reach commercial status.

- All absorption/regeneration tests should be run at the high temperatures and pressures consistent with gasification atmospheres, generating data that show repeatability and consistency.
- Evaluation tests should be conducted to verify theoretical model predictions. The verified theoretical models can then be used to provide a basis for scale-up.
- Integrated absorption/regeneration and sulfur recovery tests at the PDU size should be run. The size of the test should be large enough that scale-up to a commercial size can be done.

INTRODUCTION

The primary objective of this investigation is to develop a viable process for hot gas desulfurization of coal derived gas to be used by Molten Carbonate Fuel Cells (MCFC). Previous studies and reports have indicated that high temperature desulfurization processes have sufficient advantages over low temperature systems to warrant further development. Iron oxide based sorbents have been developed at Morgantown Energy Technology Center (METC) in the past, and at the same time, work in this area has been done at Air Products and Chemicals, Inc., Institute of Gas Technology (IGT), Giner, Inc., and the University of Kentucky, among others.

This report covers the work that has been performed at METC in developing a zinc ferrite hot gas desulfurization process, beginning with laboratory scale investigations in July 1980 and extending through May 1984. The laboratory scale work summarized herein was conducted on a two-inch diameter test reactor, the initial phase using simulated fixed-bed gasifier gas. The test results are summarized in this volume, with additional data and information contained in accompanying appendices.

At the completion of the first phase of laboratory scale testing in March 1983, METC proceeded with zinc ferrite testing using side-stream gas from the METC fixed bed gasifier. Using a six-inch diameter reactor, tests were conducted through the end of 1983 on various gasified coals.

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1.1 BACKGROUND OF SORBENT DEVELOPMENT

Many organizations, including private companies, and METC have been involved in sorbent development for the removal of sulfur compounds from hot fuel gas streams.

METC, Air Products, and Girdler Chemical, Inc. - Iron Oxide

In the mid 1970's, work at METC resulted in the development of iron oxide sorbent on fly ash and silica supports having improved strength characteristics and regenerable properties as compared to unsupported iron oxide. Tests at METC indicated that iron oxide is typically capable of removing better than 90 percent of the H_2S in a hot gas stream at temperatures between 1000-1500°F. Regeneration with air was completed through up to 70 cycles with appreciable but generally acceptable loss in activity. The sulfur was removed from the sorbent mostly in the form of SO_2 . Largely because of the high cost of treating regeneration tail gas, a process based on iron oxide was not considered by METC to have good prospects at the time, and development was discontinued.

Based on the iron oxide developmental work at METC, additional work was carried out by Air Products and Chemicals, Inc., and Girdler Chemical, Inc. until March 1978. Several sorbents were tested with varying amounts of iron oxide from varying sources, and with fly-ash or silica supports. An economic analysis was made, determining the cost of an iron oxide desulfurization system using air regeneration, and an optimum set of operating conditions was presented. In addition, a simulation model was developed that could predict the

performance of a fixed bed iron oxide reactor in absorption and regeneration modes.

An interesting result reported by Air Products is that high yields of elemental sulfur are possible with steam/air regeneration at high steam/air ratios. This has been reported by other researchers, and was later verified at METC. The necessity of adding steam (or nitrogen) to air for regeneration is to moderate the high temperature wave in a fixed bed reactor resulting from the exothermic sulfide - oxygen reaction, thus preserving the sorbent structure and reactivity that deteriorate at excessively high temperatures.

IGT - Zinc Oxide and Other Sorbents

The Institute of Gas Technology (IGT) studied improvements in high temperature fuel gas desulfurization with an objective of obtaining elemental sulfur directly during regeneration. IGT tested various commercial sorbents containing ZnAl_2O_4 , ZnCr_2O_4 , Cr_2O_3 , and CuCr_2O_4 , among other compounds, and determined that zinc oxide containing solids can be regenerated with oxygen containing gases. Experiments with zinc chromite and zinc aluminate indicated that elemental sulfur is obtained upon regeneration with air. The formation of elemental sulfur is thought by IGT to proceed by a mechanism which involves the spinel crystal structures of these compounds.

Giner - Zinc oxide and Other Sorbents

Giner, Inc. screened fifty-five elements, their carbonates, and their oxides in order to select promising materials for regenerable high temperature desulfurization. These elements were screened for the extent of reaction with H_2S , based on free energy change in the reaction. Based on this screening process, several materials appeared to be promising candidates: oxides of zinc, vanadium, copper, and tungsten. The physical and chemical properties of these candidate sulfur sorbents were surveyed, and bench scale experiments

were conducted with the most promising candidate of the group, vanadium sesquioxide (reduced form of vanadium pentoxide). A vanadium oxide-containing sorbent was found to have a low (3 percent) sulfur capacity at 1200°F, but was thought to be capable of lowering sulfur concentration of a fuel mixture to less than 10 ppm. In addition, vanadium oxide was completely regenerated with air at 1200°F, with no apparent reduction in capacity over several cycles.

It was later found that the thermodynamic basis used to calculate the potential H₂S absorption by vanadium oxide was erroneous and therefore the observed lowering of H₂S concentration to less than 10 ppm may be a surface phenomenon rather than the result of bulk reaction to a thermodynamic equilibrium level.

METC - Zinc Ferrite

In light of the knowledge gained during METC'S development program for a regenerable iron oxide sorbent, zinc ferrite evolved as a likely candidate for initial testing. This compound has the same crystal structure as the magnetite form of iron oxide (i.e., the spinel structure) and is easily made synthetically by heating iron oxide and zinc oxide powders together in 1:1 molar proportions. It was reasoned that this material could have a combination of the absorption efficiency of zinc oxide, i.e., reducing H₂S concentration to 1 ppm, and the capacity and regenerability that iron oxide is known to have. It is also known from metallurgical practice that zinc ferrite is difficult to reduce, and so it was surmised that there would be a lesser probability of elemental zinc volatilization than would be expected in the case of zinc oxide. Zinc ferrite may also possess an economic advantage over zinc oxide in that it occurs naturally in the mineral franklinite as well as in certain by-products of the metallurgical industry such as open-hearth sludge.

At this stage of development there was more interest in the absorptive and regenerative properties of the active material than

in its strength. Therefore, a sorbent was simply prepared by adding small amounts of bentonite binder and water and extruding the mixture. Details are given in Appendix A. For comparison it was decided to test a commercial nominally 100 percent zinc oxide sorbent, Harshaw Zn-0401 E, 3/16 inch diameter by 1/2 inch long.

Before testing these sorbents, a few tests were first carried out with an iron oxide-silica sorbent developed by METC in conjunction with Air Products and Chemicals, Inc., coded 811X3-1X1. Based on Air Products' and METC experience in testing iron oxide, it was decided to use a mixture of 50 percent steam and 50 percent air by volume for regeneration in future tests. This mixture produces a temperature rise in the regeneration reaction zone of about 500° to 700°F in the two-inch reactor. The calculated temperature rise for an adiabatic reactor is more than twice this; therefore, on a large scale it may be necessary to remove heat from the sorbent bed by the introduction of heat exchange surfaces, unless a lower air/steam ratio mixture is used as regenerant.

1.2 DEVELOPMENT AND TESTING OF ZINC FERRITE AT METC

The need to reach the 1 ppm level required for fuel cells led METC to begin investigating a zinc ferrite sorbent which showed promise of achieving low sulfur levels while retaining its reactivity and regenerability. Screening tests initiated in July 1980 were performed in a two-inch diameter reactor using bottled gases to simulate the composition of gas from gasification of coal. In these tests it was found that this sorbent achieved a high level of removal of both H₂S and COS and was regenerable through up to four cycles of absorption and regeneration. The chemistry of this process is as follows:

REGENERATION: $2\text{FeS} + 3/2 \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 2\text{SO}_2$

$\text{ZnS} + 3/2 \text{O}_2 \rightarrow \text{ZnO} + \text{SO}_2$

$\text{ZnO} + \text{Fe}_2\text{O}_3 \rightarrow \text{ZnFe}_2\text{O}_4$

The stoichiometry of the absorption reactions indicates that if all of the iron and zinc can be reacted to sulfide, an approximately 35 weight percent sulfur loading can be obtained. High sulfur loadings are an important consideration in avoiding excessively large beds or frequent regeneration. The screening tests demonstrated that the zinc ferrite average loading was about 15 percent, or less than half the theoretical loading, but substantially better than the six percent achieved by zinc oxide under the same reactor conditions. Figure 1-1 shows the comparison of zinc ferrite and zinc oxide from these tests.

Preliminary parameters for testing zinc ferrite at atmospheric pressure were established early in the lab scale test program which enabled METC to concentrate on various other operating conditions and goals. Typical of these parameters were:

Sulfidation Temperature, 1000-1200°F

Sulfidation Space Velocity, 1000-2000 h⁻¹

Regeneration Temperature, 1000°F

Regeneration Space Velocity, 500-600 h⁻¹

Regeneration Steam/Air Ratio, 50/50 V/V

Upon completion of the lab-scale screening tests in March 1983, a larger 6-inch diameter fixed-bed absorber/regenerator was constructed and tests were carried out from June to December 1983 using a slipstream of fuel gas from the 42-inch, pressurized, stirred, fixed-bed gasifier at METC. This gasifier is representative of fixed bed gasifiers such as the Lurgi. A fixed bed design for the absorber was chosen for these tests to provide design data for large-scale fixed-bed reactors. Besides reactor

METC Simulated Gas Test Results

FIGURE 1-1

scale up, an objective was to investigate absorption with a real gas.

Experiments in the test unit were conducted under conditions of relatively high space velocity with absorption tests continuing until hydrogen sulfide breakthrough occurred. High sulfur capture efficiencies comparable to lab-scale results were observed. With an inlet concentration of approximately 2,000 to 3,000 ppm, outlet concentrations of H₂S of under 10 ppm were usually achieved, representing a capture efficiency of over 99.5 percent. The sharpness of the breakthrough curves indicated a narrow H₂S concentration profile moving through the reactor even at relatively high space velocities. Sulfur loadings of up to 30 weight percent were obtained in the front part of the reactor. These are all desirable features for an absorption process. Perhaps more importantly, no serious adverse reactions of the sorbent with tars and other "real" gas contaminants were observed. Some carbon accumulation which occurred in the bed was determined to be the result of conversion of iron in the sorbent to iron carbide. The carbon, however, was burnt off during regeneration, restoring the bed to its original condition. A side benefit also observed was an apparent elimination of some fuel gas ammonia (approximately 20 percent) based on the amount found in regeneration tail gas. Regenerability of the sorbent was also established through up to four cycles.

In anticipation of using the zinc ferrite process in conjunction with the KRW-PDU, a series of lab-scale tests were conducted from March to May 1984 with the revamped two-inch diameter, internally aluminized reactor using simulated KRW coal gas, both air and oxygen-blown. Utilizing a zinc ferrite sorbent supplied by United Catalysts, eight absorption tests were conducted which demonstrated that H₂S can be removed to a level of a few ppm before breakthrough.

2.0 SUMMARY OF TESTING

2.1 LABORATORY-SCALE TESTING WITH SIMULATED LURGI GASIFIER GAS

Prior to initiating laboratory-scale evaluations, a series of equilibrium models were written to determine the expected levels of H_2S in equilibrium with various sorbents at various temperatures. A discussion of this modeling is presented in Appendix B.

The laboratory-scale testing was conducted with a test unit consisting of a 2-inch diameter by 2-foot 6-inch long reactor made from AISI Type 316 stainless steel schedule 80 pipe, fitted with ASA 300-pound flanges and an internal 1/8-inch mesh sorbent support. A number of 1/4-inch and 1/2-inch couplings are connected along the reactor length for installation of thermocouples, etc. The reactor is equipped with three shell-type electric heaters controlled separately by individual powerstats. Its operating pressure is limited to about 30 psia. Operating temperatures up to 1800°F or more can be achieved. An engineering drawing of the reactor and schematic drawings of the test unit are included as Appendix C.

Cylinders of the various gases needed to simulate the products of coal gasification, and air for sorbent regeneration are joined to a manifold through regulators and flowmeters. Water can be added to the gas mixture leaving the manifold by means of a pressurized tank of distilled water through a flowmeter. When the reactor is operating in the absorption mode, a preheater of coiled Type 304 stainless steel tube, 1/4-inch diameter by 60-feet long surrounded by two shell-type electric heaters is used to heat the mixture of gases and vaporized water to the desired temperature. This mixture flows upward through a one kilogram sorbent bed in the reactor having a depth of about 18 inches, and leaves at the top after desulfurization.

Reactor effluent gases pass into a water-cooled condenser where steam is condensed, and then are discharged into an exhaust hood via

a scrubber containing United Catalysts G-72D zinc oxide extrusions, which removes any remaining hydrogen sulfide to environmentally safe levels.

In the regeneration mode, regenerant gases, normally air and steam, pass through a preheater, where they are heated to the operating temperature. The gases flow downward through the reactor, from where they pass through a condenser or alternately through a bath of ice-cooled propanol which serves to knock out elemental sulfur and steam condensate. The regeneration tail gases are then vented via the zinc oxide scrubber to the hood.

A Baseline Industries 1030A gas chromatograph is installed for gas analysis. Gas samples are metered to the chromatograph from sampling points shown on the schematic drawing of the test unit in Appendix C. Alternatively, the hydrogen sulfide and sulfur dioxide content of gases can be measured by detector tubes. Temperatures are monitored by a Doric readout and a Honeywell continuous recorder coupled to independent dual thermocouples.

The laboratory-scale test program was conducted in a sequence that developed from test conclusions and a logical requirement for further related information. The sequence of events with summarized results and follow-up logic is shown on Table 2-1. For each of the tests, summary sheets were prepared and selected data were plotted. These sheets are included as Appendix D.

2.1.1 Investigation of Regeneration Conditions of Iron Oxide/Silica (Tests 001-006)

Before initiating tests on zinc oxide-based sorbents, it was decided to establish a suitable regeneration procedure by testing a sample of iron oxide-silica sorbent developed jointly by METC and Air Products and Chemicals, Inc. This sorbent, coded 811X3-1X1 and in

TABLE 2-1

SUMMARY OF LABORATORY SCALE TESTING

<u>Test Sequence</u>	<u>Significant Results</u>
2.1.1 Iron Oxide Silica	Shakedown Apparatus
2.1.2 Preliminary Sorbent Comparisons	
a. Zinc Ferrite	Sorbent Loading - 21 wt% S @ 1000°F, 1000h ⁻¹ SV 1000°F Regeneration @ 600h ⁻¹ SV Reaction wave at 1750°
b. Zinc Oxide	Sorbent Loading - 19 wt% S @ 1000°F, 1000h ⁻¹ SV 1000°F Regeneration @ 600h ⁻¹ SV Reaction wave at 1750°F
Next logical sequence was to determine effect of temperature on each sorbent - Changed to simulated Lurgi gas with high H ₂ S and high H ₂ O. Increased SV to 2000 h ⁻¹ .	
2.1.3 Effect of Temperature on H ₂ S Absorption	
a. Zinc Ferrite	Some decline in breakthrough time and decrease in loading - Unsure if due to temp., composition of gas, or S.V. up to 2000h ⁻¹ .
b. Zinc Oxide	Noticeable decline of reactivity at 1400°F. Peak sulfur loading @ 1200°F.
Zinc ferrite peak loading was 15% vs. oxide peak at 8% @ 1200°F. Next logical sequence was to determine effect of steam content in view of lowered capacity observed by introducing Lurgi gas.	
2.1.4 Effect of Steam on H ₂ S Absorption	
a. Zinc Ferrite	Insufficient testing to determine effect of H ₂ O.
b. Zinc Oxide	Insufficient testing to determine effect of H ₂ O.
Next logical sequence was to determine effect of steam/air ratio on Zn Ferrite regeneration. Lower ratio would produce more desirable off gas.	

TABLE 2-1 (Cont.)

SUMMARY OF LABORATORY SCALE TESTING

<u>Test Sequence</u>	<u>Significant Result</u>
2.1.5 Effect of Steam/Air Ratio on Regeneration	25/75 ratio resulted in 1800°F peak and sintering of bed. Went back to 50/50.
At this time, the general conclusions were:	
Run at 1200°F, 2000h ⁻¹ S.V.	
Regenerate at 1000°F, 600h ⁻¹ S.V., 50/50 steam air	
Zn Ferrite more resistant to sintering and has higher loading, 15% vs. 10%	
Decided to look at some other compounds, e.g., Vanadium, Franklinite, & IFP Zinc Oxide.	
2.1.6 Absorption of H ₂ S by Vanadium Compounds	Vanadium Pentoxide does not reduce below 10ppm H ₂ S.
2.1.7 Absorption of H ₂ S by Franklinite Ore	Inconclusive results due to method of preparing sorbent beads.
2.1.8 Evaluation of IFP Zinc Oxide	Results comparable to Harshaw ZnO with optimum at 1000°F. No further action.
In view of the results favoring Zn Ferrite, variations of Zinc Ferrite composition and operating conditions were explored.	
2.1.9 Effect of Zinc Content in Zinc Ferrite on H ₂ S	Reduced ZnO and increased Fe ₂ O ₃ results in loss of capacity after regeneration
At this point, United Catalysts prepared several 5 kg samples of Zinc Ferrite with various binders.	
2.1.10 Evaluation of UCI 1442 Zinc Ferrite	Loaded to 15.5% at 1200°F and 2000h ⁻¹ S.V. First indication of sulfate formation.

TABLE 2-1 (Cont.)

SUMMARY OF LABORATORY SCALE TESTING

<u>Test Sequence</u>	<u>Significant Result</u>
2.1.11 Absorption of H ₂ S by Nickel	Tests with and without H ₂ S in inlet gas showed H ₂ S evolution from reactor walls. Nickel absorption inconclusive.
Logical to test empty reactor for sulfur evolution.	
2.1.12 Sulfur pickup by Empty Reactor	Pickup and evolution roughly equivalent to iron sulfide equilibrium.
2.1.13 Parametric Studies of Zinc Ferrite for Computer Simulation	Tested UCI 1443 for sulfidation under various conditions of H ₂ O, S.V., and temperature. No regeneration cycles.
2.1.14 Evaluation of UCI Zinc Ferrite to be Used in Side Stream Tests - Similar to 1443 in Preparation	Verified sulfidation at 1200°F, 1286h ⁻¹ S.V. Regeneration at 1000°F, 50/50 Steam-Air.

the form of 1/4-inch diameter extrusions, contains about 45 percent by weight of iron oxide, the remainder being mostly silica. Air Products had investigated the regeneration of a similar material, coded 814X3-1X6, using various mixtures of steam and air as regenerant with particular interest in quantifying any elemental sulfur formed during regeneration.

In tests 001 to 006, (Table 2-2), three cycles of sulfidation and regeneration were completed with three separate loadings of 811X3-1X1 at reactor inlet temperatures of 1000°F. For sulfidation, a gas mixture similar to that used by Oldaker, et al., i.e., simulated METC fixed-bed gasifier gas, was employed except that carbon oxides, hydrocarbons, and oxygen were replaced by nitrogen. The space velocity of 800 to 1,000 hourly was also about the same and sulfidation was continued until breakthrough. For regeneration, three different mixtures of steam and air were examined; 95/5, 90/10, and 50/50 percent by volume. Again, the space velocity for regeneration of about 600 hourly was in the same range as those employed by Oldaker, et al.

Before and after sulfidation in test 001, sorbent samples were characterized for surface area, density, and pore volume and also analyzed for sulfur content by high-temperature combustion techniques. Additionally, mineral and elemental analyses by X-ray techniques were conducted after sulfidation. It is noteworthy that there was satisfactory agreement between the sulfur analyses by the two methods. Of interest was the finding that the iron content of sulfided sorbent was in the form of pyrite, hematite, and magnetite, roughly in the ratio 1:1:2.

Test 002 was a regeneration with 95/5 percent steam-air mixture heated to 1000°F. The test was continued for 39 hours during which virtually all the absorbed sulfur was liberated, about 75 percent as elemental sulfur and the bulk of the rest as hydrogen sulfide as measured by the Tutwiler method. Sulfur analysis of regenerated sorbent confirmed that regeneration was virtually complete.

TABLE 2-2
INVESTIGATION OF REGENERATION CONDITIONS OF IRON OXIDE/SILICA

Test No.	Test Type	Sorbent	Sorbent Wt. (gm)	Sulfur Loading Before Break-through. Wt, %	Gas Feed Composition Vol. % (l)	H ₂ S Vol. %	Space Velocity (Vol/Vol Hr)	Linear Velocity (cm/sec)	Temp. °F	Pressure	Sorption Time Before Breakthrough or Regeneration Time (Hrs)	Exit Gas Composition H ₂ S (ppm) SO ₂ (%) Sulfur (g)
001	Sulfidation	Iron oxide/silica	936	4.7	METC	0.7	800	8.1	1000	Atmospheric	8	85 ppm
002	Regeneration	Iron oxide/silica	936	N/A	95% steam 5% air		600	4.9	1000	Atmospheric	39	7.2% H ₂ S, No SO ₂ . 122 gm. elemental sulfur
003	Sulfidation	Iron oxide/silica	936	4.47	METC	2.7	1013	8.2	1000	Atmospheric	4.5	22 ppm H ₂ S
004	Regeneration	Iron oxide/silica	936	N/A	90% steam 10% air		622	4.9	1000	Atmospheric	20.5	5000-6000 ppm H ₂ S. 0.3 ppm SO ₂ 19.4 g elemental sulfur
005	Sulfidation	Iron oxide/silica	1000	10.4	METC	2.7	900	8.2	1000	Atmospheric	3	1 to 6 ppm H ₂ S
006	Regeneration	Iron oxide/silica	1000	N/A	50% steam 50% air		600	5.4	1000	Atmospheric	7.5	1000-1200 ppm H ₂ S. 4-7% SO ₂ 2.5g elemental sulfur

(1) METC gas composition: 14.6% H₂, 75.8% N₂, 6.9% H₂O, 2.7% H₂S.

For the second regeneration, test 004, the regenerant was a 90/10 percent steam-air mixture. Elemental sulfur formed was about 15 percent of the recovered total, the remainder being a mixture of hydrogen sulfide and sulfur dioxide in comparable proportions.

A third regeneration was carried out in test 006 with a 50/50 percent steam-air mixture. In this case, elemental sulfur represented only about 1.5 percent of total sulfur. The bulk of the sulfur was liberated as sulfur dioxide accompanied by a small amount of hydrogen sulfide. Samples of regenerated sorbent were characterized for BET surface area, pore volume for pores up to 600Å, and skeletal density by helium pycnometry, and also analyzed for mineral and elemental content.

There was little noticeable difference in surface area, skeletal density, and pore volume between sulfidized and regenerated sorbent. These were, respectively, about 1 m²/g, 3.25 g/m³, and 2.2 mm³/g.

Figure 2-1 illustrates the extent to which hydrogen sulfide was removed in sulfidation tests 001, 003, and 005 before breakthrough. A surprising result was the low initial exit level, less than 10 ppm, of hydrogen sulfide particularly in test 005. This level is an order of magnitude less than is predicted for iron oxide and comparable to that achieved in later tests with zinc oxide-based sorbents. This may perhaps be a consequence of the small zinc oxide content, about 7 percent by weight, of the sorbent, whose iron oxide content is a by-product of the steel industry. Table 2-3, based on literature data, gives values of hydrogen sulfide in gases of various steam content, over the range of temperatures of interest, in equilibrium with zinc oxide.

In spite of the substantial elemental sulfur formation when regenerating with high steam-air ratio mixtures, preliminary economic calculations suggest that a process based on this, for sulfur recovery, probably would not be feasible in most cases

IRON OXIDE SULFIDATION

TESTS 001,003,005

FIGURE 2-1

TABLE 2-3

HYDROGEN SULFIDE/ZINC OXIDE EQUILIBRIUM VALUES

Volume of Steam in Gas	H ₂ S Concentration (ppm) in Wet Exit Gas					
	450°C (842°F)	500°C (932°F)	550°C (1022°F)	600°C (1112°F)	650°C (1202°F)	700°C (1292°F)
50	1.7	3.7	7.3	13.2	22.0	34.5
40	1.4	3.0	5.9	10.6	17.6	27.6
30	1.0	2.2	4.4	7.9	13.2	20.7
20	0.69	1.5	2.9	5.3	8.8	13.8
10	0.35	0.75	1.5	2.6	4.4	6.9
5	0.17	0.37	0.7	1.3	2.2	3.5

because of the large steam requirement and the potential difficulty of condensing sulfur and disposing of effluent steam. Since addition of 50 percent of steam to air produced a satisfactory moderating effect on regeneration temperatures, it was decided to conduct future regeneration tests using this mixture as the regenerant. Later experiments sought to optimize the steam content.

2.1.2 Preliminary Sorbent Comparison

2.1.2.1 Zinc Ferrite (Tests 007-012)

Tests 007 to 012 (Table 2-4) with the same charge of sorbent had as their purpose determination of the hydrogen sulfide removal capability of zinc ferrite sorbent and verification of its regenerability. As in the previous tests with iron oxide, both sulfidation and regeneration were at 1000°F. The regenerant was a 50/50 percent by volume steam-air mixture.

Figure 2-2 shows that, for all three sulfidation tests, hydrogen sulfide was removed to a level of about 2 to 4 ppm before breakthrough. This compares with a figure of about 1 ppm calculated, from equilibrium considerations, for zinc oxide (see Appendix B). It is also evident that, after two regenerations, there was no noticeable loss of absorption capacity. This absorption capacity is somewhat greater than, though comparable with, that of the iron oxide sorbent in test 005, if the latter's large content of silica is taken into consideration.

During regenerations, a reaction zone moves through the sorbent bed in about 8 hours accompanied by a temperature peak of up to 1750°F depending on steam dilution. This is illustrated in Figure 2-3 for test 008. The regeneration off-gas contained about 5 to 10 percent sulfur dioxide by volume on a dry basis. Significant amounts of hydrogen sulfide, of the order of 1000 ppm, were also present in the regeneration off-gas as well as small quantities of elemental sulfur. Thus it appeared that zinc ferrite has the capability of removing

TABLE 2-4
PRELIMINARY ZINC FERRITE TEST RUNS

Test No.	Test Type	Sorbent	Sorbent Wt. (gm)	Sulfur Loading Before Break-through Wt., %	Gas Feed Composition Vol. % (1)	H ₂ S Vol. %	Space Velocity (Vol/Vol H ₂ r)	Linear Velocity (cm/sec)	Temp. °F	Pressure	Sorption Time Before Breakthrough or Regeneration Time (Hrs)	Exit Gas Composition H ₂ S (ppm) SO ₂ (%) Sulfur (g)
007	Sulfidation	zinc ferrite	800	21.3	METC	2.7	1000	8.1	1000	Atmospheric	7	1-2 ppm H ₂ S
008	Regeneration	zinc ferrite	800	N/A	50% steam 50% air	-	600	4.9	1000	Atmospheric	12.5	2000 ppm H ₂ S 4-9% SO ₂
009	Sulfidation	zinc ferrite	800	18.7	METC	2.7	1000	8.1	1000	Atmospheric	6	2-4 ppm H ₂ S
010	Regeneration	zinc ferrite	300	N/A	50% steam 50% air	-	600	4.9	1000	Atmospheric	12.5	2000-3000 ppm H ₂ S 4-10% SO ₂
011A	Sulfidation	zinc ferrite	300	N/A	METC	3.0	1000	8.1	1000	Atmospheric	0.5 (Aborted)	
011B	Sulfidation	zinc ferrite	800	21.38	METC	2.7	1000	8.1	1000	Atmospheric	7	2-6 ppm H ₂ S
012A	Regeneration	zinc ferrite	800	N/A	50% steam 50% air		600	4.9	1000	Atmospheric	12.5	2000-3000 ppm H ₂ S 4-10% SO ₂

(1) METC gas composition: 14.6% H₂, 75.8% N₂, 6.9% H₂O, 2.7% H₂S.

ZINC FERRITE SULFIDATION

TESTS C07,009,011B (THREE CYCLES ON SAME SORBENT)

FIGURE 2-2

ZINC FERRITE REGENERATION

TEST 008

FIGURE 2-3

hydrogen sulfide to levels comparable with zinc oxide and is also regenerable.

BET surface area, pore volume for pores up to $600\text{\AA}$, and skeletal density determinations were made before test 007, after test 008, and after test 011B. Over the series there was a fall off in surface area from $5.8\text{ m}^2/\text{g}$ (initial, unsulfidized) to $1.4\text{ m}^2/\text{g}$ (final, sulfidized). Correspondingly, pore volume declined from $12.2\text{ mm}^3/\text{g}$ to $2.9\text{ mm}^3/\text{g}$. Skeletal density changed from 5.2 to 4.4 g/cm^3 , accounted for by the lower density of sulfide compared with oxide.

The sorbent was analyzed for sulfur by the high-temperature combustion technique after test 008 (regenerated) and after test 011B (sulfidized). Sulfur content averaged 0.4 and 25.4 percent by weight, respectively. The latter figure is significantly higher than that obtained by parallel X-ray elemental analysis (16.0 percent), though in better agreement with that deduced from X-ray diffraction mineral analysis (23 percent). Mineral analysis, after test 011B, averaged 28.5 percent FeS, 38.5 percent ZnS, and 33.0 percent ZnFe_2O_4 . In contrast with a corresponding analysis for the iron oxide sorbent, no pyrite (FeS_2) was detected.

2.1.2.2 Zinc Oxide (Tests 013-015)

As a basis for comparison, a commercial nominally 100 percent zinc oxide sorbent, Zn-0401E 3/16 inch diameter, was tested which was obtained from Harshaw Chemical Company. Some of its characteristics are given in their brochure, Harshaw Catalysts:

Apparent Bulk Density	1.2 g/cm^3
Crushing Strength	3.6 kg
Surface Area	$3\text{ m}^2/\text{g}$
Pore Volume	$0.26\text{ cm}^3/\text{g}$ (For pore sizes down to $100\text{\AA}$)

It is advertised to remove sulfur compounds from producer, coke oven, hydrogen, and hydrocarbon gas streams.

Tests 013 to 015, (Table 2-5), two sulfidations and one regeneration at nominally 1000°F, demonstrated that this sorbent, after one regeneration, lost none of its absorption efficiency or capacity under the test conditions employed, which were the same as for the previous regeneration tests with zinc ferrite. Hydrogen sulfide content was brought down to a level of about 2 to 8 ppm, much the same as for zinc ferrite. This is illustrated in Figure 2-4.

During regeneration, as for zinc ferrite, a similar temperature wave moved through the sorbent bed in a similar time frame. Figure 2-5 compares the sulfur dioxide content of regeneration off-gas during test 014 (zinc oxide) with the average of that from tests 008 and 010 (zinc ferrite). These results are also seen to be generally similar. The lower sulfur dioxide concentration in the case of zinc ferrite may be accounted for by the accompanying production of elemental sulfur and hydrogen sulfide and oxidation of ferrous to ferric iron. No elemental sulfur was observed to condense out from the zinc oxide regeneration off-gas.

BET surface area, pore volume for pores up to 600Å, and skeletal density were measured before test 013 (fresh), and after test 015 (sulfidized). A mineral analysis was done after test 013. Results show a decline of surface area and pore volume from 3.2 m²/g and 6.5 mm³/g to 1.1 m²/g and 2.0 mm³/g, respectively. Skeletal density changed from 6.4 g/cm³ to 3.8 g/cm³. The measured surface area of fresh sorbent was in good agreement with the manufacturer's value. It should be noted that the manufacturer's value for pore volume is for uncrushed extrusions by mercury porosimetry in contrast to the tests, which are for crushed extrusions by nitrogen adsorption. The mineral analysis of sulfidized sorbent indicated a composition of 15 percent ZnO and 85 percent ZnS on a weight basis. As for sulfidized zinc ferrite, the zinc sulfide content was distributed between αZnS and βZnS in the approximate ratio 1:3.

Pore Volume 0.26 cm³/g (For pore sizes down to 100Å)

It is advertised to remove sulfur compounds from producer, coke oven, hydrogen, and hydrocarbon gas streams.

Tests 013 to 015, (Table 2-5), two sulfidations and one regeneration at nominally 1000°F, demonstrated that this sorbent, after one regeneration, lost none of its absorption efficiency or capacity under the test conditions employed, which were the same as for the previous regeneration tests with zinc ferrite. Hydrogen sulfide content was brought down to a level of about 2 to 8 ppm, much the same as for zinc ferrite. This is illustrated in Figure 2-4.

During regeneration, as for zinc ferrite, a similar temperature wave moved through the sorbent bed in a similar time frame. Figure 2-5 compares the sulfur dioxide content of regeneration off-gas during test 014 (zinc oxide) with the average of that from tests 008 and 010 (zinc ferrite). These results are also seen to be generally similar. The lower sulfur dioxide concentration in the case of zinc ferrite may be accounted for by the accompanying production of elemental sulfur and hydrogen sulfide and oxidation of ferrous to ferric iron. No elemental sulfur was observed to condense out from the zinc oxide regeneration off-gas.

BET surface area, pore volume for pores up to 600Å, and skeletal density were measured before test 013, fresh, and after test 015, sulfidized. A mineral analysis was done after test 013. Results show a decline of surface area and pore volume from 3.2 m²/g and 6.5 mm³/g to 1.1 m²/g and 2.0 mm³/g, respectively. Skeletal density changed from 6.4 g/cm³ to 3.8 g/cm³. The measured surface area of fresh sorbent was in good agreement with the manufacturer's value. It should be noted that the manufacturer's value for pore volume is for uncrushed extrusions by mercury porosimetry in contrast to the tests, which are for crushed extrusions by nitrogen adsorption. The mineral analysis of sulfidized sorbent indicated a composition of 15

TABLE 2-5
PRELIMINARY ZINC OXIDE TEST RUNS

Test No.	Test Type	Sorbent	Sorbent Wt. (gm)	Sulfur Loading Before Break-through Wt., %	Gas Feed Composition Vol. % (1)	H ₂ S Vol. %	Space Velocity (Vol/Vol Hr)	Linear Velocity (cm/sec)	Temp. °F	Pressure	Sorption Time Before Breakthrough or Regeneration Time (Hrs)	Exit Gas Composition H ₂ S (ppm) SO ₂ (%) Sulfur (g)
013	Sulfidation	zinc oxide	1000	18.7	METC	2.7	1000	7.9	1000	Atmospheric	9	5-9 ppm H ₂ S
014	Regeneration	zinc oxide	1000		50% steam 50% air		600	4.8	1000	Atmospheric	12	3-14% SO ₂ 0.16 gm elemental sulfur
015	Sulfidation	zinc oxide	1000	18.8	METC	2.7	1000	7.9	1000	Atmospheric	9	2-7 ppm H ₂ S

(1) METC gas composition: 14.6% H₂, 75.8% N₂, 6.5% H₂O, 2.7% H₂S.

ZINC OXIDE SULFIDATION

TESTS 013, 015 (HARSHAW ZN-0401)

FIGURE 2-4

SORBENT REGENERATION

ZINC OXIDE AND ZINC FERRITE

FIGURE 2-5

2.1.3 Effect of Temperature on H₂S Absorption

2.1.3.1 Zinc Ferrite (Tests 016-031)

Tests 016 to 031 (Table 2-6) were conducted to determine the absorption performance of zinc ferrite over a range of temperatures from 600°F to 1500°F. Interest in lower temperatures is mainly concerned with the lower equilibrium hydrogen sulfide levels expected. The higher temperatures are of interest because of prospective thermal efficiency gains. All regenerations were at a nominal temperature of 1000°F.

The composition of the hydrogen sulfide carrier gas was changed to that typical of a commercial Lurgi air-blown dry-ash fixed-bed gasifier, but with H₂S content increased to 2.7% to shorten the breakthrough time consistent with operations that could be completed within a day.

For tests 016 and 017 at 1000°F, both absorption and regeneration space velocities were doubled to 2000 and 1200 hourly, respectively, in order to complete tests to breakthrough during a day shift. This proved to be injudicious in the case of regeneration because, after a satisfactory absorption run in test 016, there was a temperature peak of over 1900°F in the regeneration reaction zone (Figure 2-6). In test 018, at 600°F with a new loading of sorbent, hydrogen sulfide breakthrough occurred immediately. After about 2 hours the inlet gas temperature was raised to 1000°F and hydrogen sulfide was reduced to 100 ppm. At this point the sorbent was regenerated and a further absorption test attempted at 1000°F. Initially, hydrogen sulfide came through at the expected level of 7 ppm but breakthrough occurred within half an hour. Test 018 includes the latter regeneration and absorption tests on the same test data sheet.

TABLE 2-6
EFFECT OF TEMPERATURE ON ZINC FERRITE PERFORMANCE

Test No.	Test Type	Sorbent	Sorbent Wt. (gm)	Sulfur Loading Before Break-through, Wt., %	Gas Feed Composition Vol. % (l)	H ₂ S Vol. %	Space Velocity (Vol/Vol Hr)	Linear Velocity (cm/sec)	Temp. °F	Pressure	Sorption Time Before Breakthrough or Regeneration Time (Hrs)	Exit Gas Composition H ₂ S (ppm) SO ₂ (%) Sulfur (g)
016	Sulfidation	zinc ferrite	643	14.1	Lurgi	2.7	2000	15.2	1000	Atmospheric	2.25	9-13 ppm H ₂ S
017	Regeneration	zinc ferrite	643	N/A	50% steam 50% air	-	1200	9.1	1000	Atmospheric	5	8-13% SO ₂ 7.7 gm elemental sulfur
018	Sulfidation	zinc ferrite	643	-	Lurgi	2.7	2000	15.2	600	Atmospheric	(Aborted)	6000 ppm H ₂ S immediately
019	Sulfidation	zinc ferrite	643	N/A	Lurgi	2.7	2000	15.2	1000	Atmospheric	2.5	3-10 ppm H ₂ S
020	Regeneration	zinc ferrite	643	N/A	50% steam 50% air	-	600	4.9	1000	Atmospheric	6.75	3.5-14% 4.1 gm. elemental sulfur
021	Sulfidation	zinc ferrite	643	12.5	Lurgi	2.7	2000	15.2	1000	Atmospheric	2	3-5 ppm H ₂ S
022	Regeneration	zinc ferrite	643	N/A	50% steam 50% air	-	600	4.9	1000	Atmospheric	6.75	3.5-13.6% SO ₂
023	Sulfidation	zinc ferrite	643	1.56	Lurgi	2.7	2000	15.5	800	Atmospheric	0.5	5 ppm H ₂ S

TABLE 2-6 (Cont.)

Test No.	Test Type	Sorbent	Sorbent Wt. (gm)	Sulfur Loading Before Break-through, Wt., %	Gas Feed Composition Vol. % (1)	H ₂ S Vol. %	Space Velocity (Vol/Vol Hr)	Linear Velocity (cm/sec)	Temp. °F	Pressure	Sorption Time Before Breakthrough or Regeneration Time (Hrs)	Exit Gas Composition H ₂ S (ppm) SO ₂ (%) Sulfur (g)
024	Sulfidation	zinc ferrite	643	15.6	Lurgi	2.7	2000	15.2	1200	Atmospheric	2.5	9-13 ppm H ₂ S
025	Regeneration	zinc ferrite	643	N/A	50% steam 50% air	-	600	4.9	1000	Atmospheric	5.25	3.1-12.8% SO ₂
026	Sulfidation	zinc ferrite	643	9.4	Lurgi	2.7	2000	15.2	1400	Atmospheric	1.5	1-3 ppm H ₂ S
027	Regeneration	zinc ferrite	643	N/A	50% steam 50% air	-	600	4.9	1000	Atmospheric	6.5	2.9-12.8% SO ₂
028	Sulfidation	zinc ferrite	643	5.26	Lurgi	2.7	2000	15.2	1500	Atmospheric	0.5	4 ppm H ₂ S
029	Sulfidation	zinc ferrite	643	1.56	Lurgi	2.7	2000	15.2	1500	Atmospheric	0.25	2 ppm H ₂ S
030	Regeneration	zinc ferrite	643	N/A	50% steam 50% air	-	600	4.9	1000	Atmospheric	1.25	4-5% SO ₂
031	Sulfidation	zinc ferrite	643	N/A	Lurgi	2.7	2000	15.2	1000	Atmospheric	0.25	600 ppm H ₂ S

(1) Lurgi gas composition: 28.1% N₂, 2.9% CH₄, 17.1% H₂, 11.9% CO, 9.7% CO₂, 27.6% H₂O, 2.7% H₂S.

ZINC FERRITE REGENERATION

TEST 017

FIGURE 2-6

It appeared from test 018 that the kinetics of absorption at 600°F are too poor to reach equilibrium hydrogen sulfide. However, it should be pointed out that the hydrogen sulfide flow rate in the simulated gas is an order of magnitude larger than would be expected in practice. It also seems clear that the sorbent was damaged by the doubled regeneration space velocity so there might be some doubt about the conclusion.

The reactor was filled with a new loading of zinc ferrite in test 019, its composition being routinely confirmed by mineral analysis. Initially, its performance was checked at 1000°F against previous tests at the same conditions and it performed according to expectations. Regeneration in test 020 reverted to the original practice of using a 600 hourly space velocity. Test 021, a repeat sulfidation at 1000°F, again proved to be normal. In future tests the lower regeneration space velocity was readopted.

After the regeneration in test 022, test 023 was completed at 800°F. Hydrogen sulfide exited the reactor at 5 ppm initially and at 900 ppm after half an hour. Therefore, reaction kinetics at 800°F are better than at 600°F but still poor at this temperature. This was a disappointing result, as it had been anticipated that the spinel structure of zinc ferrite might give superior kinetics. Because of the short duration of absorption, the subsequent regeneration was included on the same test data sheet. In test 024, absorption temperature was raised to 1200°F. Hydrogen sulfide was down to 9 to 15 ppm for 2.5 hours. After a fourth regeneration, there was a further increase of temperature in test 026 (absorption) to 1400°F. Unexpectedly, the hydrogen sulfide removal level before breakthrough was superior to that found at 1200°F and comparable to that at 1000°F. Absorption capacity however, was inferior, breakthrough occurring after about 1.5 hours.

The next sulfidation, after regeneration in test 027, was at 1500°F in test 028 when hydrogen sulfide was initially removed also to the unexpectedly low level of 4 ppm but only for about half an hour.

ZINC FERRITE SULFIDATION

TESTS 021,023,024,026,028

FIGURE 2-7

Surface area and pore volume of sulfidized material were unusually low at $0.5 \text{ m}^2/\text{g}$ and $0.7 \text{ mm}^3/\text{g}$, respectively. Because the sorbent had been inadvertently overheated to 1600°F during overnight storage before test 028, the test was repeated in test 029 with a new batch of sorbent. The results of this test were essentially the same, indicating that the overnight heating was not the cause of the poor performance in test 028. To test whether the sorbent was permanently damaged at 1500°F , a further sulfidation at $1,000^\circ\text{F}$ in test 031 was attempted after regeneration in test 030. Breakthrough occurred immediately. Surface area and pore volume after test 031 were $2.2 \text{ m}^2/\text{g}$ and $5.2 \text{ mm}^3/\text{g}$ which are normal, suggesting that sintering may not be the main reason for the poor performance.

Mineral analysis after test 028 gave 48.5 percent FeO , 28.7 percent ZnS , 5.3 percent ZnFe_2O_4 , and 17.4 percent ZnO , indicating that most ferric iron in zinc ferrite had been reduced to ferrous iron. No sulfur was absorbed as FeS contrary to experience at lower temperatures.

Another mineral analysis, after test 031, gave 91.8 percent ZnFe_2O_4 and 8.2 percent ZnS . Therefore, it appears that the sorbent had been mostly reconverted to zinc ferrite after the sulfidation excursion at 1500°F and subsequent regeneration though its absorption capacity was very small, at least at the low-hydrogen sulfide level required, indicating irreparable though unaccountable damage.

Figure 2-7 illustrates the effect of temperature on hydrogen sulfide removal by zinc ferrite for tests 021 to 028. It is apparent that there is some decline in absorption capacity starting at 1400°F . There appears to be no significant fall in the level of hydrogen sulfide removal with temperature. Because the same loading of sorbent was used in tests 019 to 028, it remains to be seen whether regeneration after absorption at 1200° and 1400°F restores the sorbent to its original condition. However, the similarity between

tests 028 and 029 suggests that no damage was incurred by the sorbent in tests 024 and 026 and subsequent regenerations.

2.1.3.2 Zinc Oxide (Tests 032-041)

In tests 032 to 041, (Table 2-7) a parallel investigation (to that of zinc ferrite) of the effect of temperature on the absorptive power of zinc oxide was conducted. The series began with test 032 at 800°F. Hydrogen sulfide was removed to 3 ppm for 1.5 hours until breakthrough. Under these conditions zinc ferrite reached a comparable removal level but substantially lower capacity. Runs 034 and 036 at 1000°F and 1200°F respectively, paralleled the corresponding tests for zinc ferrite with a similar degree of hydrogen sulfide removal but substantially lower absorption capacity. A noticeable departure in absorption capacity became evident in test 038 at 1400°F. Though removal level was virtually the same, sorbent capacity was less than half. At this point regeneration in test 039 was aborted as sulfur dioxide was being evolved at much less than the normal rate. Sulfidation test 040 at 1500°F with a new batch of zinc oxide sorbent was again similar to the corresponding test for zinc ferrite, sulfide removal level being down to 2 ppm for about half an hour.

The above effects of temperature on zinc oxide sulfidation are illustrated in Figure 2-8. When comparing these with the corresponding data for zinc ferrite, it should be borne in mind that the weight of zinc oxide sorbent for each test was substantially greater (1000 g compared to 643 g).

Comparatively, zinc ferrite and zinc oxide appear to be very similar in their absorptive capabilities, particularly in regard to the concentration level of hydrogen sulfide attainable in treated gas. The main difference detected is in absorption capacities (or sulfur loadings), which is illustrated in Figure 2-9. Both sorbents achieved maximum sulfur loadings between 1000° and 1200°F, zinc ferrite absorbing more than 15 percent and zinc oxide about

TABLE 2-7
EFFECT OF TEMPERATURE ON ZINC OXIDE PERFORMANCE

Test No.	Test Type	Sorbent	Sorbent Wt. (gm)	Sulfur Loading Before Break-through, Wt., %	Gas Feed Composition Vol. % (1)	H ₂ S Vol. %	Space Velocity (Vol/Vol Hr)	Linear Velocity (cm/sec)	Temp. °F	Pressure	Sorption Time Before Breakthrough or Regeneration Time (Hrs)	Exit Gas Composition H ₂ S (ppm) SO ₂ (%) Sulfur (g)
032	Sulfidation	Zinc oxide	1000	6.04	Lurgi	2.7	2000	15.2	800	Atmospheric	1	3 ppm H ₂ S
033	Regeneration	Zinc oxide	1000	N/A	50% steam 50% air	-	600	4.9	1000	Atmospheric	6	5-4% SO ₂
034	Sulfidation	Zinc oxide	1000	8.0	Lurgi	2.7	2000	15.2	1000	Atmospheric	2	1-3 ppm H ₂ S
035	Regeneration	Zinc oxide	1000	N/A	50% steam 50% air	-	600	4.9	1000	Atmospheric	7.5	3.7-14.8% SO ₂
036	Sulfidation	Zinc oxide	1000	8.0	Lurgi	2.7	2000	15.2	1200	Atmospheric	0.25	6-15 ppm H ₂ S
037	Regeneration	Zinc oxide	1000	N/A	50% steam 50% air	-	600	4.9	1000	Atmospheric	6.75	3.7-14.8% SO ₂
038	Sulfidation	Zinc oxide	1000	2.0	Lurgi	2.7	2000	15.2	1400	Atmospheric	0.5	2-3 ppm H ₂ S
039	Regeneration	Zinc oxide	1000	N/A	50% steam 50% air	-	600	4.9	1000	Atmospheric	19	Regeneration Aborted
040	Sulfidation	Zinc oxide	1000	1.0	Lurgi	2.7	2000	15.2	1500	Atmospheric	0.25	2 ppm H ₂ S

(1) Lurgi gas composition: 28.1% N₂, 2.9% CH₄, 17.1% H₂, 11.9% CC, 9.7% CO₂, 27.6% H₂O, 2.7% H₂S.

ZINC OXIDE SULFIDATION

TESTS 038,038,034,032 (HARSHAW ZN-0401)

FIGURE 2-8

SULFUR LOADING

ZINC FERRITE AND ZINC OXIDE

FIGURE 2-9

8 percent at the conditions of the investigation. These figures are conservative since they were calculated from hydrogen sulfide flow rate up to the last recorded point before breakthrough. At the lower end of the temperature range covered, 800°F, zinc oxide appears to react more rapidly with hydrogen sulfide permitting a larger capacity before breakthrough. In contrast zinc ferrite performs substantially better at 1000°, 1200°, and 1400°F in terms of absorption capacity. At the higher temperatures, it may be that zinc oxide is more prone to sintering or pore blockage. Above 1400°F zinc ferrite is reduced to a mixture of zinc and ferrous oxides which may cause irreversible damage to the sorbent.

There is some evidence that, at least at 1000°F, zinc ferrite sulfur loadings can be substantially greater when influent gas steam content is smaller, such as in tests 007, 009, and 011B where sulfur loadings either approached or exceeded 20 percent. Under the same conditions, in the case of zinc oxide, the effect is more marked and sulfur loadings approached 20 percent in tests 013 and 015. Oldaker et al. found that increased steam content resulted in smaller absorption capacities for their iron oxide sorbents.

Conclusions, Plans and Recommendations

The principal finding at this stage of the project was that zinc ferrite and also iron oxide containing some zinc ferrite had hydrogen sulfide absorption performances very similar to those of zinc oxide. Extruded sorbents made from these compounds were demonstrated to perform with varying ability to remove H₂S in the temperature range 800°F to 1400°F, at a space velocity of 2000 hourly and an inlet gas H₂S concentration of 2.7 percent. Sorbents were also shown to be regenerable with a 50/50 percent v/v steam-air mixture at 1000°F and 600 hourly space velocity with little loss of absorptive power over up to 5 cycles.

Both zinc ferrite and zinc oxide appear to perform optimally in the middle of the temperature range, where absorption capacity is

greatest. Surprisingly, the experimental results indicated no trend to a lower degree of hydrogen sulfide removal with rise in temperature. Zinc ferrite appeared to be superior to zinc oxide in terms of its absorption capacity and resistance to sintering or pore blockage at higher temperatures.

In the experimental tests thus far, hydrogen sulfide was removed to a level of below 10 ppm, which is an order of magnitude away from the goal for molten carbonate fuel cells. However, most of the tests utilized a gas containing 27 percent by volume of steam. Since equilibrium considerations lead one to expect the attainable hydrogen sulfide level to be directly proportional to steam content, utilization of gas with low-steam content could be one way to approach the goal, bearing in mind that an excessively reducing gas may damage the sorbent.

2.1.4 Effect of Steam on H₂S Absorption

2.1.4.1 Zinc Ferrite (Tests 043 and 050-053)

Most of the previous test tests were carried out employing a simulated gas containing 27 percent by volume of steam. The hydrogen sulfide levels achieved by absorption with zinc oxide and zinc ferrite agreed well with the thermodynamically predicted values, indicating that the resistance to mass transfer of diffusion and reaction rate was sufficiently low so that equilibrium could be attained. Additional tests were carried out to determine whether this equilibrium could also be reached under conditions where no steam was added to the simulated gas at two different space velocities. (See Table 2-8)

Test 43 at 1000°F with a new batch of zinc ferrite was analogous to test 42R for zinc oxide (see below) and resulted in a similar hydrogen sulfide level. After regeneration in test 50, test 51 was carried out at the lower space velocity of 720 hourly and a

TABLE 2-8
EFFECT OF STEAM ON ZINC FERRITE PERFORMANCE

Test No.	Test Type	Sorbent	Sorbent Wt. (gm)	Sulfur Loading Before Break-through, Wt., %	Gas Feed Composition Vol. % (1)	H ₂ S Vol. %	Space Velocity (Vol/Vol Hr)	Linear Velocity (cm/sec)	Temp. °F	Sorption Time Before Breakthrough or Regeneration Time (Hrs)	Exit Gas Composition H ₂ S (ppm) SO ₂ (%) Sulfur (g)
C43	Sulfidation	Zinc Ferrite	643	12.5	Lurgi (dry)	3.7	1442	34.9	1000	3.75	0.5-0.9 ppm H ₂ S
G50	Regeneration	Zinc Ferrite	643	N/A	50% steam 50% air	-	600	15.4	1000	8.25	10.4-16% SO ₂
D51	Sulfidation	Zinc Ferrite	643	7.9	Lurgi (dry)	3.7	721	17.4	900	4.0	0.2-1.6 ppm H ₂ S
D52	Regeneration	Zinc Ferrite	643	N/A	50% steam 50% air	-	600	15.4	1000	9.75	10.8-14.4% SO ₂
D53	Sulfidation	Zinc Ferrite	643	14.2	Lurgi (dry)	3.7	721	17.4	1000	5.0	2-5 ppm H ₂ S

(1) Lurgi gas composition (dry): 38.87% N₂, 4.0% CH₄, 23.7% H₂, 16.16% CO, 13.53% CO₂, 3.7% H₂S.

temperature of 900°F. The sorbent was regenerated again in test 52 and a further sulfidation carried out in test 53 at the same space velocity of 720 hourly but at 1000°F. The hydrogen sulfide levels attained are plotted in Figure 2-10 together with the average of those from tests 16, 21, and 47 for comparison. The time scale is normalized to give a constant hydrogen sulfide flow rate into the reactor.

For about half the time to breakthrough the hydrogen sulfide level in tests 51 and 53 was somewhat lower than in test 43 analogous to the case of zinc oxide but, in contrast, plateaued at about the same level for the rest of the time to breakthrough. This suggests that resistance to mass transfer of hydrogen sulfide into the sorbent is appreciably higher for zinc ferrite than for zinc oxide. Sulfur takeup at 900°F was about half that at 1000°F which is comparable to the case for simulated gas containing 27 percent v/v of steam.

2.1.4.2 Zinc Oxide (Tests 042R and 045-046)

In test 42R (Table 2-9) at 1000°F with a new batch of zinc oxide, steam was deleted from the simulated gas previously employed at a space velocity of 2000 hourly reducing the space velocity to 1440 hourly. After regeneration in test 45, the space velocity in test 46 was halved to 720 hourly. The exit hydrogen sulfide levels in tests 42R and 46 are shown in Figure 2-11 together with those in test 34 for comparison. The time scale is normalized to a constant flow of hydrogen sulfide into the reactor. The steam content at the reactor exit in tests 42R and 46 is expected to be about 4.5 percent assuming that the "shift" reaction is at equilibrium. At the higher space velocity of test 42R equilibrium does not appear to be reached. The lower space velocity of test 46 results in a somewhat lower hydrogen sulfide level which is about that expected for solid-gas equilibrium free of diffusional resistances associated with higher space velocities.

ZINC FERRITE SULFIDATION

TESTS AVG(16,21,47),043,051,053

FIGURE 2-10

TABLE 2-9
EFFECT OF STEAM ON ZINC OXIDE PERFORMANCE

Test No.	Test Type	Sorbent	Sorbent Wt. (gm)	Sulfur Loading Before Break-through, Wt. %	Gas Feed Composition Vol. % (1)	H ₂ S Vol. %	Space Velocity (Vol/Vol Hr)	Linear Velocity (cm/sec)	Temp. °F	Sorption Time Before Breakthrough or Regeneration Time (Hrs)	Exit Gas Composition H ₂ S (ppm) SO ₂ (%) Sulfur (g)
042R	Sulfidation	Zinc Oxide	1000	8.0	Lurgi (dry)	3.7	1442	34.9	1000	3.5	0.8-1.2 ppm H ₂ S
045	Regeneration	Zinc Oxide	1000	N/A	50% steam 50% air		600	15.4	1000	10.0	7.8-12% SO ₂
046	Sulfidation	Zinc Oxide	1000	8.1	Lurgi (dry)	3.7	721	17.6	1000	4.0	0.2-1 ppm H ₂ S

(1) Lurgi gas composition (dry): 38.87% N₂, 4.0% CH₄, 23.7% H₂, 16.16% CO, 13.53% CO₂, 3.7% H₂S.

ZINC OXIDE SULFIDATION

TESTS 042R, 046, 034 (HARSHAW ZN-0401)

FIGURE 2-11

2.1.5 Effect of Steam/Air Ratio on Regeneration (Tests 047-049)

In considering the Foster Wheeler RESOX process for sulfur recovery, it is known that a 25/75 volume percent steam-air mixture would produce a more compatible regeneration offgas. Tests 47, 48, and 49 (Table 2-10), were designed to establish whether use of such a regeneration gas composition is practical.

Test 47 was a typical sulfidation at a temperature of 1000°F and a space velocity of 2000 hourly. For regeneration in test 48, a 25/75 volume percent steam-air mixture was employed with the usual space velocity of 600 hourly. The temperature in the hot reaction zone exceeded 1800°F and in a subsequent sulfidation in test 49, under the same conditions as in test 47, breakthrough of hydrogen sulfide occurred in about half an hour instead of the normal two and one half hours, as shown in Figure 2-12. This smaller sulfur loading before breakthrough is attributed to sintering, resulting from the high regeneration temperature. From this, it may be concluded that, even in the case of the 2-inch diameter reactor where some heat of regeneration can escape through the reactor sides, regeneration gas recycle would be necessary to avoid sintering when using such a rich air-steam mixture. For an adiabatic reactor still more recycle would be required. Later work, however, established that recycle of gases containing SO₂ is undesirable because of sulfate formation in the sorbent.

2.1.6 Absorption of H₂S by Vanadium Compounds (Tests 044 and 054-059)

As previously mentioned, vanadium oxide was thought to have the potential to remove hydrogen sulfide to even lower levels than zinc oxide. To investigate this possibility, test 44 (Table 2-11) at 1000°F was carried out employing zinc ferrite sorbent containing a small quantity, 3 weight percent, of zinc vanadium oxide prepared by a method reported in the literature. Analyses of the mixed sorbent, before and after sulfidation, are shown in Table 2-12. In the

TABLE 2-10
EFFECT OF STEAM/AIR RATIO ON REGENERATION

Test No.	Test Type	Sorbent	Sorbent Wt. (gm)	Sulfur Loading Before Break-through, Wt., %	Gas Feed Composition Vol. % (1)	H ₂ S Vol. %	Space Velocity (Vol/Vol Hr)	Linear Velocity (cm/sec)	Temp. °F	Sorption Time Before Breakthrough or Regeneration Time (Hrs)	Exit Gas Composition H ₂ S (ppm) SO ₂ (%) Sulfur (g)
047	Sulfidation	Zinc Ferrite	643	12.5	Lurgi	2.7	2000	48.2	1000	4.0	0.8-5 ppm H ₂ S
043	Regeneration	Zinc Ferrite	643	N/A	25% steam 75% air	-	600	15.4	1000	5.0	7.4-12.6% SO ₂
049	Sulfidation	Zinc Ferrite	643	3.31	Lurgi	2.7	2000	48.2	1000	1.0	6 ppm H ₂ S

(1) Lurgi gas composition: 28.1% N₂, 2.9% CH₄, 17.1% H₂, 11.9% CO, 9.7% CO₂, 27.6% H₂O, 2.7% H₂S.

ZINC FERRITE SULFIDATION

TEST 047, 049

FIGURE 2-12

TABLE 2-11
ABSORPTION OF H₂S BY VANADIUM COMPOUNDS

Test No.	Test Type	Sorbent	Sorbent Wt. (gm)	Sulfur Loading Before Break-through, Wt., %	Gas Feed Composition Vol. %	H ₂ S Vol. %	Space Velocity (Vol/Vol Hr)	Linear Velocity (cm/sec)	Temp. °F	Sorption Time Before Breakthrough or Regeneration Time (Hrs)	Exit Gas Composition H ₂ S (ppm) SO ₂ (%) Sulfur (g)
044	Sulfidation	Zinc Ferrite/ Vanadium Oxide	619	13.1	Lurgi (Dry)	2.7	2000	50.9	1000	3.0	1.2-7.0 ppm H ₂ S
054	Sulfidation	Zinc Oxide/Vanadium Catalyst	974	4.0	Lurgi (1)	2.7	1000	27.4	1200	3.25	92-114 ppm H ₂ S
055	Sulfidation	Zinc Oxide	500	6.1	Lurgi (1)	2.7	2000	27.4	1200	3.5	5.6-7 ppm H ₂ S
056	Regeneration	Zinc Oxide/Vanadium Catalyst	974	N/A	50% Steam 50% Air		600	15.4	1000	4.75	4.5-14.6% SO ₂
057	Sulfidation	Zinc Oxide/Vanadium Catalyst	974	5.2	Lurgi (1)	2.7	1000	27.4	1200	3.5	10.5-18 ppm H ₂ S
058	Regeneration	Zinc Oxide/Vanadium Catalyst	974	N/A	50% Steam 50% Air		600	15.4	1000	6.0	5-12.8% SO ₂
059	Sulfidation	Zinc Oxide/Vanadium Catalyst	974		Lurgi (1)	2.7	1000	27.4	1200	3.0 (Aborted)	1000-3600 ppm H ₂ S

(1) Lurgi gas composition: 28.1% N₂, 2.9% CH₄, 17.1% H₂, 11.9% CO, 9.7% CO₂, 27.6% H₂O, 2.7% H₂S.

TABLE 2-12
PERCENT TOTAL INTEGRATED INTENSITY OF VARIOUS SORBENTS*

Test No.	Test Type	Sorbent	Before or After Run	CaSO ₄	Fe ₂ O ₃	FeS	V ₂ C ₃	ZnO	αZnS	βZnS	ZnAl ₂ O ₄	ZnAl ₂ O ₄	Zn ₂ SiO ₄
044	Sulfidation	Zinc Ferritel ¹ Plus Zinc Vanadium Oxide	Before					12.0	2.0	4.7		81.3	
			After			19.3			12.2	55.0		13.5	
060	Sulfidation	Franklinite Ore	Before									95.6 ²	4.4
073	Sulfidation	IFP ZnO	After	17.0				8.0	26.0	49.0			
074	Regeneration	IFP ZnO	After	11.0				63.0			26.0		
075	Sulfidation	Zinc Ferrite	Before		27.0			Trace				73.0	

Notes:

* Percent total integrated intensity refers to the intensity of a Bragg diffraction reflection from a sample which is directly proportional to the concentration of the crystalline phase; the amorphous phase of the sample is not included in the results.

1. The small amount of zinc vanadium oxide present was indistinguishable from zinc ferrite.
2. ZnFe₂O₄ is indistinguishable from (Zn, Mn, Fe) (Fe, Mn)₂O₄.

mixture the X-ray analytical technique is unable to distinguish between zinc ferrite and zinc vanadium oxide. The hydrogen sulfide level attained was about the same as for 100 percent zinc ferrite, so the addition of zinc vanadium oxide did not appear to have any effect. However, as the zinc vanadium oxide contained a small amount of zinc sulfide, left over in its preparation, the result may be inconclusive.

At this point, it was noticed that the thermodynamic calculations leading to the conclusion that vanadium oxide absorbs hydrogen sulfide to a low level may be in error. This is because there is a gross disagreement between the heat of formation of V_2S_3 obtained from two sources. It is thought that the National Physical Laboratory value of -125 kcal/mole is more accurate than the National Bureau of Standards value of -227 kcal/mole. This means that vanadium oxide would be inferior to zinc oxide (or zinc ferrite) in respect of attainable hydrogen sulfide level.

Nonetheless, because the Giner experimental results with vanadium gave a low H_2S level, contradicting thermodynamic reasoning, tests 54 to 59 were carried out for verification. These tests employed a Harshaw Catalysts vanadium catalyst V-0701T composed of 10 percent V_2O_5 , mounted on a support of silica containing alumina. The BET surface area, skeletal density and pore volume up to $600\text{\AA}$ of the material, were measured and are shown in Table 2-13. These agree well with the manufacturer's values which are also shown. In test 54 the bottom half of the reactor was charged with zinc oxide and the top half with the vanadium catalyst. The test was with simulated Lurgi gas at a temperature of 1200°F (649°C) and a space velocity of 1000 hourly. Following the practice of Giner, Inc., gas was passed for 1 hour to reduce the catalyst before admitting hydrogen sulfide. It was expected that the exit hydrogen sulfide level would be below the about 10 ppm level leaving the zinc oxide part of the bed. Instead, the levels were about 100 ppm. Analysis of fresh and sulfidized catalysts gave sulfur contents of 0.043 and 0.147 weight percent, respectively (Table 2-14). To confirm that

TABLE 2-13
STRUCTURAL CHANGES IN VARIOUS SORBENTS

Test No.	Test Type	Sorbent	BET Surface Area (m ² /g)		Skeletal Density (g/cm ³)		Pore Volume (mm ³ /g)	
			Before	After	Before	After	Before	After
054	Sulfidation	Harshaw Vanadium Catalyst V-0701T	.45 (139)+		3.56		338 (450)+	
060	Sulfidation	Franklinite	0.86		5.44		0.74	
061	Sulfidation	IFP Zinc Oxide	11.7 (11.0)*		4.74 (4.29)*		38.1 (330)*	
066	Regeneration	IFP Zinc Oxide		11.8 (11.4)*		4.26 (4.26)*		37.4 (280)*
073	Sulfidation	IFP Zinc Oxide		5.2		3.74		17.6
074	Regeneration	IFP Zinc Oxide		(6.4)*		(4.17)*		(220)*
075	Sulfidation	Zinc Ferrite		(4.6)*		(5.27)*		(390)*

+ Manufacturer's value (pore volume by mercury porosimetry).

* Performed by Coors/Spectro Chemical (pore volumes by mercury porosimetry for pores down to 120Å diameter).

Note: Except where noted, performed by METC. Skeletal density by helium pycnometry; pore volume by nitrogen adsorption for pores up to 600Å diameter.

the level of hydrogen sulfide from the zinc oxide was as expected, test 55 was carried out with the reactor half full of zinc oxide only. The expected hydrogen sulfide level of less than 10 ppm was confirmed.

The catalyst was replaced in the reactor and regenerated together with the zinc oxide in test 56. In test 57, a repeat of test 54, hydrogen sulfide exit levels were about 10 ppm, even during the initial reduction period, indicating that the small amount of sulfur left in the bed after regeneration was being liberated.

The combined bed was regenerated again in test 58, and a final test 59 was carried out. In this test, for 3 hours during the reduction period with no hydrogen sulfide inflow, hydrogen sulfide levels exceeded 1000 ppm and the test was aborted. It thus appears that, at least with the reduction cum regeneration procedure now being employed, vanadium oxide is incapable of reducing hydrogen sulfide level lower than zinc oxide. A sulfur analysis of vanadium catalyst after test 59 (see Table 2-14) gave a sulfur content of 0.12 weight percent suggesting that it had been incompletely regenerated. Since the vanadium oxide tests were carried out to confirm the findings of Giner, Inc., they were asked to check the results with their smaller scale apparatus. Further tests with vanadium oxide-containing sorbents were suspended at this point.

Later experiments indicated that there is some pickup and release of sulfur by the reactor walls, but it is not thought that this effect invalidates the above findings.

2.1.7 Absorption of H₂S by Franklinite Ore (Test 060)

Zinc ferrite occurs naturally as the mineral franklinite. A quantity of it was obtained from New Jersey Zinc Company to measure its sorptive properties for comparison with the synthetic material. The as-mined ore contains substantial amounts of willemite, Zn₂SiO₄,

TABLE 2-14
ANALYSIS OF FRESH AND SULFIDIZED SORBENTS

Test No.	Test Type	Sorbent	Elemental Sulfur by Combustion (% w/w)		Elemental Sulfur by X-Ray (% w/w)	
			Before	After	Before	After
044	Sulfidation	Zinc Ferrite			2.20	29.11
054	Sulfidation	Harshaw Vanadium Catalyst V-0701T	0.043	0.147		
059	Sulfidation ¹		0.12			
073	Sulfidation	IFP ZnO		34.74		
074	Regeneration	IFP ZnO				0.026

¹ Sulfidation was aborted because of high H₂S level during an initial reduction period.

and magnetite, Fe_3O_4 , in addition to zinc ferrite. The bulk of the willemite was removed by Oak Ridge National Laboratory using a Frantz isodynamic magnetic separator. The x-ray analysis of the enriched ore is shown in Table 2-12. Since magnetite and zinc ferrite are not distinguishable, they are both included under franklinite which will also include some manganese ferrite. The ore was also analyzed by atomic absorption spectroscopy and is shown in Table 2-15. The elemental concentrations are expressed as oxides.

TABLE 2-15
ANALYSIS OF ENRICHED FRANKLINITE ORE

Elemental Content (Weight Percent)	SO_2	CaO	Fe_2O_3	K_2O	MnO	SiO_2	ZnO	Al_2O_3
Sample 1	0.12	0.16	63.89	≤ 0.0008	6.66	2.57	15.66	2.26
Sample 2	0.18	0.26	64.76	≤ 0.0008	7.09	5.70	15.57	1.93

It proved impossible to extrude the ore, which was ground to less than 200 mesh, according to the usual procedure. Instead it was formed manually into small spherical beads and heat treated in the same manner as synthetic zinc ferrite. In test 60 an attempt was made to use this sorbent for desulfurization. A temperature of 1000°F and a space velocity of 1000 hourly were employed. Hydrogen sulfide broke through immediately at a level exceeding 4000 ppm. The surface area, porosity, and skeletal density of fresh crushed pellets are given in Table 2-13. The surface area of about $1 \text{ m}^2/\text{g}$ would lead one to expect better absorptive properties. Therefore, it is possible that the poor performance can be attributed to the method of making the pellets which were much harder and brittler than the extrusions of synthetic zinc ferrite. The pore volume of about $1 \text{ mm}^3/\text{g}$ is indicative of the hardness and brittleness of the sorbent. Alternately, the poor absorptivity may be attributed to the greater crystallinity of the naturally occurring material.

2.1.8 Evaluation of IFP Zinc Oxide (Tests 061-074)

The Institut Francais du Petrole (IFP) has developed a high temperature regenerable zinc oxide sorbent, a sample of which was obtained for testing on simulated coal-derived gases. The IFP zinc oxide was tested in multiple sulfidation and regeneration cycles at 1000°F to determine the efficiency of regeneration, and to determine if there was any loss of capacity after multiple cycles. (Table 2-16)

Four sulfidations were conducted on the IFP zinc oxide at 1000°F and space velocity of 2000 hourly, using a simulated Lurgi gas with 27 percent steam. After an initial sulfidation with exit H₂S levels above 20 ppm, subsequent sulfidations resulted in H₂S levels below 10 ppm (Figure 2-13). Regenerability was determined to be good, and little loss of surface area was detected after three sulfidations.

Sulfidations at 800°F and 1200°F revealed the apparent optimum temperature to be 1000°F, with a 50 percent drop in breakthrough time at 800°F and an 87 percent drop in breakthrough time at 1200°F (Figure 2-14). The lower activity at 800°F is attributed to slower kinetics, whereas rapid breakthrough at 1200°F is attributed to possible sintering. A test at 1000°F conducted on the same sorbent after the 1200°F test indicated rapid breakthrough at 1000°F. This result suggests that damage to the sorbent at 1200°F affects its performance at the higher temperature.

Comparison of the IFP zinc oxide with the Harshaw zinc oxide (see Figure 2-15) shows that, at a temperature of 1000°F, the IFP zinc oxide breaks through 1 hour sooner than the Harshaw ZnO.

Performance of the IFP zinc oxide was poorer than the Harshaw ZnO at temperatures of 800°F and 1200°F. The order in which performance falls off for the different temperatures was also different with IFP's poorest performance at 1200°F, whereas Harshaw's poorest performance was at 800°F (Figure 2-16). This was not expected since IFP's sorbent was developed for high-temperature applications and

TABLE 2-16
INVESTIGATION OF IFP ZINC OXIDE

Test No.	Test Type	Sorbent	Sorbent Wt. (gm)	Sulfur Loading Before Break-through Wt. %	Gas Feed Composition Vol. % (1)	H ₂ S Vol. %	Space Velocity (Vol/Vol Hr)	Linear Velocity (cm/sec)	Temp. °F	Sorption Time Before Breakthrough or Regeneration Time (Hrs)	Exit Gas Composition H ₂ S (ppm) SO ₂ (%)
061	Sulfidation	IFP Zinc Oxide	892	6.8	Lurgi	2.7	2000	48.2	1000	2.5	30 ppm H ₂ S
062	Regeneration	IFP Zinc Oxide	892	N/A	50% steam 50% air	-	600	15.4	1000	4.75	8.8-14.4% SO ₂
063	Sulfidation	IFP Zinc Oxide	892	9.0	Lurgi	2.7	2000	48.2	1000	3.5	2.5-6.5 ppm H ₂ S
064	Regeneration	IFP Zinc Oxide	892	N/A	50% steam 50% air	-	600	15.4	1000	7.0	2.1-11.6% SO ₂
065	Sulfidation	IFP Zinc Oxide	892	9.0	Lurgi	2.7	2000	48.2	1000	3.0	6.5-9.5 ppm H ₂ S
066	Regeneration	IFP Zinc Oxide	892	N/A	50% steam 50% air	-	600	15.4	1000	7.0	4.7-15% SO ₂
067	Sulfidation	IFP Zinc Oxide	892	5.8	Lurgi	2.7	2000	48.2	1000	3.0	8-18 ppm H ₂ S
068	Regeneration	IFP Zinc Oxide	892	N/A	50% steam 50% air	-	600	15.4	1000	7.5	3.1-14% SO ₂
069	Sulfidation	IFP Zinc Oxide	892	4.5	Lurgi	2.7	2000	41.6	800	2.0	14 ppm H ₂ S
070	Regeneration	IFP Zinc Oxide	892	N/A	50% steam 50% air	-	600	15.4	1000	7.75	6.0-15.2% SO ₂

TABLE 2-16 (Cont.)

Test No.	Test Type	Sorbent	Sorbent Wt. (gm)	Sulfur Loading Before Break-through Wt. %	Gas Feed Composition Vol. % (1)	H ₂ S Vol. %	Space Velocity (Vol/Vol Hr)	Linear Velocity (cm/sec)	Temp. °F	Sorption Time Before Breakthrough or Regeneration Time (Hrs)	Exit Gas Composition H ₂ S (ppm) SO ₂ (%)
071	Sulfidation	IFP Zinc Oxide	892	1.1	Lurgi	2.7	2000	54.8	1200	1.0	15 ppm H ₂ S
072	Regeneration	IFP Zinc Oxide	892	N/A	50% steam 50% air	-	600	15.4	1000	7.5	4.5-12.4% SO ₂
073	Sulfidation	IFP Zinc Oxide	892	-	Lurgi	2.7	2000	48.2	1000	0.25	28,000 ppm H ₂ S
074	Regeneration	IFP Zinc Oxide	892	N/A	50% steam 50% air	-	600	15.4	1000	12.75	14-16% SO ₂

(1) Lurgi gas composition: 28.1% H₂, 2.9% CH₄, 17.1% H₂, 11.3% CO, 9.7% CO₂, 27.6% H₂O, 2.7% H₂S.

IFP ZINC OXIDE SULFIDATION

TESTS 067,065,063,061 (IFP MEP 682)

IFP ZINC OXIDE SULFIDATION

TESTS 067,069,071 (IFP MEP 682)

ZINC OXIDE SULFIDATION

TESTS 067,034

ZINC OXIDE SULFIDATION

TESTS 032,034,036 (HARSHAW ZN-0401)

FIGURE 2-16

supposedly was resistant to sintering. These tests, although not conclusive, indicate that the Harshaw zinc oxide performs better than the IFP sorbent, probably attributable to differences in binders. Figure 2-17 shows a similar plot for zinc ferrite for comparison purposes. This plot also indicates that zinc ferrite is a better performer at 1000°F and 1200°F, but not at 800°F.

The results and conclusions from the METC tests were reviewed by IFP. Appendix D includes correspondence from IFP in which they take exception to the METC conclusions which were somewhat negative. In particular, they emphasized that the IFP sorbent is designed for removal of bulk H₂S rather than trace levels of H₂S.

2.1.9 Effect of Zinc Content in Zinc Ferrite (Tests 075-079)

Large quantities of solid iron oxide waste containing zinc ferrite are available from the steel industry. It was therefore thought desirable to test a mixture of zinc ferrite and iron oxide for its hydrogen sulfide absorptive properties with a view to the possible utilization of this inexpensive waste.

Test tests 75 to 79, (Table 2-17), three sulfidations and two regenerations, were carried out using a sorbent made from a mixture having a molar ratio, Fe₂O₃/ZnO of 2.5/1. The same charge was used throughout and both absorption and regeneration were conducted at 1000°F. Space velocity during absorption was 2,000 hourly.

In test 75 hydrogen sulfide was removed to about the same level as previously found for 100 percent zinc ferrite. Sulfur loading before breakthrough was also comparable. In tests 77 and 79, however, after normal regenerations, though initially hydrogen sulfide level was similar to that in test 75, the sulfur loading was significantly less.

BET surface area, skeletal density, and pore volume for the sulfided sorbent from test 75 are given in Table 2-13. The values are

ZINC FERRITE SULFIDATION

TESTS 021,023,024

FIGURE 2-17

TABLE 2-17
TEST RUNS TO DETERMINE EFFECT OF ZINC CONTENT

Test No.	Test Type	Sorbent	Sorbent Wt. (gm)	Sulfur Loading Before Break-through Wt. %	Gas Feed Composition Vol. % (1)	H ₂ S Vol. %	Space Velocity (Vol/Vol Hr)	Linear** Velocity (cm/sec)	Temp. °F	Sorption Time Before Breakthrough or Regeneration Time (Hrs)	Exit Gas Composition H ₂ S (ppm) SO ₂ (%)
075	Sulfidation	Zinc Ferrite	643	17.2	Lurgi	2.7	2000	48.2	1000	4.25	4-5 ppm H ₂ S
076	Regeneration	Zinc Ferrite	643	N/A	50% steam 50% air	-	600	15.4	1000	9.25	14.2-15.1% SO ₂
077	Sulfidation	Zinc Ferrite	643	1.6	Lurgi	2.7	2000	48.2	1000	1.5	3.0 ppm H ₂ S
078	Regeneration	Zinc Ferrite	643	N/A	50% steam 50% air	-	600	15.4	1000	18.5	7-13.8% SO ₂
079	Sulfidation	Zinc Ferrite	643	7.8	Lurgi	2.7	2000	48.2	1000	2.0	5.5. ppm H ₂ S

(1) Lurgi gas composition: 28.1% N₂, 2.9% CH₄, 17.1% H₂, 11.9% CO, 9.7% CO₂, 27.6% H₂O, 2.7% H₂S.

comparable to those obtained in previous tests with 100 percent zinc ferrite, the surface area and pore volume being somewhat greater. This indicates that there are grounds for expecting that substantial sorptive power is retained after repeated regenerations before breakthrough at the same hydrogen sulfide level as for 100 percent zinc ferrite.

2.1.10 Evaluation of UCI Zinc Ferrite (Tests 080-088)

United Catalysts, Inc., was contracted to prepare, initially, four experimental 5 kg samples of 3/16-inch diameter zinc ferrite extrusions along the lines developed at METC, except that an organic binder (Methocell) was used instead of bentonite and water. The samples were prepared by dry blending an equimolar mixture of ZnO and Fe_2O_3 (with the addition of 20 weight percent alumina in one case), mix mulling with Methocell, extruding into 3/16-inch diameter extrusions, drying, and calcining. The properties of the samples are shown in Table 2-18.

Pore distribution sheets for these samples are included with the test summary sheets in Appendix D.

TABLE 2-18
PROPERTIES OF INITIAL ZINC FERRITE SAMPLES

	Sample No.			
	L1442	L1443	L1444	L1445
Calcination Temperature, °F	1500	1600	1500	1100
Bulk Density, lbs/cu ft	65	66.5	71.0	66.0
DWL Crush Strength, lbs/mm	2.3	2.0	1.7	0.7
Surface Area, m ² /g	6.6	5.9	25.8	9.6
Molar Ratio ZnO/Fe ₂ O ₃	1	1	1	1
Weight percent Alumina	0	0	20	0
Pore Volume, cm ³ /g	0.36	0.37	0.22	0.32
Mean Pore Diameter, Å	1,520	2,000	1,095	1,400
Mean Crystallite Size, Å				
ZnFe ₂ O ₄	>2000	>2000	321 (67%)*	776 (~95%)
Fe ₂ O ₃			2000 (~33%)	>2000 (~5%)
ZnAl ₂ O ₄			80	

* Figures in parentheses indicate weight percent in sample.

Surface areas were measured by BET nitrogen adsorption, pore volumes by mercury porosimetry for pores down to 29 Å, and mean crystallite sizes by x-ray diffraction techniques. Samples L1442, L1443, and L1444 were made with Pfizer CX-6139 iron oxide and French Process zinc oxide A2066 from American Smelting and Refining Company. Sample L1445 was made from Pfizer CX-6143 iron oxide and Sherwin Williams HSA zinc oxide.

Inspection of the properties of the four samples resulted in the choice of L1442 as being most suitable for further testing. L1443, which was calcined at the higher temperature of 1600°F, did not appear to have superior crush strength, which might be expected. L1444, containing alumina, contained a large quantity of unconverted Fe₂O₃ and had a lower crush strength. L1445 calcined at a low temperature though having a high surface area, and pore volume had a low crush strength.

Results of Testing L1442 Zinc Ferrite Sorbent

A batch of L1442 sorbent was tested in the lab-scale test unit under conditions of temperature, space velocities, and gas composition simulating, approximately, those to be encountered in future scaled-up, side-stream tests. Conditions for the five sorbent sulfidations and four regenerations performed are summarized in Table 2-19.

The sorbent was analyzed before test 080 in its fresh form and after the final sulfidation test 088. The analysis is shown in Table 2-20.

The hydrogen sulfide level at the reactor exit for tests 080 and 082 at 1000°F is plotted in Figure 2-18. Breakthrough time is about 2 hours in both cases. The higher H₂S level in test 080 before breakthrough is accounted for by sulfur pickup from the reactor sides, the preceding test 079 being a sulfidation test. The estimated average sulfur loading of the sorbent of a little over 6 weight percent is about half that achieved previously with METC sorbent.

Figure 2-19 is a plot of H₂S levels for tests 084, 086, and 088 at the higher temperature of 1200°F. The sulfur loading for the first test was a little greater than that for the preceding test at 1000°F, but this fell during the second and third tests to less than half the value for the first. This is accounted for by the excessive reduction of the sorbent to FeO, perhaps owing to the reactor temperature occasionally exceeding the nominal 1200°F value. In contrast to previous experience, no FeS was found in the mineral analysis of the sulfidized sorbent (see Table 2-20).

TABLE 2-19

SUMMARY OF L1442 ZINC FERRITE SORBENT TESTS
CONDITIONS AND RESULTS

	Test No./Test Type								
	080 Sulfida- tion	081 Regenera- tion	082 Sulfida- tion	083 Regenera- tion	084 Sulfida- tion	085 Regenerat- tion	086 Sulfida- tion	087 Regenerat- tion	088 Sulfida- tion
Space Velocity, h ⁻¹	2000	600	2000	600	2000	600	2000	600	2000
Superficial Linear Velocity, cm/s	48.2	15.4	48.2	15.4	48.2	15.4	48.2	15.4	48.2
Temperature, °F	1000	1000	1000	1000	1200	1000	1200	1000	1200
Breakthrough or Regeneration Time, h	2.0	8.25	2.0	8.0	2.25	10	1.5	7.25	1.0
H ₂ S Plateau Concentration Before Break- through, ppm (Dry Basis)	80		10		10		10		10
Final SO ₂ Concentration Vol. Percent (Dry Basis)		0.04		0.8		0.09		0.12	
Sulfur Loading, Weight Percent	6.25		6.25		7.0		4.7		3.1

- Notes: 1. The reactor was charged with 643 g of sorbent, the same charge being used for all the tests.
 2. The reactor pressure was slightly above ambient.
 3. The composition of the simulated Lurgi gas employed, in volume percent is 2.7 H₂S, 27.66 H₂O, 9.78 CO₂, 11.68 CO, 17.11 H₂, 2.90 CH₄, and 28.17 N₂.
 4. Regeneration gas was a 50/50 volume percent steam/air mixture.

ZINC FERRITE SULFIDATION

(T080,T082) UNITED CATALYSTS L-1442

FIGURE 2-18

ZINC FERRITE SULFIDATION

(T084,T086,T088) UNITED CATALYSTS L-1442

FIGURE 2-19

A sample of the final sulfidized sorbent contained 15.5 weight percent sulfur, well below the theoretical maximum indicating that the ultimate sulfur loading could be greater under appropriate process conditions.

TABLE 2-20
ANALYSIS OF L1442 ZINC FERRITE SORBENT BEFORE AND AFTER TESTING

Measurement by:	Fresh Sorbent		Sulfidized Sorbent
	Before Test 080		After Test 088
	METC	United Catalysts	METC
BET Surface	6.95	6.6	2.20
Area, m ² /g			
Skeletal Density, g/cm ³	5.40		4.67
Pore Volume, mm ³ /g	13.6		2.34
Porosity, %	6.9		1.1
Sulfur by Combustion, wt %	0.13		15.5
Mineral Analysis, Percent			
Total Integrated Intensity			
Franklinite (Including Fe ₃ O ₄)	100		41 (24)*
α ZnS	0		5 (8)
β ZnS	0		19 (57)
ZnO	0		24 (11)
FeO	0		11 (Trace)

* Figures in parentheses are for a duplicate sample.

- Notes:
1. Skeletal density by helium pycnometry.
 2. Porosity by nitrogen adsorption for pores up to 600Å diameter.
 3. Sulfidized sorbent from bed inlet.

During the sulfidation tests with regenerated sorbent, sulfur dioxide concentration in exit gas was also measured. In the initial stages the value was on the order of 100 to 200 ppm, but this dropped to negligible levels in less than an hour of on-stream time. This sulfur dioxide is thought to originate from residual sulfur compounds (mainly sulfides and sulfates) remaining in the sorbent after regeneration. A special study of this phenomenon was contracted to SRI International.

The condensate from exit gas during sulfidation tests 086 and 088 was analyzed for zinc and iron. The values obtained were 71.5 and 2.0 for zinc, and 52.4 and 16.5 ppm for iron, respectively. These levels are thought to be acceptable for potential applications.

In the course of the series of tests the surface area of the sorbent fell to about a third of its original value and the pore volume to about a fifth (Table 2-20). This is, undoubtedly, partly accountable for by the higher specific volume of the sulfidized sorbent. These changes are thought to be acceptable for a practical sorbent.

Supplementary tests of the L1442 sorbent were contracted to RTI, in particular, to determine the effect of the addition of simulated tars and hydrogen chloride to the gas composition employed at METC. The tests were performed at a pressure of 150 psig in the temperature range 1000 to 1400°F in a small reactor containing 500 gm of sorbent. Principal findings are that phenolic compounds are largely deoxygenated and aromatic hydrocarbons dealkylated to some extent. Analysis of condensate from the exit gas did not indicate a significant carry-over of zinc and iron. However, combined sulfate and sulfide sulfur in the condensate, roughly in the ratio 10/1, was about 2 percent of the sulfur entering the reactor (H_2S concentration of inlet gas was 0.12 volume percent). Analysis of sorbent after about 5 hours on-stream time at a space velocity of about 2000 hourly indicated that some coke formation had occurred on

the order of 10 percent of the sulfur loading, which was about 2 weight percent of the sorbent.

Most of the hydrogen chloride in the inlet gas passed through the reactor unreacted and appeared in the exit gas condensate.

2.1.11 Absorption of H₂S by Nickel (Tests 089 and 090)

Since hydrogen sulfide (and other sulfur compounds) may need to be lowered substantially below 1 ppm, tests 089 and 090 were designed to determine whether sulfur compounds in simulated coal gas leaving a zinc oxide-containing sorbent, might be lowered by passage through a nickel-containing sorbent, utilizing the phenomenon of chemisorption.

For sulfidation Run 089, 500 grams of United Catalyst G-72D (a high surface area commercial zinc oxide sorbent) and 333 grams of G-65RS (a prereduced and stabilized nickel methanation catalyst) 3/16-inch diameter extrusions were placed in the reactor with the nickel sorbent bed uppermost. Simulated coal gas was the same as for tests 080 to 088. Temperature was nominally 1000°F and space velocity 2000 hourly (based on combined bed volume). Gas flow was maintained for 2 hours. The minimum hydrogen sulfide concentration achieved in the reactor exit gas was 16 ppm. It was surmised that hydrogen sulfide was being picked up from the reactor sides which were in a sulfidized condition from the previous test. For test 090, the reactor was refilled with the same quantities of fresh sorbents and test 089 repeated, except that the gas contained no hydrogen sulfide. In spite of this, the reactor exit gas contained 20 to 50 ppm of H₂S over a 10-hour, on-stream period. This hydrogen sulfide content was attributed to pickup from the reactor sides. The investigation of trace sulfur removal by chemisorption was curtailed at this point and plans made to install a quartz reactor system, thus precluding sulfur pickup. ERC was contracted to perform an independent study of trace sulfur removal.

Samples of the G-72D and G-65RS sorbents from test 089 were analyzed. The results are shown in Table 2-21.

The analytical results indicate that there is a moderate fall in the surface area and pore volume of the G-65RS sorbent. A considerable amount of sulfur was absorbed by it in the form of nickel sulfide, Ni_3S_2 .

2.1.12 Sulfur Pickup by Empty Reactor (Tests 091-095)

In the previous tests attempting to lower hydrogen sulfide to ultra-low levels, the release of sulfur from the reactor sides into the simulated coal gas intolerably affected the concentration measurements. To establish the magnitude of the effect, tests 091 to 095 were designed in which the empty stainless steel reactor was subjected to sulfidation and regeneration, and sulfur release into a simulated coal gas stream measured.

In test 091, regeneration gas was passed through the empty reactor from test 090 under the same conditions as previous regeneration tests. A considerable amount of sulfur dioxide was evolved, the concentration (dry gas basis) falling from 0.44 to 0.04 volume percent over 5.5 hours.

Simulated Lurgi gas containing 1000 ppm H_2S was subsequently passed through the reactor at the space velocity of 2000 hourly and a temperature of 1000°F in test 092. H_2S initially was lowered to 200 ppm. This level gradually rose to the inlet concentration after 4.5 hours showing that a substantial amount of sulfur was being removed from the gas by the reactor sides. A plot of the exit H_2S level is shown in Figure 2-20.

Test 093 was identical to test 092 except that the hydrogen sulfide feed into the inlet gas was shut off. However, H_2S was found in the exit gas at a level of 300 to 400 ppm over a 5-hour on-stream

TABLE 2-21
ANALYSIS OF G-72D AND G-65RS SORBENTS

	Fresh Sorbent Before Run 089		Sulfidized Sorbent After Run 089	
	G-72D	G-65RS	G-72D	G-65RS
BET Surface Area, m ² /g	44.2	41.5	24.4	33.5
Skeletal Density g/cm ³	4.91	3.85	4.47	3.82
Pore Volume mm ³ /g	82	159	134	123
Weight Percent Sulfur by Combustion	0.0	0.0	16.8	5.9
Mineral Analysis Percent Total Integrated Intensity				
ZnO	100		68	
α-ZnS			6	
β-ZnS			26	
Ni (metal)		84		66
Ni ₃ S ₂				12
α-Al ₂ O ₃		16		21
CaAl ₂ O ₄		Trace		Trace

Notes: 1. Skeletal density by helium pycnometry.
2. Pore volume by nitrogen adsorption for pores up to 600Å diameter.

ZINC FERRITE SULFIDATION

T092 EMPTY REACTOR SULFIDATION

period. This concentration roughly corresponds to a level in equilibrium with iron sulfide. The H_2S level is plotted in Figure 2-21.

In test 094, the empty reactor was regenerated as in test 091 except that after 2.5 hours, when SO_2 had fallen from 7 percent to 0.2 percent, regeneration was accelerated by stepping up the air flow and shutting off the steam flow. The test was continued until the SO_2 level in the exit gas was 0.01 volume percent. At this point, as in test 095, flow of Lurgi gas without H_2S was resumed as in test 093. H_2S was still found in the exit gas, albeit at a lower level of about 30 ppm, except for a brief initial period when it was about 200 ppm.

The above tests clearly demonstrated that pickup and release of sulfur from and to the gas stream by the reactor cannot be neglected, particularly when very low concentration levels are being examined. Subsequently, the lab-scale unit was revamped with an internally aluminized stainless steel reactor and an alternate quartz reactor.

2.1.13 Parametric Studies of Zinc Ferrite for Computer Simulation (Tests 096-127)

A contract was placed with Professor J. T. Schrodt, University of Kentucky, to further develop a dynamic fixed-bed sulfidation/regeneration model which had been developed for a similar process.

To provide an experimental base for validation of the model, a series of 32 sulfidation test tests were performed under various conditions of temperature, gas composition, gas space velocity, gas linear velocity, and bed depth. The sorbent employed was United Catalysts' L1443 zinc ferrite. L1443 differs from L1442 (tested in tests 080 to 088) only in being calcined at 1600°F instead of 1500°F. This difference in calcination temperature has a minimal

ZINC FERRITE SULFIDATION

T093 H₂S LEACHING FROM EMPTY SULFIDED REACTOR

FIGURE 2-21

effect on sorbent properties while resulting in a stronger extrusion. Table 2-22 gives the matrix of approximate conditions for the tests. Analysis of the sorbent on completion of certain tests is given in Table 2-23.

In tests 099, 102, and the even number sequence to 126, the reactor was regenerated to remove sulfur pickup on the reactor sides. Except for test 099, when it was empty, the reactor was filled with fresh sorbent for the subsequent sulfidation before regeneration to save dismantling and reassembling time.

Test 096 was carried out to closely approximate the conditions expected in the planned coal-gasifier, side-stream tests. Exit hydrogen sulfide level is plotted in Figure 2-22. The complete breakthrough of hydrogen sulfide took about 50 hours, breakthrough at the 10 ppm level occurring about 25 hours into the test. Analysis of the sorbent at the end of the test (Table 2-23) indicates that its surface area has not significantly diminished in comparison with fresh material (Table 2-18). Mineral and sulfur analysis indicates that the sorbent has been completely converted to sulfides of iron and zinc. Carbon analysis shows that a small amount of carbon has been formed.

Tests 097 to 101 were practice tests designed to establish the best accelerated conditions involving space velocity, hydrogen sulfide concentration, and bed depth in order to obtain a complete breakthrough curve in a normal working day. Based on these tests, space velocities were set in the range 2000 to 3600 h⁻¹, H₂S concentration 3.1 to 6.2 mole percent, and bed depth 7 inches (half the normal bed depth). Steam concentrations to be investigated were 0 and 10 mole percent.

Figure 2-23 shows the H₂S breakthrough curves for tests 103 and 105 at 1000°F and 0 and 10 volume percent steam, respectively. Though the difference between them is not marked, there is some evidence

TABLE 2-22

MATRIX OF CONDITIONS FOR SULFIDATION TESTING OF L1443
ZINC FERRITE FOR DYNAMIC SIMULATION STUDY

Run No.	Gas Flow Rate, scfh	Space Velocity h^{-1}	Superficial Linear Velocity cm/s	Temperature, $^{\circ}\text{F}$	Bed Depth, in.	On-Stream Time, h	H ₂ O in Inlet Gas Mole %	H ₂ S Inlet Gas Mole %
096	12	800	5	1000	7	50	0	0.5
097	60	8800	25	1000	3.5	6.5	0	1.5
098	37	5400	15	1000	3.5	12	0	1.5
100	37	5400	15	1000	3.5	3.6	0	0
101	37	5400	15	1000	3.5	4.7	0	3.2
103	39	3200	16	1000	7	4.4	0	6.2
105	43	3600	18	1000	7	5.3	10	5.6
107	43	3600	18	1200	7	2.5	10	5.6
109	39	3200	16	1200	7	1.3	0	6.2
111	39	3200	16	1200	7	0.5	0	6.2
113	43	3600	18	1400	7	0.5	10	5.6
115	24	2000	10	1000	7	5.7	10	5.6
117	24	2000	10	1200	7	2.2	10	5.6
119	24	2000	10	1400	7	0.5	10	5.6
121	43	3600	18	1000	7	2.4	10	3.1
123	43	3600	18	1200	7	2.3	10	3.1
125	43	3600	18	1400	7	0.3	10	3.1
127	24	2000	10	1000	5	1.1	10	5.6

- Notes: 1. The runs tabulated are sulfidations; in each case the reactor was charged with a fresh batch of sorbent and regenerated.
2. Regeneration runs are not tabulated.
3. The reactor pressure was slightly above ambient.
4. Simulated Lurgi gas (Table 2-6) was employed except that steam and H₂S flows were changed.
5. Regeneration gas was a 50/50 volume percent steam/air mixture.

TABLE 2-23

ANALYSIS OF L1443 ZINC FERRITE SORBENT
IN CERTAIN SULFIDATION RUN

	Run No.									
	96		97	105	111		113		127	
	Middle	Top			Middle	Top	Middle	Top	Bottom	Top
BET Surface Area, m ² /g	10.1	9.9							3.2	5.7
Skeletal Density, g/cm ³	4.09	4.10							4.54	5.26
Pore Volume, mm ³ /g	12.8	12.11							5.3	9.4
Sulfur by Combustion, wt %	37.6	35.2							26.9	1.4
Carbon by Combustion, wt %	0.53		32.4*	0.06						
Mineral Analysis, % Total Integrated Intensity										
Hematite, Fe ₂ O ₃					28	10				
Franklinite/Magnetite, ZnFe ₂ O ₄ /Fe ₃ O ₄					22	66				
Zincite, ZnO							45	55		
α-ZnS				14						
β-ZnS	64	58	65	44	50	24	10	9		
FeO							45	37		
FeS	36	42	35	42						

* Analysis of dust found deposited in sorbent.

Notes: 1. Skeletal density by helium pycnometry.

2. Pore Volume by nitrogen adsorption for pores up to 600Å diameter.

ZINC FERRITE SULFIDATION

TEST 098

FIGURE 2-22

ZINC FERRITE SULFIDATION

TESTS 103, 105 L-1443 UNITED CATALYSTS

FIGURE 2-23

that after given periods of time H_2S is being absorbed at a greater rate in the presence of steam.

In Figure 2-24 are shown the H_2S breakthrough curves for tests 105, 107, and 113 at 1000°, 1200°, and 1400°F, respectively. In each case, steam concentration is 10 volume percent. There is a marked difference in the total absorption capability, which progressively decreases with temperature. This is in contrast to previous experience when the absorption capability at 1200°F exceeded that at 1000°F. The difference is probably because of FeO formation at the lower steam concentration. There is also a marked increase in the steepness of the curves with temperature. This is probably in large part because of the temperature effect on intrinsic reaction rate, though the effect of sorbent deterioration on both reaction rate and diffusion of H_2S into the sorbent must also be taken into account.

Mineral analysis at the end of test 113 (Table 2-23) shows that most of the iron in the sorbent has been converted to wustite, Fe_xO , the zinc being partially converted to sulfide. This is in contrast to test 105 where virtually all of the zinc and iron are in the form of sulfide. Thus, at the higher temperature of 1400°F, the iron and most of the zinc in the sorbent appear to be inaccessible to sulfidation at prevailing conditions.

The H_2S breakthrough curves for tests 115, 117, and 119, at a space velocity of 2026 h^{-1} , which are analogous to tests 105, 107, and 113 at a space velocity of 3600 h^{-1} , are shown in Figure 2-25. The mass flow rate of H_2S through the sorbent is about 1.8 times less than previously. This results in the proportionately longer absorption times for a given H_2S concentration breakthrough. The 1200°F curve is closer to the 1000°F in the new series suggesting that less sorbent deterioration has occurred at the higher temperature.

In tests 121, 123 and 125, the space velocity was raised to 3600 h^{-1} and the H_2S concentration lowered to 3.1 volume percent, the mass flow rate of H_2S remaining the same as in tests 115, 117, and 119.

ZINC FERRITE SULFIDATION

TESTS 105, 107, 113 L-1443 UNITED CATALYSTS

FIGURE 2-24

ZINC FERRITE SULFIDATION

TESTS 115, 117, 119 L-1443 UNITED CATALYSTS

FIGURE 2-25

The H₂S breakthrough curves are plotted in Figure 2-26. In this case, the 1200° and 1400°F curves are similar to those in the previous two series. The 1000°F curve, however, is anomalous, particularly in the early stages when H₂S appears to be absorbed at a lower rate than expected.

The three series of tests are also plotted in Figures 2-27, 2-28, and 2-29 at 1000°, 1200°, and 1400°F, respectively, to bring out the effect of space velocity and H₂S concentration on the rate of absorption of H₂S. H₂S is plotted against normalized time, defined as the time for a given mass flow of H₂S through the reactor. In effect, the time scale for tests 105, 107, and 113 has been expanded by a factor of 1.0, that for the rest remaining unchanged.

2.1.14 Evaluation of UCI Zinc Ferrite Sorbent to be Used in Sidestream Tests (Tests 128-132)

The higher calcination temperature of the L1443 sample used in the preceding tests did not appear to give superior properties, particularly crush strengths. Therefore this confirmed that the lower calcination temperature, L1442 zinc ferrite, would be satisfactory for scaled-up testing.

Two additional final 5 kg samples (L1504 and L1505) were, therefore, obtained from United Catalysts, who used the same preparatory technique as for the L1442 sample except that the sources of the raw materials were changed. In L1504 the iron oxide was that used by United Catalysts in their high-temperature shift catalyst. That in L1505 for comparison was Fisher-certified iron oxide. In both cases the zinc oxide was a high surface area grade from AZO Chemical, being preferred because of its low arsenic content.

An additional 5 cu ft of L1504 zinc ferrite was later procured. The properties of the two samples and the 5 cu ft batch are given in Table 2-24. Pore Volume sheets for these samples are included with the test summary sheets in Appendix D. As in Table 2-19 surface

ZINC FERRITE SULFIDATION

TESTS 121, 123, 125 L-1443 UNITED CATALYSTS

FIGURE 2-26

ZINC FERRITE SULFIDATION

TESTS 105,115,121 L-1443 UNITED CATALYSTS

FIGURE 2-27

ZINC FERRITE SULFIDATION

TESTS 107, 117, 123 L-1443 UNITED CATALYSTS

FIGURE 2-28

ZINC FERRITE SULFIDATION

TESTS 113, 119, 125 L-1443 UNITED CATALYSTS

FIGURE 2-29

TABLE 2-24

PROPERTIES OF FINAL ZINC FERRITE SAMPLES

	L1504 5 kg Sample	L1504 5 cu ft batch	L1505 5 kg Sample
Calcination Temperature, °F	1500	1500	1500
Bulk Density, lbs/cu ft		85	
DWL Crush Strength, lbs/ Extrusion		16	
Surface Area, m ² /g	6.1	3.2	3.1
Molar Ratio ZnO/Fe ₂ O ₃	1	1	1
Pore Volume, cm ³ /g	0.29	0.25	0.22
Mean Pore Diameter, Å	2500	2900	2300
Mean Crystallite Size, Å			
ZnFe ₂ O ₄	(92)*	>2000 (84)	(96)
Fe ₂ O ₃	(4)	>2000 (7)	(2)
ZnO	(4)	>2000 (9)	(2)

* Figures in parentheses indicate weight percent in sample.

Note: 1. Pore volume by mercury porosimetry down to 30Å pore diameter.

areas were measured (by the manufacturer) by BET nitrogen adsorption, pore volumes by mercury porosimetry, and mean crystallite sizes by X-ray diffraction techniques.

Some of the L1504 5 kg sample was tested in the lab-scale unit at the anticipated working temperature of 1200°F. The results of these tests are summarized in Table 2-25. The sorbent performed much as expected absorbing more than 10 weight percent of sulfur except in test 128, when bad temperature control allowed the temperature to exceed 1400°F at times. The hydrogen sulfide concentration is plotted in Figure 2-30.

The exit gas condensate from test 129 was collected and sampled at hourly intervals and analyzed for zinc, iron, and sulfate to determine the extent of zinc and iron sulfate carryover from the sorbent bed. The results are given in Table 2-26.

The figures appear to indicate that at 1200°F much more zinc than iron is found in the condensate. The amount of sulfate ion is comparable to that of zinc suggesting that zinc is carried over from the sorbent predominantly in sulfate form.

Conclusions

The laboratory-scale development and evaluation of high-temperature, coal gas desulfurization sorbents was brought to a conclusion. The main accomplishment was the evaluation of commercially prepared samples of zinc ferrite sorbent based on a composition developed at METC. Variables in the sample preparations included calcination temperature and alumina addition. The sorbent chosen for larger-scale evaluation in a sidestream of gas from the METC 24 TPD fixed-bed gasifier consisted of 50 mole percent each of Fe_2O_3 and ZnO with an organic methocel binder, calcined at 1500°F. The methocel binder was chosen upon the recommendation of United Catalysts, Inc. to give greater reactivity and acceptable crush strength.

TABLE 2-25

SUMMARY OF L1504 ZINC FERRITE SORBENT TESTS

	Test No./Test Type				
	128/ Sulfidation	129/ Sulfidation	130/ Regeneration	131/ Sulfidation	132/ Regeneration
Space Velocity, h^{-1}	1285	1285	385	1285	385
Superficial Linear Velocity. cm/s	48.2	48.2	15.4	48.2	48.2
Temperature, °F	1200	1200	1000	1200	1000
Breakthrough or Regeneration Time, h	2	6		5.5	2
H ₂ S Plateau Concentration Before Break- through ppm (Dry Basis)	5	10		12	
Final SO ₂ Con- centration, Volume Percent (Dry Basis)			0.06		8
Sulfur Loading, Weight Percent	4	12		11	

- Notes:
1. The reactor was charged with 1000 g of sorbent, one charge being used for Test 128, another for the remaining runs.
 2. The reactor pressure was slightly above ambient.
 3. The composition of the simulated Lurgi gas employed in volume percent is 2.70 H₂S, 27.66 H₂O, 9.78 CO₂, 11.68 CO, 17.11 H₂, 2.90 CH₄, and 28.17 N₂.
 4. Regeneration gas was a 50/50 volume percent steam/air mixture.
 5. Test 132 was a partial regeneration to obtain incompletely regenerated extrusions for analysis.

ZINC FERRITE SULFIDATION

TESTS 128,129,131 (L1504)

FIGURE 2-30

TABLE 2-26
CONDENSATE ANALYSIS DURING TEST 129

	Hourly Intervals					
	1	2	3	4	5	6
Zinc, ppm (wt) Zn	67.8	58.8	39.8	70.9	31.3	232
Iron, ppm (wt) Fe	0.013	<0.002	0.003	0.002	0.087	0.012
Sulfate, ppm (wt)SO ₄	353	116	76	66	94	77

Sorbent performance was close to that of the previously tested METC developmental sorbent. In particular, sulfur absorption capacity decreased above about 1200°F.

Tests of the trace sulfur absorption capability of a nickel methanation catalyst were attempted but were inconclusive because of interference by the release of sulfur from the stainless steel reactor.

Several complete hydrogen sulfide breakthrough curves were generated in support of a dynamic modeling study. These permitted making qualitative inferences about the absorption mechanism. The rate of absorption of hydrogen sulfide appears to be controlled by a combination of gas-solid reaction kinetics and diffusion to the reaction site. A complicating factor is the structural changes taking place in the sorbent such as the reduction of the sorbent to wustite or magnetite.

2.2 BENCH SCALE SIDESTREAM TESTING USING METC FIXED BED GAS

The installation of the sidestream test unit in a sidestream of the DOE/METC fixed-bed gasifier provided the opportunity to test the hot gas desulfurization process on a real coal gas with all the associated tars, oils, particulates, and additional sulfur compounds present in coal gas. The primary differences between the lab-scale and sidestream testing are outlined in Table 2-27. The purpose of the scaled-up testing was to demonstrate the capability of this process to desulfurize gasifier gas to ppm levels at temperatures

TABLE 2-27

OPERATING CONDITIONS OF LAB-SCALE AND SIDESTREAM TEST UNIT

Conditions	Lab-Scale Test Unit	Sidestream Test Unit
<u>Sulfidation</u>		
Gas Composition:		
1. Majors (CO, CO ₂ , H ₂ , N ₂ , CH ₄)	Gases from cylinders simulating air-blown Lurgi gasifier	Actual DOE/METC fixed-bed gasifier; both air-blown and oxygen-blown compositions
2. Moisture	27% as added steam	4-5% on air-blown gas; 53% on oxygen-blown gas
3. Sulfur	27,000 ppm H ₂ S from cylinder	2300-3800 ppm H ₂ S (on air-blown) plus COS, thiophenes, CS ₂ and others
Tars	None	Typical of DOE/METC fixed-bed gasifier (~1 wt% tar)
Particulates	None	Typical of DOE/METC fixed-bed gasifier after primary and secondary cyclone (~1 g/Nm ³)
Pressure	Atmospheric	Gasifier pressure (100-250) psig)
<u>Regeneration:</u>		
Gas Composition:		
1. Steam	50-75%	80%
2. Air	25-50%	10-20%
3. Nitrogen	0	0-8%
Pressure	Atmospheric	5 psig

between 1000 and 1200°F. Items of particular interest were as follows:

- Effect of tars
- Effect of particulates
- Effect of sorbent on organic sulfur compounds such as thiophene
- Regeneration characteristics of the larger reactor

The bench-scale sidestream test unit was designed, and procurement of components practically completed during FY 82. During FY 83, the unit was assembled and installed in a location where it could be connected to the METC fixed bed or fluidized bed gasifier.

Skid-mounting of the unit gives it portability should it be desired to remove it to another test site. Figure 2-31 is a flow sheet of the bench-scale test unit.

The design throughput of the sidestream test unit is an order of magnitude larger than that of the laboratory-scale unit. The larger size of the sidestream test unit and its operation on an actual hot raw coal gas were expected to establish with much greater confidence the capability of sorbents under test to achieve the desired goal to remove sulfur compounds to low levels (1-10 ppm) to withstand the effects of other contaminants, and to be regenerable.

In particular, the zinc ferrite sorbent, which showed promise in the laboratory-scale tests, was singled out for evaluation.

The description of the sidestream test apparatus is presented in Appendix E.

Four series of test tests on the zinc ferrite sorbent were conducted to coincide with scheduled testing of the METC 24 TPD fixed bed gasifier. These tests were designated 101 through 104. A thorough compilation of the data as reported by METC is included as Appendices F through I.

PROCESS FLOW-SHEET FOR HDT GAS DESULFURIZATION BENCH-SCALE TEST UNIT

FIGURE 2-31

For each of the gasifier tests, the most pertinent results have been extracted and summarized in the following sections.

2.2.1 Gasifier Run No. 101

Gasifier Run 101 comprised the first series of tests on the sidestream test unit. The objectives were as follows:

- a. To shake down the hot gas desulfurization skid-mounted test unit using a sidestream from the fixed-bed gasifier.
- b. To conduct a sulfidation test on hot producer gas to determine effects, if any, of tar vapors, particulates, and other trace constituents.
- c. To conduct a regeneration with minimum effect on the integrity of the sorbent.
- d. To conduct a second sulfidation on producer gas to determine any loss of desulfurization capacity, after regeneration.

During Gasifier Run 101, five tests were conducted on the sidestream test unit, outlined in Table 2-28.

TABLE 2-28
HOT-GAS DUSULFURIZATION TESTS - GASIFIER RUN 101

Test No./ Type	Durat ion (Hrs)	Gasifier Coal Type	Gasifier Oxidant	HGD Reactor Temp. (°F)	HGD Reactor Pressure (Psig)	Inlet Sulfur (ppm H ₂ S)	Exit Sulfur (ppm H ₂ S)
001/ Sulfidation	29.6	Arkwright	Air	1025	160	2300	2
002/ Regeneration	14.4						
003/ Sulfidation	24.6	Arkwright	Air	1018	143	3600	1.6
004/ Regeneration	18.8						
005/ Sulfidation	23.2	Arkwright	Air/O ₂	1012	91	3800	3

Desulfurization Capacity

Lab-scale testing of zinc ferrite showed that the level to which H_2S concentration in the treated gas can be reduced is limited by equilibrium constraints. Test results from sidestream Test 001 are shown in Figure 2-32. The results indicate that equilibrium H_2S levels are obtained at approximately 1 to 3 ppm. These results match the results previously obtained on lab-scale tests with simulated gas that did not contain tars or oils. This indicates that tars and oils and/or particulates in the coal gas do not inhibit the level to which H_2S is reduced in the gas. Figure 2-33 shows the breakthrough curve for Test 003, which was carried out after a regeneration. The data show that H_2S is reduced to the same low levels after a regeneration. However, the data also indicate that it took approximately 4 hours to obtain less than 4 ppm H_2S . This is attributed to sulfur remaining in the sorbent after regeneration, and is a function of the quality and duration of the regeneration. The time to breakthrough also appears to have been reduced from approximately 29 hours to 22 hours. However, during Test 003, the sulfur concentration of the inlet gas was higher (0.36% during Test 003 versus 0.23% during Test 001). The total sulfur removed (as calculated by inlet sulfur minus exit sulfur) was actually higher for Test 003 (8.06 lb) than for Test 001 (6.49 lb).

Removal of thiophene from the gasifier gas in Tests 001 and 003 is shown in Figure 2-34. Thiophene levels of 4-8 ppm were measured at the reactor exit and appeared to increase during breakthrough, as with the other sulfur compounds (H_2S and COS). COS levels were typically below 1 ppm prior to breakthrough.

Sulfidations that followed the process of regeneration exhibited an SO_2 leakage phenomenon. This is attributed to sulfates in the reactor which released SO_2 when exposed to a reducing gas. Figure 2-35 shows the level and duration of SO_2 leakage during Test 005. The figure shows that the SO_2 level dropped to 1 ppm within the first hour.

HYDROGEN SULFIDE BREAKTHROUGH PLOT

HGD - SULFIDATION TEST #01

GAS FROM THE 42-INCH FIXED BED GASIFIER RUN #101

FIGURE 2-32

GAS CHROMATOGRAPH AND DETECTOR TUBE DATA WAS TAKEN FROM OLD PLOT

HYDROGEN SULFIDE BREAKTHROUGH PLOT

HGD - SULFIDATION TEST #03

GAS FROM THE 42-INCH FIXED BED GASIFIER RUN #101

GAS CHROMATOGRAPH WAS NOT WORKING DURING SULFIDATION TEST #03

FIGURE 2-33

THIOPHENE BREAKTHROUGH CURVE
ZINC FERRITE SULFIDATION
SIDESTREAM TEST UNIT TESTS 001 AND 003

FIGURE 2-34

ZINC FERRITE SULFIDATION

INITIAL H₂S AND SO₂ CONCENTRATION

FIGURE 2-35

Sorbent Characterization

In conducting the three sulfidations and two regenerations during Gasifier Run 101, the sorbent integrity over several cycles was of interest. In order to characterize the sorbent before and after these tests, the following analyses were carried out.

- Total carbon
- Total sulfur
- BET surface area
- Crush strength
- Porosity
- Mineral Analysis
- Skeletal Density

Table 2-29 outlines most of the data obtained on samples of the sorbent removed from the reactor at 10-inch intervals (except for one at midbed) after the third sulfidation. The sorbent was in the sulfided state as indicated by the total sulfur numbers. A high degree of sulfur capture is indicated by the total sulfur concentrations of 25 to 31 weight-percent for approximately the first half of the reactor, whereas the second half of the reactor picked up less sulfur since the concentration of sulfur in the gas was already greatly reduced. This is shown graphically in Figure 2-36.

Conclusions

The first series of tests to evaluate the performance of zinc ferrite, hot-gas desulfurization sorbent in a side-stream of METC's 24 TPD, fixed-bed coal gasifier was carried out successfully with only minor difficulties. The concentration of sulfur compounds in the exit gas from the hot-gas desulfurization unit was generally less than 10 ppm. However, this disregards sulfur compounds condensing out in the tar and aqueous condensates which, expressed as equivalent gas concentration, amounts to about 100 ppm.

The tests established that desulfurization performance of the sorbent was satisfactory in the temperature range 1000 to 1100°F,

TABLE 2-29

SORBENT ANALYSIS AFTER TEST 005, ZINC FERRITE L-1504, UNITED CATALYSTS

Bed Height (Inches)	Total Carbon (% Wt)	Total Sulfur (% Wt)	BET Surface Area (Sq M/G)	Skeletal Density (G/CC)(3)	Porosity % (5)	Crush Strength (Kg DWL) ± S.D.(7)	Skeletal Density (G/CC)(8)	Porosity % (9)
0(1)	1.97	29.88	1.43	4.37	0.93	7.0 ± 3.3	-	-
6	1.88	31.41	1.49	4.55	0.93	8.4 ± 3.5	-	-
16	2.58	27.78	2.09	4.26	1.68	7.3 ± 3.5	3.84	27.9
23	2.89	25.92	2.43	4.33	1.96	8.1 ± 3.1	-	-
26	3.48	28.97	2.24	4.34	2.26	4.4 ± 2.1	3.84	36.1
36	2.37	7.29	2.30	4.86	1.76	4.2 ± 2.6	-	-
46(2)	3.27	8.60	3.11	5.14	2.75	2.4 ± 1.8	4.57	50.2
--METC FRESH SORBENT	0	0.13	3.13	6.16	2.59	6.3 ± 2.8	-	-
--UCI			3.2	85(4)	-	7.2	-	60.6(6)
ABSORBER FINES	6.93	26.29						

NOTES:

1. Bottom/Inlet during sulfidation - Outlet during regeneration
2. Top/Outlet during sulfidation - Inlet during regeneration
3. Skeletal Density by Helium Pycnometry
4. Bulk Density (Lbs/Cu Ft)
5. Porosity by Nitrogen Adsorption for pores up to 600Å diameter
6. Porosity by Mercury Porosimetry for pores down to 30Å diameter
7. Crush strength data are average and standard deviation of 15 measurements
8. Skeletal density by mercury porosimetry
9. Porosity by mercury porosimetry for pores down to 120Å diameter.

SORBENT PELLET ANALYSIS

GASIFIER RUN 101 - THREE SULFIDATIONS

FIGURE 2-36

at pressures up to 150 psig, and at a space velocity of 2000 h^{-1} . On removal from the reactor, the sorbent contained about 10 percent of zinc ferrite fines but most of this may be the result of breakage in the removal process. The strength of the sorbent extrusions appeared to be unimpaired.

The sorbent was active in promoting the carbon monoxide "shift" conversion reaction to hydrogen. It also absorbed alkali metals and halides to a large extent, subsequently releasing them during regeneration. These may have been associated with particulates in the feed gas. There was some evidence that vanadium, calcium, and mercury were similarly removed to some extent.

2.2.2 Gasifier Run No. 102

During Gasifier Run 102, seven tests were conducted as outlined in Table 2-30. The principal purpose of these tests was to provide hot desulfurized gas to a combustion test unit.

The sidestream unit was operated in two periods with different batches of the zinc ferrite sorbent. During the first period the gasifier was fed with Arkwright coal, and during the second with Blacksville coal briquettes. The gasifier was operated in the airblown mode.

- First Period

The reactor contained the customary 20.4 kg of sorbent but, contrary to the first test series, reactor furnace temperatures were set at 1100°F , compared to 1000°F previously, which, it was hoped, would increase the sulfur absorption rate and result in longer times to breakthrough. Gasifier pressure was about 150 psig.

The unit was operated for two short absorption spells (Test Nos. 006 and 008), with an intermediate regeneration (Test No. 007).

TABLE 2-30

HOT GAS DESULFURIZATION TESTS - GASIFIER RUN 102

Test No./ Type	Duration (hrs)	Gasifier Ccal Type	Gasifier Oxidant	HGD Reactor Temp (°F)	HGD Reactor Pressure (psig)	Inlet Sulfur (ppm H ₂ S)	Exit Sulfur (ppm H ₂ S)
006/ Sulfidation	4.1	Arkwright	Air	1149	134	3140	5
007/ Regeneration	13.3	-	-	-	-	-	-
008/ Sulfidation	7.0	Arkwright	Air	1143	143	3560	5
009/ Sulfidation	8.1	Blacksville Briquettes	Air	1044	94	5830	1
010/ Regeneration	17.8	-	-	-	-	-	-
011/ Sulfidation	18.8	Blacksville Briquettes	Air	1005	122	3610	60
012/ Regeneration	27	-	-	-	-	-	-

In Test No. 006, gas was passed through the unit at a space velocity of $2,000\text{h}^{-1}$ for about an hour, which was then increased to $8,000\text{h}^{-1}$ to give the gas flow required by the combustor. After a further 2 hours, H_2S breakthrough began and gas to the combustor was cut off. A renewed breakthrough occurred after 2 more hours at a space velocity of $2,000\text{h}^{-1}$. The reactor pressure drop gradually increased and exceeded the maximum instrument reading of about 160 inches of water at the higher space velocity, well above the bed lifting pressure.

The sorbent was regenerated in Test No. 007 for about 10 hours. Because of the low sulfur loading it was found necessary to increase the air/steam ratio above normal. Nonetheless, temperatures barely reached 1300°F and pressure drop on completion still exceeded the instrument maximum.

In Test No. 008, gas was immediately supplied to the combustor at the same conditions as in Test No. 006. H_2S breakthrough again occurred after about two hours. Gas to the combustor was cut off and the unit continued on-stream at the lower space velocity of $2,000\text{h}^{-1}$ for a further four hours until a renewed breakthrough occurred. At this point the reactor pressure drop exceeded 50 psig, based on unit inlet and outlet pressure indicators, and it was decided to replace the sorbent before carrying out further tests. The sorbent was found to have agglomerated to a great extent, especially at the reactor exit, apparently because of coke formation and the high differential pressures.

H_2S breakthrough profiles are shown on Figures 2-37 and 2-38.

- Second Period

For this period the reactor was refilled with fresh sorbent. Reactor furnace temperatures were set at 1000°F , a temperature

HYDROGEN SULFIDE BREAKTHROUGH PLOT

HGD - SULFIDATION TEST #06

GAS FROM THE 42-INCH FIXED BED GASIFIER RUN #102

TEMP = 1149 F (520 C)

PRESS = 134 PSIG

SPACE VELOCITY = 2023 HOURLY

* = DETECTOR TUBE

□ = GAS CHROMATOGRAPH

FIGURE 2-37

GAS CHROMATOGRAPH DATA WAS TAKEN FROM OLD PLOT

HYDROGEN SULFIDE BREAKTHROUGH PLOT

HGD - SULFIDATION TEST #08

GAS FROM THE 42-INCH FIXED BED GASIFIER RUN #102

GAS CHROMATOGRAPH DATA WAS TAKEN FROM OLD PLOT

FIGURE 2-38

which had given lower reactor pressure drops previously. Gasifier pressure was about 100 psig.

Two absorption tests (Test Nos. 009 and 011) and two regenerations (Test Nos. 010 and 012) were carried out. In Test No. 009, after an initial short time at $2,000\text{h}^{-1}$, the space velocity was stepped up to $5,000\text{h}^{-1}$; the additional gas flowed to the combustor. This flow was half that in Test Nos. 006 and 008, to provide a longer on-stream time to breakthrough and a more acceptable reactor pressure drop. Breakthrough of H_2S occurred after about six hours, when the pressure drop was about 6 psig. Upon cutting off the flow to the combustor, reactor pressure drop fell to 1.5 psig. A renewed breakthrough occurred after a further hour, when the pressure drop had increased to 1.75 psig.

The sorbent was regenerated in Test No. 010 by the regular procedure and reactor pressure drop returned to approximately its original level.

In Test No. 011 no gas was supplied to the combustor, gas flow through the reactor being at a space velocity of $2,000\text{h}^{-1}$ throughout. H_2S breakthrough occurred after about 19 hours. Reactor pressure drop rose from 0.5 psi to 1 psi after 10 hours and then more rapidly to about 6 psi finally, exceeding the bed lifting pressure.

A second regeneration was carried out in Test No. 012 and the sorbent removed. No agglomeration was found.

H_2S breakthrough profiles for tests 009 and 011 are shown on Figures 2-39 and 2-40.

HYDROGEN SULFIDE BREAKTHROUGH PLOT

HGD - SULFIDATION TEST #09

GAS FROM THE 42-INCH FIXED BED GASIFIER RUN #102

NO SAMPLES WERE TAKEN THE FIRST 10 HOURS

FIGURE 2-39

HYDROGEN SULFIDE AND SULFUR DIOXIDE PLOT

HGD - SULFIDATION TEST #11

GAS FROM THE 42-INCH FIXED BED GASIFIER RUN #102

TEMP = 1005 F (558 C)

PRESS = 122 PSIG

SPACE VELOCITY = 1966 HOURLY

* = DETECTOR TUBE (H₂S)

□ = GAS CHROMATOGRAPH

○ = DETECTOR TUBE (SO₂)

FIGURE 2-40

- Sorbent Characterization

The sulfidized sorbent after Test No. 008 was sampled on removal at points along the reactor length. The results are shown in Tables 2-31 and 2-32. At the reactor inlet most of the zinc oxide in the reduced zinc ferrite sorbent has been converted to sulfide, but a significant amount remains, probably as a result of the diffusional limitations. A substantial part of the sorbent's iron content is found to be in the form of cementite (iron carbide). At the reactor outlet the sorbent's zinc content is predominantly in the form of zinc oxide, as expected. Virtually all of the iron appears in the form of iron carbide and no magnetite is detected. Sulfur content is seen to fall from about 25 weight percent at the reactor inlet to near zero at the reactor outlet. Carbon content varies from about 5 weight percent at the inlet to about 8 weight percent at the outlet. This can be explained by the fact that, at the inlet, a good part of the iron in the sorbent is in the form of pyrrhotite (FeS_x), whereas at the outlet, no pyrrhotite is detected.

The surface area and pore volume of the sorbent, particularly towards the outlet, are significantly greater than for the fresh material. This is attributed to the increased porosity resulting from reduction of magnetite in the sorbent to iron and iron carbide. The increased porosity is accompanied by a significantly lower crush strength, which may be the main reason for the large amount of fines formed in the removed sorbent. The fines which passed through a No. 12 screen amounted to about a third of the total sorbent.

Conclusions

The general performance of the sorbent was similar to that in the previous series of tests during gasifier Run No. 101 with low molecular weight sulfur compounds removed to less than about 10 ppm.

TABLE 2-31

ANALYSIS OF MINERALS BY X-RAY DIFFRACTION
IN SULFIDED ZINC FERRITE
GASIFIER RUN 102
TEST 008

Bed Height (Inches)	Hematite Fe_2O_3	Franklinite ZnFe_2O_4 and/or Magnetite Fe_3O_4 (4)	Zincite ZnO	Alpha ZnS	Beta ZnS	Pyrrhotite FeS	Cementite Fe_3O
		Percent	TII (3)				
0(1)			10.9	29.1	38.1	10.1	11.9
6			11.5	32.6	33.4	8.7	13.9
16			15.9	28.6	27.4	5.3	22.7
23			27.6	18.0	19.1	1.3	34.0
26			39.5	10.3	9.8	-	40.4
36			38.4	12.2	9.8	-	39.6
46(2)			58.6	-	1.1	-	40.3
Fresh Sorbent	4.	89.	6.0	-	-	-	-

NOTES:

1. Bottom/Inlet during sulfidation - Outlet during regeneration.
2. Top/Outlet during sulfidation - Inlet during regeneration.
3. Percent TII = Percent Total Integrated Intensity; directly proportional to the concentration of the crystalline phase. Amorphous phase is not accounted for.
4. Franklinite and Magnetite have the same crystal structure and, therefore, cannot be readily distinguished by the diffraction pattern.

TABLE 2-32
SORBENT ANALYSIS OF SULFIDED ZINC
FERRITE GASIFIER RUN 102
TEST 008

Bed Height (Inches)	Total Carbon (% Wt)	Total Sulfur (% Wt)	Bet Surface Area (SO M/G)	Skeletal Density (G/CC)(3)	Porosity %(4)	Crush Strength (Kg DWL) ± S.D.(5)	Skeletal Density (G/CC)(6)	Porosity %(7)
0(1)	4.88	24.61		4.39		3.1 ± 0.9	-	-
6	5.86	24.41					-	-
16	7.51	19.67	4.68	4.57	4.22	1.7 ± 1.6	4.50	46.9
23	7.65	13.15					-	-
26	7.67	7.11	4.72	5.58	6.45	1.6 ± 1.6	4.31	53.2
36	8.18	7.22	6.53	5.72	6.36	1.6 ± 1.3	-	-
46(2)	7.98	0.28	4.46	6.20	7.73	1.2 ± 0.9	5.61	69.4
								-
Fresh Sorbent	0	0.13	3.13	6.16	2.59	6.3 ± 2.8	6.16	60.6(8)

NOTES:

1. Bottom/Inlet during sulfidation - Outlet during regeneration.
2. Top/Outlet during sulfidation - Inlet during regeneration.
3. Skeletal Density by Helium Pycnometry.
4. Porosity by Nitrogen Adsorption for pores up to 600Å diameter.
5. Average and standard deviation of 15 measurements.
6. Skeletal density by mercury porosimetry.
7. Porosity by mercury porosimetry for pores down to 120Å diameter.
8. Porosity by mercury porosimetry for pores down to 30Å diameter.

It was found that, at the higher space velocities necessary to provide gas to the METC combustion test unit, diffusional resistance resulted in the sorbent picking up less than half the anticipated amount of sulfur. This diffusional resistance may be accentuated by the conversion of magnetite in the sorbent to iron carbides.

The formation of iron carbides, resulting from the high CO/CO₂ ratio in the gas which was desulfurized, appears to weaken the sorbent considerably and, upon removal in the sulfidized form, it contained a large quantity of fines.

On these grounds, it appears advisable to operate the desulfurization process at conditions of gas composition and temperature such that iron in the sorbent is not reduced from magnetite to iron and iron carbide. Appendix G also contains an analysis on the effect of fuel gas composition and temperature on sorbent composition.

The particulate loading of the gas stream to the desulfurization unit was again of the order of $1\text{g}/\text{Nm}^3$ and median particle diameter in the range 20 μm to 25 μm . This combination of particulate loading and size resulted in an unacceptable reactor pressure drop, high enough to lift the sorbent bed (operation was in an upward flow mode.)

2.2.3 Gasifier Run No. 103

The sidestream unit was operated with a single batch of sorbent in the reactor for four sulfidation periods and three intermediate regeneration periods as outlined in Table 2-33. The gasifier was operated in the air-blown mode and fed with Blacksville, Arkwright, and Kittanning coals.

As usual, the reactor contained 20.4 kg of zinc ferrite extrusions. Reactor furnace temperatures were set at 1,000°F throughout all the sulfidation and regeneration periods. A lower space velocity than

TABLE 2-33

HOT GAS DESULFURIZATION TESTS - GASIFIER RUN 103

Test No./ Type	Duration (Hrs)	Gasifier Coal Type	Gasifier Oxidant	HGD Reactor Temp (°F)	HGD Reactor Pressure (psig)	Inlet Sulfur (ppm H ₂ S)	Exit Sulfur (ppm H ₂ S)
013/ Sulfidation	45.8	Blacksville	Air	1027	117	5980	2.5
014/ Regeneration	25.2	-	-	-	-	-	-
015/ Sulfidation	40.1	Arkwright	Air	1036	120	5590	25
016/ Regeneration	20.2	-	-	-	-	-	-
017/ Sulfidation	55.6	Kittanning/ Arkwright	Air	1017	168	1180/ 6270	10
018/ Regeneration	12.3	-	-	-	-	-	-
019/ Sulfidation	23.5	Arkwright	Air	1026	235	3860	3

previously of 1000 h^{-1} for the sulfidation was thought to give a more acceptable pressure drop. The space velocity during the regenerations was about 500 h^{-1} .

In Test No. 013, with the gasifier providing gas from Blacksville coal at about 120 psig, breakthrough of hydrogen sulfide occurred after about 46 hours during which time the exit gas H_2S level was about 5 ppm initially, but drifted to about 10 ppm later. The reactor pressure drop gradually rose from about 2 inches to more than 100 inches of water, slowly at first, but more rapidly later. Pressure drop fluctuations occurred when condensate was dumped from the reactor exit condenser, causing gas surges through the sorbent which dislodged bed particulates. Regeneration of the sorbent in Test No. 014 required about 24 hours, the steam-to-air volume ratio being about 85/15. Reactor pressure drop gradually fell, more rapidly at first from about 20 to 2 inches of water.

Test 015, the second sulfidation in which the gasifier provided gas from Arkwright coal at about 120 psig, lasted 40 hours and was terminated prematurely because of an excessive pressure drop increase from about 2 inches, initially to about 160 inches of water. H_2S levels were similar to those in the first sulfidation, except initially when both H_2S and SO_2 were high because of sulfur compounds left in the sorbent after regeneration.

Test 016 was the second regeneration of the sorbent. In this case, the steam-to-air ratio was decreased stepwise from 85/15 initially to 75/25 during the first few hours to ensure that the temperature in the reaction zone reached the desired level of about 1500°F . The duration was consequently rather shorter, about 20 hours. Pressure drop was about 70 inches of water for the first few hours and then rapidly fell to about 5 inches of water at the same time that the steam/air ratio was decreased, i.e., the air flow was increased.

In Test 017, the third sulfidation of the series, gas was provided from Kittanning coal at 120 psig for about 43 hours until this coal

was used up. Then, for a further 13 hours until H₂S breakthrough, the gas came from Arkwright coal at about 240 psig. H₂S levels were less than 10 ppm for the Kittanning coal gas except for a short initial period when the values were again high, resulting from residual sulfate in the sorbent; for the Arkwright coal gas, H₂S levels slowly drifted up to the 20 ppm level.

In Test 018, the third regeneration, the steam/air ratio was again decreased stepwise from 85/15 to 75/25 but more rapidly than before, resulting in a shorter duration of about 12 hours.

Test 019 was the fourth and final sulfidation of the test series. Gas was again derived from Arkwright coal but, in contrast to Test 015, the gasifier pressure was twice as high, at 240 psig. Because the gasifier was shut down prematurely, H₂S breakthrough did not occur and the test lasted about 24 hours.

The H₂S breakthrough profiles of tests 013 through 019 are shown on Figures 2-41 through 2-44.

- Sorbent Characterization

The sulfidized sorbent after Test No. 019 was sampled, on removal, at points along the reactor length and characterized by various techniques. The results are shown in Tables 2-34 and 2-35. As found previously at similar gas conditions, the sorbent is seen to contain large amounts of cementite, particularly towards the reactor outlet. Pyrrhotite is only found near the reactor inlet where there is also some unsulfidized magnetite. The bulk of the zinc oxide at the reactor inlet has been converted to sulfide.

Table 2-35 shows that the sorbent contains up to 25 weight percent sulfur at the reactor inlet. Carbon content, lower at the inlet, exceeds 7 weight percent towards the outlet. Values of surface area and pore volume at the reactor inlet are

HYDROGEN SULFIDE BREAKTHROUGH PLOT

HGD - SULFIDATION TEST #13

GAS FROM THE 42-INCH FIXED BED GASIFIER RUN #103

TEMP = 1027 F (552 C)

* = DETECTOR TUBE

PRESS = 117 PSIG

□ = GAS CHROMATOGRAPH

SPACE VELOCITY = 1006 HOURLY

FIGURE 2-41

HYDROGEN SULFIDE AND SULFUR DIOXIDE PLOT

HGD - SULFIDATION TEST #15

GAS FROM THE 42-INCH FIXED BED GASIFIER RUN #103

FROM HOUR 11 THROUGH 29, H₂S DETECTOR TUBE WAS TOO LOW TO READ

FIGURE 2-42

HYDROGEN SULFIDE AND SULFUR DIOXIDE PLOT

HGD - SULFIDATION TEST #17

GAS FROM THE 42-INCH FIXED BED GASIFIER RUN #103

AT HOUR 40, CALIBRATION OF THE GAS CHROMATOGRAPH WAS PERFORMED AND WAS FOUND TO BE OFF SEVERAL ppm

FIGURE 2-43

HYDROGEN SULFIDE BREAKTHROUGH PLOT

HGD - SULFIDATION TEST #19

GAS FROM THE 42-INCH FIXED BED GASIFIER RUN #103

TEMP = 1026 F (552 C)

* = DETECTOR TUBE

PRESS = 235 PSIG

□ = GAS CHROMATOGRAPH

SPACE VELOCITY = 1012 HOURLY

FIGURE 2-44

TABLE 2-34

ANALYSIS OF MINERALS BY X-RAY DIFFRACTION
IN SULFIDED ZINC FERRITE
GASIFIER RUN 103

Bed Height (Inches)	Hematite Fe_2O_3	Franklinite ZnFe_2O_4 and/or Magnetite Fe_3O_4 ⁽⁴⁾	Zincite ZnO	Alpha ZnS	Beta ZnS	Pyrrhotite FeS	Cementite Fe_3C
		PERCENT TII (3)					
0 ⁽¹⁾		33.9	6.8	12.8	37.3	9.2	-
6		25.7	6.9	18.6	35.4	11.7	1.7
16		14.6	15.9	21.0	25.9	9.4	13.3
23		2.8	52.9	6.5	2.5	-	35.2
26		-	65.0	<0.5	<0.5-	-	35.0
36		-	64.8	-	0.4	-	34.8
46 ⁽²⁾		-	62.7	-	1.1	-	36.2
Fresh Sorbent	4.	89.	6.0	-	-	-	-

NOTES:

1. Bottom/Inlet during sulfidation - Outlet during regeneration.
2. Top/Outlet during sulfidation - Inlet during regeneration.
3. Percent TII = Percent Total Integrated Intensity; directly proportional to the concentration of the crystalline phase. Amorphous phase is not accounted for.
4. Franklinite and Magnetite have the same crystal structure and, therefore, cannot be readily distinguished by the diffraction pattern.

TABLE 2-35

SORBENT ANALYSIS OF
SULFIDED ZINC FERRITE
GASIFIER RUN 103
TEST 019

Bed Height (Inches)	Total Carbon (% Wt)	Total Sulfur (% Wt)	BET Surface Area (Sq M/G)	Skeletal Density (G/CC) ³	Porosity % (4)	Crush Strength (Kg DWL) $\pm$ S.D. (5)	Skeletal Density (G/CC) ⁶	Porosity % (7)
0 ⁽¹⁾	1.45	23.87						
0-6			2.06	4.59	2.01	9.0 $\pm$ 1.8		
6	2.33	25.64						
6-16			2.07	4.56	1.76	4.1 $\pm$ 2.2	4.62	55.0
16	7.62	19.75						
23	6.39	3.40	4.89	5.38	5.50	1.2 $\pm$ 0.9	4.88	61.8
26	6.35	0.58						
26-36			5.72	6.69	7.67	1.1 $\pm$ 0.7		
36	6.06	0.28						
36-46			6.22	6.66	7.89	1.0 $\pm$ 0.5		
46 ⁽²⁾	6.12	0.61					6.21	74.6
Fresh Sorbent	0	0.13	3.13	6.16	2.59	6.3 $\pm$ 2.8	—	60.6 ⁽⁸⁾

NOTES:

1. Bottom/Inlet during sulfidation - Outlet during regeneration.
2. Top/Outlet during sulfidation - Inlet during regeneration.
3. Skeletal Density by Helium Pycnometry.
4. Porosity by Nitrogen Adsorption for pores up to 600Å diameter.
5. Average and standard deviation of 15 measurements.
6. Skeletal density by mercury porosimetry.
7. Porosity by mercury porosimetry for pores down to 120Å diameter.
8. Porosity by mercury porosimetry for pores down to 30Å diameter.

comparable to those of fresh sorbent. Values towards the reactor outlet significantly exceed those for fresh sorbent which may be accounted for by the reduction of the sorbent to cementite. Similarly, sorbent crush strength is comparable to that for fresh sorbent at the reactor inlet, but is significantly lower at the outlet. About a third of the sorbent passed through a No. 12 screen as fines. This disintegration is mostly ascribed to the formation of cementite and its weakening effect.

- Particulate Analysis

During Test Nos. 013, 015, and 017, samples of inlet and outlet gas were taken to characterize the particulate content. In this series, both inlet and outlet samples were obtained for each test to get some idea of the change in particulate loading and size distribution for the gas in passing through the reactor.

The particulate loading of the inlet gas was similar for the three tests, approximately 1 to 2 g/Nm³. The median particle diameter was highest for Arkwright coal gas, ~26 μ m (Test No. 015), somewhat less for Blacksville coal gas, ~21 μ m (Test No. 013), and least for Kittanning coal gas, ~13 μ m (Test No. 017). For each test, a significant proportion of the particulate appeared to be removed by the sorbent bed, reaching about 80 weight percent in Test No. 017.

Larger particles appear to be removed preferentially, so that the median particle diameter at the outlet is significantly less than at the inlet, ~22 μ m for Arkwright coal gas, ~14 μ m for Blacksville coal gas, and ~5 μ m for Kittanning coal gas.

There appears to be a positive correlation between the median particulate size in the inlet gas and the rate of increase of reactor pressure drop in a given sulfidation test, which was highest for Arkwright coal gas, somewhat less for Blacksville

coal gas, and much less for Kittanning coal gas. Smoothed out pressure drop plots for the sulfidation tests are shown in Figure 2-45.

Conclusions

A third series of tests of the hot gas desulfurization unit in a sidestream of the METC 24 TPD fixed-bed gasifier was successfully concluded. The amount of sulfur absorbed at the lower space velocity of $1,000 \text{ h}^{-1}$ was comparable to that found at $2,000 \text{ h}^{-1}$ in previous tests. A substantial amount of the sorbent was again converted to iron carbide, which appears to resist sulfidation and also markedly reduces the crush strength and attrition resistance of the sorbent. In spite of this, low molecular weight sulfur compounds were removed to a level of less than about 10 ppm and the sorbent recovered virtually all its absorption capacity on regeneration. A greater number of cycles will be necessary to demonstrate the sorbent's long-term effectiveness.

Reactor pressure drop was studied more closely in this test series and it was found that there was a positive correlation between the median particulate diameter in gas to the unit and the rate of pressure drop increase. Very little pressure drop increase was evident during a sulfidation test for an inlet gas median particulate diameter of $13 \mu\text{m}$. Particulate gas loading was of the order of 1 g/Nm^3 . Carbon deposition may also affect the pressure drop, so the correlation should be regarded with caution.

2.2.4 Gasifier Run No. 104

The high-temperature, sidestream desulfurization unit was operated for a fourth and final series of tests during fixed-bed gasifier Run No. 104 between December 8 and 13, 1983.

In these tests the main objective was to investigate the desulfurization of lignite gas.

PRESSURE DROP ACROSS REACTOR

INCHES OF WATER

FIGURE 2-45

With a single batch of the same zinc ferrite sorbent used in all the previous tests, the unit was operated for two sulfidation periods with an intervening regeneration, as summarized on Table 2-36. The gasifier was operated in the air-blown mode, being fed with North Dakota lignite during the first sulfidation and Arkwright coal during the second.

The reactor was filled with 20.4 kg of sorbent extrusions. Furnace temperatures were set at 1000°F for the first sulfidation and 1200°F for the second. In both cases the nominal space velocity was 2000 h⁻¹. For the regeneration the furnace temperatures were set at the usual 1000°F and nominal space velocity was 500 h⁻¹.

In Test No. 020, with the gasifier providing gas from lignite at 160 to 200 psig, breakthrough of hydrogen sulfide occurred after about 45 hours on-stream time. The H₂S level was generally less than 5 ppm. Reactor pressure drop increased only slightly from about 0.15 to 0.5 psi. There was an increase of reactor temperatures approaching 100°F.

In the regeneration Test No. 021, the steam/air ratio, initially 85/15, was decreased stepwise during the first few hours to 80/20 in order to achieve reaction zone temperatures of about 1,500°F. The reactor pressure drop was very low throughout, about 0.15 psi.

Test No. 022, lasting about 16 hours, was the final sulfidation of the test series. In this case, with the gasifier providing gas from Arkwright coal at about 130 psig, the aim was to study the effect of the higher temperature on sorbent behavior.

The hydrogen sulfide level in the exit gas initially exceeded 100 ppm, gradually falling to 15 ppm after 8 hours and then resuming an upward trend shortly thereafter. The reactor pressure drop behaved similarly to that in previous tests with Arkwright coal at similar conditions, exceeding bed-lifting pressure after about 12 hours on-stream. The pressure drop, initially about 0.2 psi, was about 4 psi

TABLE 2-36

HOT GAS DESULFURIZATION TESTS
GASIFIER RUN 104

Test No./ Type	Dura- tion (Hrs.)	Gasifier Coal Type	Gasifier Oxidant	HGD Reactor Temp (°F)	HGD Reactor Pressure (psig)	Inlet Sulfur (ppm H ₂ S)	Exit Sulfur (ppm H ₂ S)
020/ Sulfidation	45.1	Lignite	Air	1040	200	2025	12
021/ Regeneration	20.3	-	-	-	-	-	-
022/ Sulfidation	15.4	Arkwright	Air	1213	124	5770	260

at the termination of the test. The temperature rise was about 50°F, somewhat less than usual, and attributed to the lesser extent of the shift reaction at the higher temperature.

H₂S breakthrough profiles for tests 020 and 022 are shown on Figures 2-46 and 2-47.

Sorbent Characterization

After Test No. 022, the sulfidized sorbent was removed from the reactor and sampled for analysis and characterization at a number of points along the reactor length. The results are detailed in Tables 2-37 and 2-38. The mineral analysis differs markedly from that in previous tests with Arkwright coal gas in that the sorbent contains large quantities of wustite, FeO. The amount of wustite is larger at the reactor exit where there is no pyrrhotite. At the reactor inlet a good part of the sorbent's iron content has been converted to pyrrhotite. There is a significant amount of unsulfidized zinc oxide at the reactor inlet, suggesting that it is somewhat inaccessible to hydrogen sulfide, which may explain why the sorbent was unable to remove it to its equilibrium level. Only a small amount of magnetite/zinc ferrite remains.

The presence of wustite is undoubtedly due to the high operating temperature of the sorbent, 1200° to 1300°F, and the relatively small water concentration in the coal gas undergoing desulfurization.

Table 2-38 shows that the sorbent contains about 22 weight percent of sulfur at the reactor inlet, which is less than found in prior comparable tests. The carbon content is quite large and comparable to previous tests where iron carbide was found (none was detected in this case). Surface areas and pore volumes were similar throughout and not much different from those of fresh sorbent. Another result is that the crush strength of the sorbent significantly exceeded that for fresh sorbent at all the sample points. Less than 5 weight

HYDROGEN SULFIDE BREAKTHROUGH PLOT

HGD - SULFIDATION TEST #20

GAS FROM THE 42-INCH FIXED BED GASIFIER RUN #104

TEMP = 1040 F (560 C)

* = DETECTOR TUBE

PRESS = 200 PSIG

□ = GAS CHROMATOGRAPH

SPACE VELOCITY = 2000 HOURLY

FIGURE 2-46

HYDROGEN SULFIDE BREAKTHROUGH PLOT

HGD - SULFIDATION TEST #22

GAS FROM THE 42-INCH FIXED BED GASIFIER RUN #104

TEMP = 1213 F (656 C)

* = DETECTOR TUBE

PRESS = 124.1 PSIG

□ = GAS CHROMATOGRAPH

SPACE VELOCITY = 2000 HOURLY

FIGURE 2-47

TABLE 2-37

ANALYSIS OF MINERALS BY X-RAY DIFFRACTION
IN SULFIDED ZINC FERRITE
GASIFIER RUN 104

Bed Height (Inches)	Hematite Fe ₂ O ₃	Franklinite ZnFe ₂ O ₄ and/or Magnetite Fe ₃ O ₄ (4)	Zincite ZnO	Wustite FeO	Alpha ZnS	Beta ZnS	Pyrrhotite FeS
Percent TII (3)							
0(1)		2.8	5.9	23.4	19.6	35.0	13.3
6		1.0	7.2	30.1	18.7	29.5	13.5
16		1.4	7.1	29.2	16.2	32.3	13.9
23		1.6	6.8	30.4	16.7	31.1	13.3
26		3.2	9.8	36.2	13.3	27.5	9.9
36		5.3	15.8	50.7	7.0	18.4	2.8
42(2)		4.9	22.9	58.6	2.8	10.8	-
Fresh Sorbent	4	89	6				

NOTES:

1. Bottom/Inlet during sulfidation - Outlet during regeneration.
2. Top/Outlet during sulfidation - Inlet during regeneration.
3. Percent TII = Percent Total Integrated Intensity; directly proportional to the concentration of the crystalline phase. Amorphous phase is not accounted for.
4. Franklinite and Magnetite have the same crystal structure and therefore, cannot be readily distinguished by the diffraction pattern.

TABLE 2-38

SORBENT ANALYSIS OF
SULFIDED ZINC FERRITE
GASIFIER RUN 104
TEST 022

Bed Height (Inches)	Total Carbon (% Wt)	Total Sulfur (% Wt)	BET Surface Area (SQ M/G)	Skeletal Density (G/CC)(3)	Porosity %(4)	Crush Strength (Kg DWL) $\pm$ S.D.(5)	Skeletal Density (G/CC)(6)	Porosity %(7)
0(1)	4.92	21.55	2.28	4.17	1.91	10.1 $\pm$ 1.8	3.99	36.5
6	6.89	19.11	1.89	3.87	1.49	9.6 $\pm$ 2.4		
16	7.51	18.85	1.64	4.18	1.02	10.6 $\pm$ 1.4		
23	7.66	18.75	1.89	3.99	1.54	9.3 $\pm$ 2.5	3.49	30.5
26	8.40	15.76	1.65	4.31	0.88	9.8 $\pm$ 2.1		
36	7.73	5.98	3.64	6.56	3.79	10.0 $\pm$ 2.3		
46(2)	7.95	4.14	2.60	7.55	2.86	9.4 $\pm$ 2.3	4.41	43.9
Fresh Sorbent	0	0.13	3.13	6.16	2.59	6.3 $\pm$ 2.8	-	60.6(8)

NOTES:

1. Bottom/Inlet during sulfidation - Outlet during regeneration.
2. Top/Outlet during sulfidation - Inlet during regeneration.
3. Skeletal Density by Helium Pycnometry.
4. Porosity by Nitrogen adsorption for pores up to 600Å diameter.
5. Average and standard deviation of 15 measurements.
6. Skeletal density by mercury porosimetry.
7. Porosity by mercury porosimetry for pores down to 120Å diameter.
8. Porosity by mercury porosimetry for pores down to 30Å diameter.

percent of the removed sorbent passed through a No. 12 screen. This relatively small amount of disintegration is associated with the sorbent's preserved crush strength, in marked contrast to previous tests when the sorbent contained substantial amounts of iron carbide.

Conclusions

The fourth and final series of tests of the hot gas desulfurization unit in a sidestream of the METC 24 TPD fixed-bed gasifier was successfully concluded. The amount of sulfur absorbed before breakthrough was similar to that in previous tests, about 20 weight percent of fresh sorbent. In the final sulfidation test, the only one in the test series in the higher temperature range of 1200° to 1300°F, much of the sorbent iron content was converted to wustite, FeO. This appeared to slow down the rate at which sulfur compounds reacted with the sorbent, and the hydrogen sulfide level attained before breakthrough was significantly higher than the equilibrium level predicted.

A smaller amount of refractory sulfur compounds in the case of lignite gas than in the case of bituminous coal gas appears to be carried through the desulfurization sorbent in the vaporized tars.

The particulate loading of the desulfurization unit exit gas was rather high in the lignite test, about 2 g/Nm³. The median particulate diameter, however, was low, about 5 μm and the pressure drop across the reactor remained very low throughout. This reinforces the conclusion previously reached that there is a strong positive correlation between rate of pressure drop increase and median particle diameter. A particulate loading of about 1 g/Nm³ and a median particle diameter of about 10 μm appear to be an acceptable specification for inlet gas to the hot gas desulfurization unit.

2.3 LABORATORY-SCALE TESTING USING SIMULATED KRW FLUIDIZED BED GAS

2.3.1 Introduction

In connection with the conceptual design of a zinc ferrite hot gas desulfurization unit by KRW Energy Systems, Inc. as part of the Waltz Mill Coal Gasification Program, a program of experiments was designed for the METC newly revamped, laboratory-scale, high-temperature desulfurization unit to investigate the performance of zinc ferrite sorbent in simulated coal gas corresponding to that anticipated from the KRW fluidized bed gasifier process development unit. The METC experiments were carried out from March to May 1984.

Laboratory Scale Unit

Details of the laboratory-scale unit are given in previous sections and the unit is a redesigned version of that employed in previous test series.

The new reactor component is 60 inches long by 2 inches diameter. It is made from 316 stainless steel and is aluminized internally to minimize hydrogen sulfide reaction with the reactor insides. It also contains an integral preheater and after cooler. The reactor is located within a 3-zone clamshell electrically heated furnace. A 12-inch section in the middle of the reactor is available to house the desulfurization sorbent. Temperatures at six points along the center line are measured by means of thermocouples situated in a stainless steel thermowell. The system is maintained at a positive pressure of 25 psig primarily to ensure flow through the on-line gas chromatograph, which measures H_2S , COS , and SO_2 concentrations in the exit gas. Process conditions are recorded by an automatic data acquisition and control system (ADACS).

Gas Conditions

It is planned to operate the KRW process development unit in both oxygen-blown and air-blown modes. Estimated compositions of the water-quenched gases entering the zinc ferrite unit are shown in Table 2-39. Gas compositions approximating these were employed at the laboratory scale in a total of eight sulfidation tests: four oxygen blown and four air blown. Carbonyl sulfide and ammonia were excluded as being of minor consequence, and the hydrogen sulfide concentration was elevated so that breakthrough could occur within a day's operation at the space velocity of 2000 h^{-1} , corresponding to a linear velocity of 15 cm/s through the reactor. The tests were conducted at 4 reactor furnace temperature settings: 1000, 1100, 1200, and 1300°F.

2.3.2 Test Results

The first two tests, Nos. 001 and 002, were designed to verify that hydrogen sulfide in simulated coal gas reacts to a negligible extent with the inside of the aluminized reactor. In Test No. 001, for convenience, simulated Lurgi air-blown gas containing 0.267 volume percent H_2S was passed through the empty reactor for about 3 hours. The H_2S level rapidly reached a plateau corresponding to the inlet H_2S level. When H_2S in the inlet gas was shut off during the following hour, the H_2S level in exit gas quickly fell to a few ppm, indicating that very little sulfidation of the reactor had taken place. This conclusion was confirmed in Test No. 002, in which a typical regeneration gas consisting of 50 volume percent each of air and steam was passed through the reactor for 2 hours. Only a few ppm of SO_2 , measured by detector tube, were detected in the reactor condenser exit gas.

Test Nos. 003, 004, 005, and 006 were carried out with simulated KRW gasifier oxygen-blown gas, containing 1 volume percent H_2S , at furnace temperature settings of 1000, 1100, 1200, and 1300°F, respectively. The reactor contained 715 g of fresh United Catalysts

TABLE 2-39

COMPOSITIONS OF GASES TO BE TREATED BY
THE ZINC FERRITE PROCESS DEVELOPMENT UNIT

Component	Oxygen-Blown Gas (Vol. %)	Air-Blown Gas (Vol.%)
CH ₄	1.2	0.63
CO	29.43	12.47
CO ₂	26.12	10.96
H ₂	11.23	13.76
H ₂ O	30.99	20.0
H ₂ S	0.59	0.301
COS	--	0.016
N ₂	0.44	41.74
NH ₃	--	0.11

L-1504 3/16-inch zinc ferrite extrusions in each test except for Test No. 003, where the amount was 593 g. Figure 2-48, shows plots of the H_2S concentration in reactor condenser exit gas against time on stream for the four tests. The H_2S levels before breakthrough are a few ppm as predicted by thermodynamic chemical equilibrium computations. However, the prediction that the level should increase with temperature is not borne out for the 1200 and 1300°F tests. In both of these, the H_2S level is lower than in the 1100°F test and comparable to the 1000°F test.

Test Nos. 007, 008, 009, and 010 were carried out with simulated air-blown gas, containing 1 volume percent H_2S , at furnace settings of 1000, 1200, 1200, and 1300°F, respectively. The reactor contained 715 g of fresh United Catalysts L-1504 3/16-inch zinc ferrite extrusions in each test. Figure 2-49 shows plots of the H_2S concentration in reactor condenser exit gas against time on stream for the four temperatures. The H_2S concentration levels attained are remarkably similar to those previously obtained for the oxygen-blown gas tests. Again, the H_2S levels above 1100°F were unaccountably lower than expected.

The amounts of sulfur absorbed by the sorbent, computed from the total gas flow through the reactor and the inlet H_2S concentration in the four tests, are shown in Figure 2-50 together with the corresponding values for the oxygen-blown gas tests for comparison. The fall-off in sulfur absorbed above 1200°F appears to be somewhat sharper for the air-blown gas case.

After breakthrough of H_2S in each test, the sorbent was cooled under nitrogen and removed from the reactor. Samples were taken from the top (gas outlet) and bottom (gas inlet) of the sorbent bed and analyzed for total sulfur, total carbon, BET surface area, pore volume, "helium" density, and mineral content. The mineral content, determined by X-ray diffraction, is shown in Tables 4 and 5 of Appendix J. Additionally, mercury porosimetry was utilized to determine percent porosity, skeletal density, and mean pore

ZINC FERRITE SULFIDATION

LAB SCALE TEST UNIT TESTS 003, 004, 005, 006

H_2S Breakthrough Curves on Westinghouse Oxygen - Blown Gas Compositions

ZINC FERRITE SULFIDATION

LAB SCALE TESTS 007, 008, 009, 010R

FIGURE 2-49

SULFUR ABSORPTION CAPACITY OF ZINC FERRITE

FIGURE 2-50

diameter. The results of the analyses are shown on Table 2-40 for Tests 003, 004, 005, and 006 and on Table 2-41 for Tests 007, 008, 009, and 010R.

The total sulfur measured in the sorbent at the reactor inlet is generally in accord with that calculated from the flow of H_2S through the sorbent (see Figure 2-49). In Tests 003, 004, 005, and 006, the values are 25.5, 27.2, 27.8, and 21.0 weight percent, respectively, and in Tests 007, 008, 009, and 010R, they are 21.1, 30.1, 28.6, and 18.4 weight percent, respectively. Total sulfur at the reactor outlet is on the order of 1 weight percent.

The total carbon measured in the sorbent at both reactor inlet and outlet is less than 0.1 weight percent, being somewhat more at the outlet.

The sorbent BET surface areas at both reactor inlet and outlet are lower at the higher operating temperatures, falling from about 2 to 3 m^2/g at 1,000°F to 0.5 to 1.5 m^2/g at 1,300°F. Pore volumes are also correspondingly lower. Surface areas at the reactor inlet, where the sorbent is predominantly in the sulfide form, are generally somewhat lower, up to about two times, than at the outlet, where only a small amount of the sorbent is sulfidized.

Fifteen extrusions from fresh sorbent and from each sample, approximately 1 cm long, were crushed between parallel flat surfaces and the crushing force was measured. Compared with the fresh sorbent, which has an average crush strength of about 8 kg/cm, the crush strength of the sorbent from the reactor inlet is generally rather higher, up to about two times, though this falls off with temperature and, at 1,300°F, the crush strength is about the same as that of fresh sorbent. The crush strength of sorbent from the reactor outlet tends to be slightly less than that of fresh sorbent at all temperatures but, because of the size of the standard deviation, this is not very significant.

TABLE 2-40
SORBENT CHARACTERIZATION: PHYSICAL AND CHEMICAL PROPERTIES
AIR BLOWN TESTS

Test Number Sample Point	007 Bottom	007 Top	008 Bottom	008 Top	009 Bottom	009 Top	010R Bottom	010R Top
Total Sulfur, (wt. %)	21.1	1.79	30.1	2.90	28.6	1.84	18.4	1.00
Total Carbon, (wt. %)	0.08	0.08	0.03	0.05	0.03	0.04	0.03	0.04
BET Surface Area, (m ² /g)	1.38	2.13	1.24	1.72	0.74	1.17	0.91	1.30
Pore Volume, (mm ³ /g)	2.01	3.02	1.92	2.43	0.75	1.71	1.36	1.89
"Helium" Density, (g/cm ³)	4.25	5.65	4.22	5.27	4.18	5.33	4.60	5.38
Crush Strength, (kg/cm)	9	8	13	5	8	7	7	6
Porosity, %	43.6	45.3	21.4	58.1	34.2	54.3	38.6	56.2
Skeletal Density (g/cm ³)	4.14	5.53	3.59	5.56	4.10	5.52	4.26	5.64
Mean Pore Diameter (μm)	0.39	0.37	0.26	0.37	0.85	0.62	0.84	0.67

Notes:

1. Typical values for fresh sorbent: 0.13 wt. % S, <0.1 wt. % C, 3.13 m²/g BET surface area, 4.32 mm³/g pore volume, 6.16 g/cm³ "helium" density, 8 kg/cm crush strength, 60.8% porosity, 0.29 μm mean pore diameter.
2. Pore volume was determined by a N₂ adsorption technique. It is a cumulative measurement of pores with diameters smaller than 600Å.
3. "Helium" density is the true sorbent density measured in helium. Density is corrected for pores, but not closed cell pores.
4. Porosity by mercury porosimetry for pores down to 120Å diameter.
5. Skeletal density by mercury porosimetry.
6. Mean pore diameter by mercury porosimetry.

TABLE 2-41
SORBENT CHARACTERIZATION: PHYSICAL AND CHEMICAL PROPERTIES
CXYGEN BLOWN TESTS

Test Number Sample Point	001 <u>Bottom</u>	003 <u>Top</u>	004 <u>Bottom</u>	004 <u>Top</u>	005 <u>Bottom</u>	005 <u>Top</u>	006 <u>Bottom</u>	006 <u>Top</u>
Total Sulfur, (wt. %)	25.5	1.08	27.2	1.69	27.8	1.76	21.0	5.43
Total Carbon, (wt. %)	0.05	0.06	0.03	0.07	0.03	0.08	0.05	0.05
BET Surface Area, (m ² /g)	2.42	1.98	1.20	2.30	0.55	1.02	0.57	1.56
Pore Volume, (mm ³ /g)	4.40	3.24	1.50	3.19	0.37	1.32	0.44	2.07
"Helium" Density, (g/cm ³)	4.61	6.47	4.26	5.49	4.15	6.50	4.50	5.27
Crush Strength, (kg/cm)	14	7	12	3	11	3	8	5
Porosity, %	31.5	64.3	31.7	61.7	38.2	58.6	38.8	58.0
Skeletal Density (g/cm ³)	3.90	5.55	4.01	5.49	4.02	5.63	4.54	5.65
Mean Pore Diameter (μm)	0.21	0.35	0.47	0.36	1.07	0.68	0.88	0.61

Notes:

1. Typical values for fresh sorbent: 0.13 wt. % S, <0.1 wt. % C, 3.13 m²/g BET surface area, 4.32 mm³/g pore volume, 6.16 g/cm³ "helium" density, 8 kg/cm crush strength, 60.8% porosity, 0.29 μm mean pore diameter.
2. Pore volume was determined by a N₂ adsorption technique. It is a cumulative measurement of pores with diameters smaller than 600Å.
3. "Helium" density is the true sorbent density measured in helium. Density is corrected for pores, but not closed cell pores.
4. Porosity by mercury porosimetry for pores down to 120Å diameter.
5. Skeletal density by mercury porosimetry.
6. Mean pore diameter by mercury porosimetry.

2.3.3 Conclusions

The series of tests carried out, in which simulated oxygen- and air-blown coal gas from the KRW process development unit was passed through zinc ferrite sorbent in a laboratory-scale unit, has demonstrated that the sorbent can function in the regime of gas composition and temperature planned for pilot-scale tests, lowering H₂S concentration to a few ppmw.

There is evidence that at 1200°F and above, wustite is formed in both oxygen and air-blown cases, resulting in a lower sorbent conversion to sulfide before hydrogen sulfide breakthrough. Thus, operation above 1200°F and at lower steam concentrations in the gases than those employed in these tests is not recommended.

The zinc ferrite high temperature desulfurization process is characterized by salient process features which have been identified from the test program at METC. For each salient feature, it is possible to identify specific system implications, key issues, and technology needs. From this approach, an assessment can be made of the zinc ferrite test program and a recommendation for future activity can be developed.

System implications serve to identify the impact that can be expected when proceeding with system design and operation. This impact can be manifested in either the zinc ferrite desulfurization system or in its effect on the balance of plant design.

Key issues are problem areas that are unresolved through the present level of testing and can be expected to have a significant impact on process development. Finally, technology needs are those tests and programs which should be undertaken to resolve or minimize the key issues.

The following salient features and their issues have been identified, based upon the results of testing discussed in this report:

SORBENT CAPACITY

System Implications:

Sorbent capacity has a direct bearing on cycle time, sorbent replacement costs, and, thus, operating costs. A primary design consideration is to relate changes in capacity with the number of regeneration cycles and the resultant increase in sorbent replacement frequency. The major implication is the cost of replacing sorbent which deteriorates with increased numbers of

regeneration cycles. Larger initial loadings of sorbent would require less frequent replacement.

Key Issues:

The reported sorbent capacities were derived from breakthrough measurements rather than equilibrium batch determinations. It is probable that commercial-scale beds, which are deeper, would have higher effective capacities resulting in less frequent replacement than is now projected. As an issue, this has yet to be demonstrated.

Technology Needs:

Large scale tests at commercial space velocities, linear velocities, and bed depths should give an indication of sorbent capacity at design levels. Also, at that size, the effect of temperature profiles within the bed and regeneration cycles should be recognized.

3.2 ABSORPTION TEMPERATURE

System Implications:

The optimum operating temperature of $1100 \pm 100^\circ\text{F}$ serves to meet the objectives of approaching maximum absorption efficiency while operating with minimal change to the sensible heat content of the gas. Higher absorption temperatures would cause sintering of the sorbent, would push the zinc ferrite out of the magnetite composition region, and could also result in zinc vapor carry-over.

Key Issues:

Testing, as reported, indicates that the optimum absorption temperature is around 1100°F . As other conditions change in the

scale-up program such as reactor size, and actual fuel gas compositions, a different optimum temperature may be established.

Technology Needs:

It will be necessary to establish optimum absorption temperatures as the sorbent development involves varying operating and test conditions in the future. The effect of the temperature profile as the reaction proceeds through the bed also needs to be established.

3.3 ABSORPTION SPACE VELOCITY

System Implications:

Absorption space velocity affects the effective absorption capacity of the sorbent by influencing breakthrough times and the frequency of regeneration. This affects capital costs for the system.

Key Issues:

Space velocity in a scaled-up reactor raises some questions:

- Does linear velocity have a significant effect?
- What is the effect of pressure at a given space velocity?
- Can test pressures and temperatures be scaled-up effectively?

Technology Needs:

A design data base should be developed from a test program specifically aimed at obtaining commercial scale-up information. KRW PDU testing is a step in this direction but the testing will be done only at low space velocities. The testing of deep beds at high space velocities will still be required for commercial scale design.

3.4 PURITY LEVEL OF EXIT GAS

System Implications:

The primary objective of the desulfurization system is to reliably produce an exit gas having a specified low level of sulfur. This is, therefore, a point of departure for breakthrough level, amount of sorbent, regeneration frequency, space velocity, and regeneration conditions.

Key Issues:

In operating the bed to ensure a low level of sulfur in the exit gas, not all of the bed can approach equilibrium at breakthrough. It is possible that other configurations would utilize the sorbent more efficiently, such as moving beds, fluidized beds, or different shapes.

Technology Needs:

Optimum bed configurations should be explored to enable more of the bed to reach equilibrium at breakthrough.

3.5 REGENERATION TEMPERATURE

System Implications:

Either extremely high or low regeneration temperatures can create sorbent problems. Low temperature regeneration serves to promote the formation of sulfates which convert to SO_2 during the subsequent initial absorption time. This necessitates a two-stage regeneration. The other extreme is that of high temperatures caused by exothermic reactions which cause thermal peaks with resultant sintering of the sorbent.

Key Issues:

The design objectives for zinc ferrite systems include control of gas temperature regeneration at 1000°F and a 1450°F maximum bed limit resulting from exothermic reactions. Methods of controlling bed temperatures by gas composition (i.e., steam content) have been explored, but active control utilizing internal bed heat exchange surfaces has not been developed.

Technology Needs:

Methods should be developed to effectively control the regeneration bed temperature and to document the effect of positive control on bed operation. The effect of the temperature profile as the reaction proceeds through the bed needs to be established.

3.6 REGENERATION GAS COMPOSITION

System Implications:

The regeneration gas composition serves to ensure that maximum quantities of SO₂ will be produced in the shortest period of time. The presence of steam or nitrogen serves to temper the exothermic reaction.

Key Issues:

It is not clear as to which regeneration gas is the best composition, i.e., O₂, N₂, air, or steam. The impact of the use of various regeneration gases on the power plant cycle needs to be established.

Technology Needs:

Further testing should be conducted at commercial scale space velocities in an attempt to optimize gas composition..

3.7 REGENERATION SPACE VELOCITY

System Implications:

In the METC test program regeneration space velocities have typically been less than one-half of the absorption flow. A low oxygen content in the regeneration gas prevents temperature buildup in the bed, and SO₂ concentrations in the regeneration gas are low.

Key Issues:

The optimum space velocity seems to be unclear. It is desirable for the regeneration time to be essentially equal to or less than the absorption time to minimize the rate of consumption of air and diluent.

Technology Needs:

Further testing should be conducted to identify the optimum regeneration space velocity while considering its effect on absorption/regeneration cycling.

3.8 REGENERATION PRODUCTS

System Implications:

The most desirable product of regeneration is a significant percentage of SO₂ in the exit gas. Other products, such as trace alkali metals and halides must be considered. If sulfates are formed, a two stage regeneration will be required to prevent release of sulfur compounds at initiation of absorption.

Key Issues:

Previous issues such as gas composition, temperature, and space velocity are uncertainties. These contribute to changes in regeneration products.

Technology Needs:

Further testing is needed on a larger scale, either in a PDU or Demonstration Test.

3.9 CHANGE OF SORBENT PROPERTIES WITH REGENERATION CYCLES

System Implications:

Changes in sorbent properties, primarily sulfur capacity, seriously affect regeneration cycles, breakthrough times and, in turn, affect replacement and operating costs.

Key Issues:

It is not entirely clear to what extent zinc ferrite properties are affected by regeneration cycles. They are known to deteriorate, but the predictable level and rate have not definitively been determined.

Technology Needs:

Sufficient applied research on zinc ferrite composition and operating characteristics should be conducted to resolve the above issues.

4.0 OVERALL ASSESSMENT OF ZINC FERRITE TEST PROGRAM

4.1 ACCOMPLISHMENTS OF TEST PROGRAM

The METC Zinc Ferrite Test Program has served to establish the basic feasibility of zinc ferrite as a regenerable sorbent for hot gas desulfurization. In particular, when compared to zinc oxide, zinc ferrite was seen to have higher loading capacity and a greater resistance to sintering.

Preliminary parameters for zinc ferrite operation were established early in the lab scale test program at atmospheric pressure which enabled METC to concentrate on various other operating conditions and results. Operating conditions were:

Sulfidation Temperature, 1000-1200°F

Sulfidation Space Velocity, 1000-2000 h⁻¹

Regeneration Inlet Temperature, 1000°F

Regeneration Space Velocity, 500-600 h⁻¹

Regeneration Steam/Air Ratio, 50/50 V/V

Throughout the balance of testing, it became apparent that a number of characteristics of zinc ferrite would become technical issues.

a. Ability to reduce the low levels of H₂S.

It was shown that the inlet gas H₂S concentration could be brought down to near the ZnO equilibrium level, usually less than 10 ppm without difficulty. This level appears suitable for gas turbine applications. For MCFC applications, a level of <1 ppm is thought to be required.

b. Reduction in Capacity with Repeated Regenerations.

Throughout the test program the quantitative effect of more than four regenerations was not determined. Indications were observed that the sorbent had reduced porosity after several regenerations which results in a downward trend in absorption capacity. This, of course, could have a significant effect on operating economics. (Note: Amax has completed tests of up to 92 cycles and has shown reduced capacity.)

c. Formation of Iron Carbide as a Result of Fuel Gas Composition.

Throughout most of the laboratory scale testing, the test gas was a simulated Lurgi gas having a high water content. In the side stream tests with actual fuel gas it was observed and confirmed that gases with a high CO/CO₂ ratio and/or low H₂O concentration at high temperatures encourage formation of iron carbide or wustite. The result of this is to incur a restricted specification on gas composition and addition of steam in some gases, i.e., KRW and Texaco.

d. Formation of Sulfates during Regeneration.

It was observed that zinc ferrite will form some zinc sulfate during regeneration with the reaction being favored by low temperatures and high oxygen concentration. High temperatures to prevent this (>1,500°F) and low steam result in sintering. The result of sulfate formation is an evolution of sulfur species with the next sulfidation unless a two stage regeneration (oxidation followed by reduction) is used.

e. Pressure Drop.

It was observed in the side-stream tests that pressure drop through the zinc ferrite bed is affected by the size of particulates in the fuel gas. The data has shown that gas

particulate control will be required up-stream of the desulfurization process.

4.2 LIMITATIONS OF ZINC FERRITE

The Zinc Ferrite Test Program has served to identify some realistic parameters that would be placed on a commercial zinc ferrite desulfurization system. Those identified thus far which would have a significant impact on design and/or operations are as follows:

a. Sulfidation Temperature.

Bed optimization around 1100°F may require multiple gas/gas heat exchangers and partial quenching of the gas from the gasifier.

b. Regeneration Temperature.

To minimize sulfate formation or sintering during regeneration of sulfided zinc ferrite, a temperature compromise is necessary. Although an increase in the temperature of the sorbent decreases the level of residual sulfate, it leads to the sintering of the sorbent and reduced capacity for subsequent desulfurization. Above 1,200°F the decomposition of sulfate is rapid.

c. Feed Gas Composition.

Strict operating limits of CO/CO₂ ratios, H₂O, and temperature are necessary to operate in the magnetite region of the sorbent. This could create efficiency problems when tailoring fuel gas compositions.

d. Regeneration Products.

The product of regeneration is a relatively low-concentration stream of SO_2 (2 to 4 percent) in nitrogen and steam. Recovery of sulfur from this stream requires a secondary cleanup train, e.g., Wellman Lord, and a sulfur recovery process. Recycle of regeneration product to a gasifier with in-situ desulfurization is another alternative.

In addition to reviewing the test results, Gilbert/Commonwealth has recently conducted a systems engineering study and conceptual design of a nominal 100 MW power plant using various gasifiers and a zinc ferrite desulfurization system. In doing this study, they have also concluded that the key systems issue of the zinc ferrite process that can have a major impact on costs is the sorbent capacity and its life over many cycles of absorption and regeneration. Long term testing with repeated cycles is required to be able to project a realistic sorbent life.

There are a number of areas in which additional research and development is necessary in order to reduce costs. These include operation at higher space velocities which reduces capital costs, extending sorbent life which reduces consumables cost, and finding a more cost effective method of regeneration tail gas treatment. Sulfur recovery constitutes over half the cost of the sulfur treatment process. A KRW PDU test was initiated in late 1986 where regeneration gas is recycled to the gasifier and sulfur removed by dolomite in the fluidized-bed gasifier. This has a potential for a large cost reduction.

SUGGESTED PROGRAMS

METC has subsequently entered into several programs with contractors to gain further insight into the salient features of zinc ferrite. These programs include:

Multicycle Durability	AMAX
Sulfate Formation	SRI International
Solid Phase Boundaries	SRI International
Kinetics and Structural Changes within Sorbent	Louisiana State University
Tail Gas Treatment	R. M. Parsons Co., Arthur D. Little
Tar Effects	Research Triangle Institute
Tar Cracking	Battelle Pacific Northwest Laboratory
Trace Sulfur Removal	Energy Research Corporation

Beyond these studies, which primarily serve to quantify the salient features of the sorbent, empirical activity on the PDU scale is warranted. The current activity that METC is involved in at the KRW gasifier site is a first step toward commercialization. Further testing of zinc ferrite reactors and systems at a commercial scale and configuration are necessary. This would serve to quantify heat transfer, temperature control, pressure drop, and other operating characteristics. Below is a listing of several research and development needs for the process to reach commercial status.

- All absorption/regeneration tests should be run at high temperature and high pressure in gasification atmospheres generating data that show repeatability and consistency.
- Test results should agree with theoretical model predictions to provide a basis for scale-up.
- Integrated absorption/regeneration and sulfur recovery tests at the PDU size should be run. The size of the test should be large enough that scale-up to a commercial size can be done.

REFERENCES

Abel, W. T., F. G. Schultz, and P. F. Langdon. 1974. "Removal of Hydrogen Sulfide from Hot Producer Gas by Solid Absorbents." Bureau of Mines Report of Investigations 7947.

Cicero, D. G., and S. C. Jain. September 1985. "Status and Overview of DOE-Funded Projects Related to Chemical Gas Stream Cleanup Program." Paper presented at the Symposium on High-Temperature Fuel Cleanup. September 19, 1985, in Chicago, Illinois.

"Coal-Derived Fuel Gases for Molten Carbonate Fuel Cells." 1979. TRW for Morgantown Energy Technology Center, Report No. DOE/METC/8085/6.

"Determination of Solid Phase Boundaries in Coal-Gas Desulfurization by Zinc Ferrite." September 1986. SRI International, Final Report No. DOE/MC/21096-2192.

Giner, Inc. October 1983. "Studies Involving High-Temperature Desulfurization/Regeneration Reactions of Metal Oxides for Fuel Cell Development." Final Report. DOE/MC/16021. NTIS/DE84003096.

Green, D. A., K. E. Leese, and W. J. McMichael. 1983. "Pollution Control in Coal Gasification." Research Triangle Institute for Morgantown Energy Technology Center. Report No. DOE/MC/16441-1406.

Grindley, T. December 1983. "Zinc Ferrite Hydrogen Sulfide Absorbent." pp. 145-172. In Third Annual Contaminant Control in Hot Coal-Derived Gas Streams Contractors' Meeting Proceedings. Science Applications, Inc. DOE/METC/184-6. NTIS/DE84000216.

_____. 1981. "Development and Testing of Regenerable Hot Coal Gas Desulfurization Sorbents." Science Applications, Inc. DOE/MC/16545-125. NTIS/DE82011114. 28 pp.

_____. 1982. "Development and Testing of Regenerable Hot Coal Gas Desulfurization Sorbents." Presented at AIChE Spring National Meeting. Report No. DOE/MC/16545-1125.

_____. 1982. "Development and Testing of Regenerable Hot Coal Gas Desulfurization Sorbents." Second Annual Contractors' Meeting on Contaminant Control in Hot Coal-Derived Gas Streams. Report No. DOE/METC/82-47.

_____. 1983. "Zinc Ferrite Hydrogen Sulfide Absorbent." Third Annual Contractors' Meeting on Contaminant Control in Hot Coal-Derived Gas Streams. Report No. DOE/METC/84-6. Grindley, T. and G. Steinfeld. 1984. "Testing of Zinc Ferrite Hydrogen Sulfide Absorbent in a Coal Gasifier Side Stream." Fourth Annual Contractors' Meeting on Contaminant Control in Hot Coal-Derived Gas Streams.

_____. 1985. "Desulfurization of Hot Coal Gas by Zinc Ferrite." In Acid and Sour Gas Treating Processes, ed. Stephen A. Newman, 419-465. Houston: Gulf Publishing Company.

_____. February 1982. "Development and Testing of Regenerable Hot Coal Gas Desulfurization Sorbents." In Overview to DOE/Fossil Energy's Gas Stream - Contaminant Control Projects. 2nd Annual Contractors' Meeting on Gas Stream Clean-Up, ed. K. E. Markel, pp. 332-359. DOE/METC/812-47. NTIS/DE820182 81.

Grindley, T., V. P. Kothari, and K. Pater. May 1983. "Coal Gas Desulfurization Activities at Morgantown Energy Technology Center." Proceedings of 12th Biennial Lignite Symposium.

Guterman, G., and P. Steiner. November 1984. "Laboratory Evaluation of Modifications to the RESOX Process, Final Report." Foster Wheeler Development Corporation. EPRI-CS-3710.

Jablonski, G., et al. 1982. "Evaluation of Gasification and Gas Cleanup Processes for Use in Molten Carbonate Fuel Cell Power Plants." Westinghouse R&D Center for Morgantown Energy Technology Center, Report No. DOE/MC/16220-1306.

Jalan, V. October 1983. "Studies Involving High-Temperature Desulfurization/Regeneration Reactions of Metal Oxides for Fuel Cell Development." Final Report. Giner, Inc. DOE/MC/16021-1486. NTIS/DE84000222.

Jalan V., and D. Wu. January 1980. "Molten Carbonate Fuel Cell Power Plant Desulfurization Systems." Final Report. November 1978-November 1979. Giner, Inc. 92 pp. DOE/ET/15370-T1. NTIS/DE83006791.

_____. 1980. "Molten Carbonate Fuel Cell Power Plant Desulfurization Systems." Giner, Inc., for U. S. Department of Energy, Report No. DOE/ET/15370-T1 & 2.

Jalan, V., et al. 1981. "Studies Involving High-Temperature Desulfurization/Regeneration Reactions of Metal Oxides for the Fuel Cell Program." Giner, Inc., for Argonne National Laboratory. Report No. ANL/J/ED3/12.

Jenkins, R. J. 1976. "Hot Low-Btu Producer Gas Desulfurization in Fixed Bed of Iron Oxide-Fly Ash." Air Products and Chemicals, Inc., for Department of Energy, Report No. DOE/FE-2033-14, 1976.

Jones, C. and J. M. Donohue. 1977. "Comparative Evaluation of High- and Low-Temperature Gas Cleaning for Coal Gasification, Combined-Cycle Powr Systems." Stone and Webster for EPRI, Report No. AF-416.

Joshi, D. K. and E. L. Leuenberger. 1977. "Hot Low-Btu Producer Gas Desulfurization in Fixed Bed of Iron Oxide-Fly Ash." Air Products and Chemicals, Inc., for Energy Research and Development Administration, Report No. ERDA/FE-2033-19, Vols. I and II.

Joshi, D. K., J. H. Olsen, M. L. Hayes, and V. Shah. 1979. "Hot Low-Btu Producer Gas Desulfurization in Fixed Bed of Iron Oxide-Fly Ash." Air Products and Chemicals, Inc., for Department of Energy, Report No. DOE/FE-2757-3.

Krishnan, G. N. and H. Wise. 1983. "Study of Sulfate Formation in Regeneration of Zinc Ferrite Sorbents." SRI International for Morgantown Energy Technology Center. Contract No. DE-AC21-83MC20092.

Markel, K. E., ed. December 1983. "Third Annual Contaminant Control in Hot Coal Derived Gas Streams Contractors' Meeting Proceedings." 481 pp. DOE/METC/84-6. NTIS/DE84000216.

_____. December 1984. "Proceedings of the Fourth Annual Contractors' Meeting on Contaminant Control in Coal-Derived Gas Streams." DOE/METC 85/3.

Markel, K. E., D. C. Cicero, ed. May 1985. "Proceedings of the Fifth Annual Contractors' Meeting on Contaminant Control in Coal-Derived Gas Streams." DOE/METC 85/6025.

_____. June 1986. "Proceedings of the Sixth Annual Contractors' Meeting on Contaminant Control in Coal-Derived Gas Streams." DOE/METC-86/6042.

"Monitoring Contaminants in Coal-Derived Gas for Molten Carbonate Fuel Cells." 1981. TRW for Argonne National Laboratory, Report No. DOE/METC/82-44.

Oldaker, E. C., A. M. Poston, and W. L. Farrior. 1975. "Removal of Hydrogen Sulfide from Hot Low-Btu Gas with Iron Oxide-Fly Ash Sorbents." Report No. MERC/TPR-75, Vols. I and II, Morgantown Energy Technology Center.

Parekh, R. D. 1982. "Handbook of Gasifiers and Gas Treatment Systems," UOP/SDC for Department of Energy, Report No. WD-TR-82/008-010.

Patel, P. S. and S. Rich, "Trace Contaminant Removal from Hot Coal Gas for Molten Carbonate Fuel Cell Application." Energy Research Corporation for Morgantown Energy Technology Center. Contract No. DE-AC21-83MC20094.

Ranade, P. V., and D. P. Harrison. 1981. "The Variable Property Grain Model Applied to the Zinc Oxide - Hydrogen Sulfide Reaction." Chem. Eng. Sci. 36(6):1079-81.

_____. 1979. "The Grain Model Applied to Solids with Variable Structural Properties." Chem. Eng. Sci. 34(3):427-32.

Robson, F. L. and W. A. Blecher. 1981. "Assessment of Fuel Gas Cleanup Systems." United Technologies Research Center for Morgantown Energy Technology Center, Report No. DOE/METC/12050-149.

Rostrup-Neilsen, J. R. 1971. "Principles Relating to the Regeneration of Sulfur-Poisoned Nickel Catalyst. J. Catal." 21(2):171-78.

Schrodt, J. T. February 1983. "Dynamic Simulation of a Fixed-Bed Zinc/Iron Oxide High-Temperature Desulfurization Process," Final Report. University of Kentucky, Department of Chemical Engineering. DOE/MC/21582-1500. NTIS/DE84000220. 165 pp.

Science Applications, Inc. December 1982. "Hot Gas Desulfurization," Annual Report. DOE/MC/16545-T1.

Steinfeld, G. 1981. "Hot Gas Desulfurization." Science Applications, Inc., for Morgantown Energy Technology Center, Report No. 1-443-13-710-00.

_____. 1982. "Hot Gas Desulfurization." Science Applications, Inc., for Morgantown Energy Technology Center, Report No. DOE/MC/16545-T1.

_____. 1984. "Status of METC Investigations of Coal Gas Desulfurization at High Temperature." Science Applications, Inc., for Morgantown Energy Technology Center, Report No. DOE/MC/16545-1553.

_____. March 1984. "Status of METC Investigations of Coal Gas Desulfurization at High Temperature." Science Applications, Inc. DOE/MC/16545-1553. NTIS/DE84003084. 140 pp.

TRW, Energy Engineering Division. May 1981. "Monitoring Contaminants in Coal-Derived Gas for Molten Carbonate Fuel Cells," Final Report. DOE/METC-44. NTIS/DE83012491.

Westmoreland, P. R. and D. P. Harrison. 1976. "Evaluation of Candidate Solids for High-Temperature Desulfurization of Low-Btu Gases." Environmental Science and Technology, 10 (659).

_____. 1976. "Evaluation of Candidate Solids for High-Temperature Desulfurization of Low-Btu Gases." Environmental Science and Technology. 10:655-61.

Westmoreland, P. R., J. B. Gibson, and D. P. Harrison. 1977. "Comparative Kinetics of High-Temperature Reaction Between HS and Selected Metal Oxides." Environmental Science and Technology. 11(5):488-91.