HOT GAS DESULFURIZATION WITH SORBENTS
CONTAINING MIXED METAL OXIDES

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FINAL REPORT

EXECUTIVE SUMMARY

This project was conducted with the funding provided by the U. S. Department of Energy. The Technical Project Officer was Mr. Suresh Jain who was succeeded by Dr. Kamalendu Das. This is the final report for this project.

In this project the sulfidation and regeneration behavior of vanadium-promoted zinc ferrite sorbents was investigated by microreactor studies and physical characterization of the promoted sorbents.

In this report, first the background of high temperature desulfurization processes using solid sorbents and of the novel sorbent research is discussed. This is followed by a discussion of the objectives of the research work. In a subsequent section the experimental setup and procedures are given. The discussion of results are presented for the fresh and used sorbent characterizations, and standard sulfidation and regeneration experiments followed by the discussion of the effects of sulfidation temperature, calcination temperature, and the water vapor content of the simulated fuel gas. Finally the major conclusions drawn from the results of this work are presented.

PROJECT SUMMARY

The advanced power generation systems such as the integrated gasification combined cycle power generators and the molten carbonate fuel cells have stringent fuel gas desulfurization requirements. Process economics dictate that this desulfurization be performed near the temperatures of the gas exiting the gasifier (538 - 816°C). The most advanced hot gas desulfurization technology is based on the zinc ferrite sorbent. This sorbent has several shortcomings: evaporation of zinc and sulfate formation limit the operating temperature range. Prebreakthrough sulfur levels below 1 ppmv, as required by the molten carbonate fuel cell applications, cannot be obtained. In addition, there is room for improvement in handling the SO₂ produced during regeneration and in reducing the other contaminants such as chloride and ammonia.

Among the novel sorbents developed recently, only the supported ZnO:V₂O₅ and CuO:MoO₃ sorbents, and the bulk ZnO:CuO:Fe₂O₃ sorbents appear to have the ability to reduce the H₂S levels below 1 ppmv. The first two sorbents have a severely limited capacity and the performance of the latter still suffers from zinc evaporation and sulfate formation.

Recent studies have shown that zinc can be stabilized by vanadium up to 750°C and that vanadium oxide can chemisorb up to 20 mol% H₂S, thus making H₂S reduction below 1 ppmv possible. Under some conditions vanadium produces large amounts of elemental sulfur. This may even be enhanced by the presence of iron and copper. Copper is instrumental in the decomposition of ammonia.

The original objective of the proposed research was to evaluate the desulfurization performance of novel sorbents consisting of different combinations of zinc, iron, vanadium, and copper oxides; and develop a sorbent

which can reduce H_2S levels to less than 1 ppmv, which can stabilize zinc, making operations above 650°C possible, and which can produce economically recoverable amounts of elemental sulfur during regeneration. This objective was to be accomplished by evaluating the sorbent performance by fixed-bed and TGA experiments supported by sorbent characterization at various reaction extents. The existing single-pellet and fixed-bed models would, then, be modified and used to explain the data. The actual funding received was less than half of the proposed budget and as a consequence all the objectives stated in the proposal could not be achieved. The new objectives were limited to the evaluation of the performance of Zn, Fe, and V-containing sorbents by fixed-bed microreactor studies and sorbent characterization.

The Zn-Fe-V-O sorbents were prepared by the impregnation of V_2O_5 on crushed zinc ferrite pellets obtained from United Catalysts, Inc. This was accomplished by using the incipient wetness technique and employing aqueous ammonium metavanadate, drying the resulting solid and calcining it. The main variables studied were the concentration of V_2O_5 in the sorbent; and the temperature of calcination.

A total of 8 test sorbents were prepared. These contained 1, 3, 4.8, or 15 mass per cent vanadium, and either calcined at 873 K or 1023 K under flowing air. The prepared sorbents were designated as ZF-V01-600, ZF-V01-750, ZF-V03-600, ZF-V03-750, ZF-V04.8-600, ZF-V04.8-750, ZF-V15-600, and ZF-V15-750. In these designations the numbers following V indicate the mass percentage of vanadium in the sorbent and the last three digits indicate the calcination temperature in $^\circ\text{C}$. Some sorbents which were initially calcined at 873 K were subjected to a second calcination step at an elevated temperature. The sorbents prepared by this two-step calcination method exhibit different characteristics than those of the

sorbents subjected to only one calcination step. The calcined sorbent was sieved and a sample was taken from the -20 +40 mesh size range.

The mass ratio of V to Zn in these sorbents are less than that required to form a eutectic mixture of ZnO and V_2O_5 (about 1.6 g V per g of Zn). The reason for this choice is that, in practice, it is better to have as little vanadium in the sorbent as possible because of the unfavorable effects of vanadium on the sorbent capacity and downstream consumption of the fuel gas.

The fresh sorbents prepared by the methods described above were characterized by atomic absorption spectroscopy for elemental analysis; X-ray diffraction for the identification of crystalline phases; and surface area, porosity and pore volume measurements.

The atomic absorption measurements have indicated that some iron has been lost during sorbent preparation; the prepared sorbents had slightly higher Zn/Fe ratios than the original zinc ferrite sorbent. Increases in Zn/Fe ratios were also observed in the used sorbents.

The X-Ray diffraction measurements of the samples containing less than 4% vanadium did not show any vanadium containing crystalline phase. The main component in these samples is the synthetic Franklinite ($ZnFe_2O_4$). Fresh ZF-V4.8-600 sorbent contains $ZnFeVO_4$ and synthetic Magnetite (Fe_3O_4) in addition to the synthetic Franklinite. Sorbent ZF-V4.8-750 does not contain Magnetite but some V_3O_4 is possibly present. Sorbent ZF-V15-600 contains $ZnFe_2O_4$ and $ZnFeVO_4$. In addition to these, sorbent ZF-V15-750 also appears to contain some Fe_2O_3 .

The surface areas of the fresh sorbents that are calcined at 873 K are almost independent of the vanadium percentage up to about 5% vanadium content and are slightly lower than that of the zinc ferrite. The surface area of the sorbent containing 15% vanadium is about 25% less than the sorbents with lower

considerably lower surface areas which decrease with the vanadium content. The results of the porosity measurements on fresh sorbents show that the porosities of the prepared sorbents decrease with increasing vanadium content and calcination temperature. The corresponding increase in the mean pore diameter indicate that small pores are lost by sintering at high temperature calcinations and that some small pores are plugged by V_2O_5 . An interesting observation is the different sorbent properties obtained by two step calcination (calcination at 873 K followed by a second calcination step at a higher temperature). The initial calcination at a lower temperature (873 K) imparts considerable stability against sintering at high temperatures.

The sorbents were evaluated with respect to their sulfidation performance by the H_2S breakthrough curves obtained in a packed-bed microreactor setup and their regenerability behavior. A quartz tube of 1 cm diameter was used as the reactor; the bed temperature was measured at the top and bottom of the sorbent bed. The reactor was operated isothermally. The packed section had a diameter of 1.5 cm and a packed height of about 2 cm. Water was introduced into the feed stream by bubbling nitrogen through distilled water and monitoring the water temperature. Sections of the setup coming in contact with H_2S were constructed from teflon or teflon coated stainless steel. The gas lines after the introduction of water are heated. Gas compositions were measured by a Varian 3400 gas chromatograph equipped with flame photometric (FPD) and thermal conductivity (TCD) detectors. A teflon column, 8' long x 1/8 in O.D., and a glass column, 6' long x 1/4 in O.D., both packed with Chromosil 310 (Supelco, Inc.) were used in the analyses. Gas samples could be analyzed every 3.5 minutes to provide time-resolved composition.

The main variables for sulfidation experiments were temperature and inlet

The main variables for sulfidation experiments were temperature and inlet H_2O concentration. The sulfidation gas composition was chosen according to the suggestions of the technical monitor. The H_2O content of the sulfidation gas was varied between 7 - 20%.

Standard sulfidation experiments were performed at 873 K with a feed gas composition of 1% H_2S , 20% H_2 , 7% H_2O , and 72% N_2 . The effects of sulfidation temperature and H_2O concentration of the sulfidation gas were studied in the subsequent experiments. In this study, sorbents in the 20/40 mesh size range were employed. The gas hourly space velocity was 4000 per hour.

The sulfidation experiments were performed on both the novel sorbents prepared in this study, and also, on zinc ferrite and zinc titanate obtained from UCI, Inc. Each sulfidation test was followed by a regeneration test and this procedure was repeated for five cycles. The regeneration gas was composed of O_2 and N_2 . In this study oxygen concentration of the regeneration gas was not varied; and no water is introduced into the regeneration gas to prevent reduction in the elemental sulfur formation. The particle size and bed dimensions were kept the same as the values used during sulfidation; the space velocity was kept at 2000 per hour. The exit gas from regeneration runs was analyzed for H_2S and SO_2 by G. C. The sulfate formation was quantified by measuring the SO_2 released from sulfate when the O_2 in the regeneration gas is replaced by N_2 . Total H_2S and SO_2 released during regeneration was determined by absorbing the exit gases in 1 N iodine solution. Sulfur formation could not be quantified accurately; approximate values were obtained by scraping the sulfur formed at the reactor exit and weighing it.

Standard regeneration experiments have been performed at 973 K with a gas composition of 10% air and 90% N_2 . Effect of regeneration temperature was

performed where regeneration was preceded by N_2 purge at $700^\circ C$ to desorb any reversibly chemisorbed H_2S .

The structural and chemical characterization of the sulfided and regenerated sorbents was carried out on selected samples. Zinc loss was determined by atomic absorption measurements. All the used sorbents have higher Zn/Fe ratios than the fresh sorbents. Highest increases in the Zn/Fe ratios are seen at high sulfidation temperatures and in sorbents with high vanadium content. The major crystalline phases observed in regenerated sorbents are generally the same as those observed in fresh sorbents. The only difference is that regenerated sorbents contain some V_2O_4 , while in fresh sorbents vanadium occurs only as $ZnFeVO_4$. The X-Ray diffraction analysis of a sulfided sample showed only pyrrhotites and Fe_9S_{10} as the sulfur containing crystals. No evidence of ZnS could be obtained indicating that sulfur compounds of zinc did not form crystalline phases during sulfidation. All sorbents containing vanadium undergo structural changes upon cycling. They lose surface area and pore volume through the loss of smaller pores. This is indicated by the increase in mean pore radius. Sorbents with high (15%) vanadium content retain their original porosity although the mean pore size increases significantly. In contrast to the vanadium-containing sorbents, the surface area of the zinc ferrite sorbent increases upon regeneration. This is due to a drastic change in the mean pore size of the sorbent. The observation that the pore sizes in the zinc ferrite sorbent decrease considerably when the sorbent is subjected to repeated sulfidation-regeneration cycles, while the pore sizes of the vanadium containing sorbents increase mildly, is difficult to explain with the available data. It might be due to the presence of different compounds with different physical properties. The physical characteristics of the sorbents calcined at 923 K by the two-step

method are very similar to those of the sorbent calcined at 873 K.

The shapes of the breakthrough curves obtained in standard sulfidation runs typically reflect the insignificance of diffusion limitations. All sorbents produced prebreakthrough H_2S levels below the detection limit of the fpd for 2.5 ml gas sample. Hydrogen sulfide levels over 1 ppmv were detectable by the gas chromatograph. These results indicate that the desulfurization levels obtained were below the equilibrium levels for zinc oxide.

Although sorbent ZF-V01-600 showed very good performance in the first cycle, its performance deteriorates rapidly as the cycle number increases. The breakthrough curves for the second and third cycles indicate an increasing diffusion limitation. The conversion of ZF-V03-600 at breakthrough is about the same as that of zinc ferrite for the first cycle, but it has higher conversions than zinc ferrite in second through fourth cycles. Its sulfur capacity is about the same as that of zinc ferrite in the fifth cycle. Sorbent ZF-V4.8-600 shows a similar behavior but has somewhat lower conversions until the fourth cycle. Its superiority seems to be in the relatively stable behavior it exhibits for cycles 2 through 5. In the fifth cycle it shows superior performance. Sorbent ZF-V15-600 shows very stable performance but consistently lower conversions. The low conversion is the result of low initial surface area and porosity due to the plugging of pores by vanadium oxide.

The sulfur capture capacity of the vanadium-promoted zinc ferrite sorbents for 873 K sulfidations is considerably higher than the recommended zinc titanate sorbents. This suggests that the addition of vanadium provides additional capacity by chemisorbing H_2S . This was confirmed by the H_2S desorption runs.

Although some sulfate formation was observed during the regeneration of zinc ferrite at 973 K, the sulfate formation in vanadium containing sorbents was

insignificant. The regeneration temperature is the most important variable affecting the sulfate formation. The sulfidation temperature does not seem to have an appreciable effect on the sulfate formation. The decomposition of the sulfate becomes slower at higher sulfidation temperatures in the case of zinc ferrite probably due to changes in the sorbent structure. Calcination temperature and the H_2O content of the fuel gas do not affect the sulfate formation significantly. Although it could not be quantified accurately, significant amounts of elemental sulfur were collected after the regeneration of vanadium-containing sorbents. Results indicate that more than 15 mass % of the sulfur can be obtained in elemental form.

Increase of sulfidation temperature from 873 K to 923 K increased the conversion in the first cycle of sulfidation of ZF-V4.8-600. In the subsequent cycles, conversion dropped continuously. This behavior may be due to active metal loss by vaporization or surface area loss due to sintering. The loss of active metal appears to play a more significant role.

ZF-V15-600 shows the same behavior as ZF-V4.8-600 at higher sulfidation temperature, that is, the conversion is consistently lower at each cycle. The interesting behavior of this sorbent is that the range of drop in the conversion is narrower than the other sorbents. Zinc ferrite shows behavior similar to those of the sorbents promoted by vanadium. The fifth cycle conversion is very close to that of ZF-V4.8-600, unlike the superior performance shown by the promoted sorbent at 873 K. This is mainly due to the fact that the adsorption of H_2S on vanadium at higher temperatures is expected to be lower.

A series of runs were made to compare the performances of sorbents prepared by single-step and two-step calcination. The sorbents calcined at 923 and 973 K by two-step calcination exhibit high conversions and have relatively stable

K by two-step calcination exhibit high conversions and have relatively stable performance throughout the 4 cycles. The most interesting observation is the behavior of sorbents calcined at 1023 K by one and two step calcination. The sorbent which was initially calcined at 1023 K in a single step showed much lower conversions than the sorbent first calcined at 873 K and then at 1023 K in two steps. This may be attributed to the structural stability imparted to the sorbent as a result of the initial low temperature calcination step.

To test the effect of fuel gas water partial pressure on the performance of the sorbents, some selected sorbents were tested for several cycles using a simulated fuel gas containing 20 % water vapor. Sorbents ZF-V15-650^{*} (two-step calcination), ZF-V4.8-750 (one-step calcination) and zinc titanate show very good stability. In fact, their performance improve with cycling. The conversion of ZF-V4.8-750 appears to approach that of ZF-V4.8-750^{*} as the number of cycles increase. Other sorbents experience a deterioration in performance upon cycling. The zinc titanate sorbent exhibits the best conversion behavior. Because of the very high conversions obtained with this sorbent, its sulfur capture capacity after the fifth cycle is the highest for sulfidations at 923 K with a gas containing 20 % water vapor. It shows a very stable behavior throughout the five sulfidation-regeneration cycles. A similar stable behavior was observed for the sorbent ZF-V15-650^{*} prepared by two-step calcination. Its conversion and capacity also increased with cycling. The main reason it exhibited lower conversion and capacity than those of zinc titanate was because substantial amount of surface area and pore volume were lost during the preparation of the promoted sorbent. Increased water content of the fuel gas decreases the conversion of ZF-V4.8-650^{*}, but increases the conversions of zinc ferrite, zinc titanate, and ZF-V15-650^{*} in the first cycle. The fuel gas water content does

cycles.

The main conclusions of this study are summarized below:

1. With all vanadium-promoted sorbents, prebreakthrough H_2S levels below the equilibrium levels for zinc oxide have been attained.
2. Some H_2S was chemisorbed by vanadium containing sorbents.
3. It was estimated that with sorbents containing vanadium, more than 15 mass % of the sulfur can be obtained in elemental form.
4. Vanadium-promoted sorbents containing 1 and 3 % vanadium had conversions similar to that of zinc ferrite, but had lower sulfur capture capacities after 5 cycles of sulfidation and regeneration.
5. The sorbent containing 4.8 % vanadium has the highest conversion and sulfur capture capacity among all the tested vanadium-promoted sorbents, and has higher conversion than zinc ferrite and higher capacity than zinc titanate after five 873 K-sulfidation - 973 K-regeneration cycles using low moisture (7 %) simulated fuel gas. When sulfided at 923 K it shows behavior similar to other vanadium-promoted sorbents and zinc ferrite.
6. The sorbent containing 15 % vanadium showed the most stable performance through five 873 K-sulfidation - 973 K-regeneration cycles using low moisture simulated fuel gas, but its conversions were low due to its low surface area and porosity. For 923 K-sulfidation its conversion was at the same level as the other promoted sorbents and zinc ferrite.
7. The sorbent ZF-V4.8-650^o, which was prepared by two-step calcination, had the highest conversion after five 923 K-sulfidation - 973 K-regeneration cycles using low moisture simulated fuel gas.
8. Calcination at high temperature stabilizes zinc in the vanadium-promoted sorbents and suppresses zinc loss during sulfidation. On the other hand ,

the surface area and porosity of the sorbent are greatly reduced.

9. If the sorbents are calcined first at low temperature and then at a higher temperature (two-step calcination), the sorbent retains the structure it has attained after the first calcination and therefore its surface area and porosity does not undergo any significant change during the second calcination step. The conversions of these sorbents did not decrease much upon cycling even at high sulfidation temperatures, because the second high temperature calcination step suppresses zinc loss during sulfidation.
10. Atomic absorption analyses of the fresh and used sorbents indicated that the Zn/Fe mass ratios increased when the vanadium-promoted sorbents were subjected to several sulfidation-regeneration cycles. Zinc loss seemed to have a more significant effect on the decrease of sorbent activity during cycling. These observations could not be explained with the available data.
11. Sorbents containing 15 mass % vanadium show stable performance through several sulfidation-regeneration cycles similar to those of zinc titanate. If these sorbents can be prepared with high surface areas and porosities, they will have stabilities comparable to that of zinc titanate but with much higher sorbent capacities.
12. Sorbents containing 4.8 % by mass vanadium or higher did not indicate any appreciable sulfate formation when regenerated at 973 K while zinc ferrite sorbent underwent some sulfate formation. Regeneration at lower temperatures caused sulfate formation in vanadium-promoted sorbents.
13. When subjected to sulfidation-reduction cycles, zinc ferrite sorbent experienced an increase in its surface area and a decrease in its porosity, while its pore size decreased significantly. On the other hand, all vanadium containing sorbents lost surface area and pore volume, and in

contrast to zinc ferrite, their pore size increased.

14. Increased water content of the fuel gas decreases the conversion of ZF-V4.8-650', but increases the conversions of zinc ferrite, zinc titanate, and ZF-V15-650' in the first cycle. The water content of the fuel gas does not seem to have an appreciable effect on sorbent conversion in the subsequent cycles.

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I. INTRODUCTION

One of the most promising areas where petroleum can be replaced by coal is the generation of electricity. There has been a considerable research effort over the last decade, to develop advanced power generation systems and fuels suitable for use in these systems. Among these, pressurized fluidized bed combusters, integrated gasification combined cycle power generators and molten carbonate fuel cells are rapidly approaching commercial stage. These applications have rather stringent fuel desulfurization requirements. For power plant combusters, a sulfur level below 100 ppmv may be adequate; but, since in the presence of alkali contaminants, H_2S may cause corrosion of turbine blades, a H_2S level below 10 ppmv will be desirable for IGCC use. For coal derived gaseous fuels to be used in molten carbonate fuel cells, their sulfur content should be limited to less than 1 ppmv to prevent poisoning of the cell electrodes.

At the coal gasifier exit fuel gas will be at 6 to 35 atm pressure and 538 to 816°C temperature. Process economics dictate that the entire coal gas cleanup process be performed near these conditions. Current high temperature desulfurization efforts are mainly focused on mixed metal oxides which are capable of decreasing the sulfur content of coal gases below 10 ppmv and which are regenerable and stable under multicycle operation.

The current hot gas desulfurization technology based on zinc ferrite needs improvement in several aspects.^(1, 2, 3, 4, 5, 6) These can be cited as the extension of the operating temperature range beyond 677°C, prebreakthrough sulfur levels less than 1 ppmv, easier and more economical handling of regeneration off-gases, increased sulfur capture capacity under practical conditions and ability to reduce other contaminants such as chloride and ammonia.

Recent research efforts concentrate on achieving these improvements through

the addition of other metal oxides such as TiO_2 to zinc oxide or zinc ferrite sorbents or by developing new mixed oxide sorbents. Most promising oxide systems belonging to the latter group are the CuO -based sorbents.^(7, 8)

II. BACKGROUND INFORMATION ON HOT GAS DESULFURIZATION

The most advanced hot gas desulfurization process based on the zinc ferrite sorbent is rapidly approaching commercial stage; recently a pilot scale process demonstration unit has been successfully operated. Tests performed at the METC have shown that a commercial zinc ferrite desulfurization sorbent capable of reducing sulfur levels to less than 10 ppm in coal gas streams at temperatures between 550°C - 650°C and pressures up to 2 mPa can be produced.⁽⁹⁾ It was shown to possess sufficient durability for fixed-bed operations.

II.A. Zinc Ferrite Process

When prepared as a mixed oxide sorbent, zinc and iron oxides will form the zinc ferrite spinel ZnFe_2O_4 . In a fixed-bed reactor, before breakthrough, a large portion of the bed will be exposed to essentially H_2S -free reducing gas containing H_2 and CO . Upon initial contact with CO and H_2 in the hot fuel gas, fresh zinc ferrite undergoes the following reaction:

With concentrated reducing gas compositions, Fe_3O_4 is further reduced to FeO and Fe .⁽¹⁰⁾ Due to slow kinetics and unfavorable chemical equilibrium at low temperatures, appreciable reduction of ZnO is not expected.^(11, 12, 13) However, recent experimental findings show that above equilibrium reduction may be possible indicating the presence of a more reactive solid phase than bulk zinc oxide.⁽¹⁴⁾ While reduction of ZnO is suppressed in the presence of H_2O , it cannot be eliminated. The evaporative loss of metallic zinc is noticeable above 600°C and becomes appreciable above 650°C.⁽⁸⁾

The majority of sulfur in the coal gas will be present as H_2S . In the

presence of water both the carbonyl sulfide and carbon disulfide will form H_2S . These reactions are expected to attain equilibrium very rapidly.

The desulfurization of fuel gas occurs through the reaction of H_2S with the reduced sorbent:

Under the conditions of desulfurization, iron is reported to form non-stoichiometric sulfur compounds FeS_x where $1 < x < 1.2$.^(10, 15, 16)

Fully sulfided sorbent can be regenerated with oxygen to reform the zinc ferrite according to the equation:

Regeneration is usually done with a gas containing a large fraction of a diluent such as N_2 or steam. In fixed-bed operations the regeneration gas compositions are adjusted to give a reaction zone temperature of about 760°C ⁽⁹⁾ because sintering becomes appreciable above 788°C ⁽¹⁶⁾. Experiments at METC showed that during oxidative regeneration a five-to-one mole ratio of steam to air is necessary to prevent the sintering of zinc ferrite.⁽¹⁷⁾ Under certain conditions of temperature and regenerating gas composition sulfate formation may prevent complete regeneration; this will be discussed in a subsequent section.

II.B. Novel Sorbent Development Efforts

Sorbent properties which are important in the applications and therefore deserve primary consideration in new sorbent development are:

- (i) hydrogen sulfide removal efficiency as indicated by the prebreakthrough H_2S levels in the desulfurizer off-gas and the sulfur loading of the sorbent which depends on the breakthrough conversion and the amount of inert material required;

- (ii) regenerability of the performance of the sorbent over multiple cycles;
- (iii) the composition of the regeneration off-gas;
- (iv) durability of physical strength; and,
- (v) behavior towards other impurities.

The development of novel hot gas desulfurization sorbents is currently at the laboratory testing stage. The recent developments are mainly due to the efforts of Flytzani-Stephanopoulos, et. al.^(7, 8, 14, 18, 19, 20) and Gangwal, et. al.^(10, 15, 21) The main objectives of these studies were to stabilize zinc or take advantage of the superior thermodynamics of CuO, by suppressing the reduction of ZnO and CuO through the formation of mixed metal oxide compounds such as ZnTiO₃, and CuAl₂O₄. A number of metal oxide combinations including oxides of iron, zinc, copper, aluminum, titanium, molybdenum and vanadium have been tried. Among these zinc oxide-titanium oxide and iron oxide-copper oxide-aluminum oxide sorbents have attracted the most attention. The outcome from these recent novel sorbent development efforts are summarized in *Table 1*. To conserve space, only the most promising sorbents are included in this table.

II.C. Sorbent Sulfur Capacity and Extent of Sulfur Removal

Sulfur capacity is given by the sulfur loading of the sorbent (g S/g sorbent) at the sulfur breakthrough point in the sulfidation cycle. The breakthrough point is the operating point when the effluent gas sulfur content exceeds a pre-determined value. Extent of sulfur removal is indicated by the amount of H₂S in the sulfidation off-gas at prebreakthrough. When the reaction and diffusion rates are sufficiently high these properties are determined by thermodynamics. On the other hand, under most practical conditions, the rates of purely chemical steps as well as the rates of diffusion in the pores of the

sorbent and in the sulfide product layer limit sorbent capacity and the degree of sulfur removal. The prediction of the sorbent behavior is further complicated by the fact that most mixed oxides form distinct crystalline phases and solid compounds and therefore generally possess different thermodynamics and reactivity than those of individual oxide components. This fact forms the basis of the recent novel sorbent development activity. With several mixed oxide sorbents subequilibrium H_2S levels were obtained indicating that chemisorption may also be an important factor in determining the degree of sulfur removal.^(7, 14) Surface area and the pore size distribution determine the rate of diffusion in the pores and through the product layer. The latter usually imparts a more severe limitation on capacity since the specific volume of the sulfided product is greater than that of the oxide causing the blocking of the small diameter pores and hence decreasing the available surface area. The new class of porous sorbents introduced by Flytzani-Stephanopoulos, et. al.^(7, 23) seems to possess superior surface area and pore size distribution characteristics and may provide an improvement over the present commercial sorbents if they can be safely and economically manufactured in large amounts and be formed into pellets of sufficient crush strength and durability. Recent pelletization studies seem to be promising.⁽¹⁴⁾

For the metal oxides under consideration, there is a trade-off between the kinetics and thermodynamics with respect to temperature. The reaction rates, therefore the sulfur capacity increase with temperature while the equilibrium concentration of H_2S in the sulfidation off-gas also increases, decreasing the degree of sulfur removal. Equilibrium constants for the reduction of metal oxides may also increase with temperature causing the formation of metallic species thus leading to increases in metal loss or to the predominance of the

unfavorable thermodynamics of the metal.

In the process demonstration unit operating with commercial zinc ferrite sorbents sulfur loading close to 30 weight percent and exhaust gas sulfur levels of less than 10 ppm have been obtained.⁽⁹⁾ The laboratory test results on the sulfur capacity and sulfur removal efficiency of the novel sorbents are summarized in Table I.

II.D. Regenerability and Multi-cycle Operation

The commercial feasibility of any sorbent system will not only depend on its sulfidation characteristics, but also on its regenerability and ability to function through many sulfidation/regeneration cycles. The commercial sorbents will be required to show adequate performance for an extended period of time between scheduled plant maintenance.

There are several factors affecting the regeneration conditions; namely, rate of regeneration reactions, SO_2 production and disposal, restoration of the properties of the sorbent to presulfidation levels, and extent of sulfate formation. Regeneration is accomplished by reacting metal sulfides with O_2 to form metal oxides. Higher oxygen concentrations result in higher regeneration rates, but also, produce hot spots resulting in sintering and loss of surface area. Therefore regeneration is usually done with air diluted with nitrogen or steam. The amount of dilution is adjusted so that the pellet temperatures do not exceed 780°C . Steam also reacts with the sulfided product to produce metal oxides at a much slower rate compared to oxygen. The concentration of steam in the regeneration gas is important in elemental sulfur formation as discussed in the next section. Sulfur dioxide, if present in the regeneration gas can also react with metal sulfides to form metal oxides and elemental sulfur, but the

Table 1. Comparison of Novel Hot-Gas Desulfurization Sorbents

Sorbent	1.7% ZnO + 3.6% V ₂ O ₅ by weight Supported by Alumina	CuO + 3MoO ₃ on Alumina 5.44 wt % Cu 2.74 wt % Mo	Porous ZnO	Porous Zinc Ferrite	Porous Copper Ferrite	Porous Copper Aluminate	Porous 3CuO:Fe ₂ O ₃ :Al ₂ O ₃	Porous CuO:MoO ₃ :Al ₂ O ₃	0.43 ZnO:TiO ₂ from TiCl ₄ Precursor	ZnO:3Fe ₂ O ₃ :3TiO ₂ from TiCl ₄ Precursor	0.86 ZnO:0.14 CuO:Fe ₂ O ₃ 2% Inorganic Binder	0.80 ZnO:TiO ₂
Reference	7	7	7, 14	7, 23	7	7, 14, 23	7, 14	7	14	14	22	22
Sulfidation T, °C	700	650	650	600	538 - 650	538 - 650	650	650	650	650	590 - 567	594 - 579
Regeneration T, °C	700	650	650	600	700	700	650	538 - 650	700	700	538	538
Degree of Sulfur Capture (Prebreak-through H ₂ S Level, ppm)	< 0.5	< 0.1	< 2 - 5	2 - 3	< 10 - 85-90	< 10 - 100	< 5	0 - < 10	< 15	< 40	0 - 2	8
Sulfur Loading (g S/g sorbent) (some entries are calculated from data in reference)	5.4 x 10 ⁻³ in dry sulfidation 1.2 x 10 ⁻³ in wet sulfidation (includes the support)	0.026 depends on H ₂ S concentration in feed	0.394	0.318 decreases during multicycle operation	0.250 - 0.300	0.066 - 0.070	0.14	0.077	0.10	0.17	0.145 - 0.134	0.07
Sulfate Formation	very little at 700 °C Eliminated by regeneration at 750 °C			Sulfate formed	Sulfate formed at 650 °C	Sulfates formed with high surface area sorbents up to 750 °C	Sulfates formed		Sulfate formation is suppressed at 650 and 700 °C regeneration	Sulfates formed	Sulfate formation at 650 °C	Sulfate formation at 650 °C but in a much smaller amount
Metal Loss	none up to 750 °C	Metal Loss observed during wet regeneration only	Dry reduction 5 - 7 wt %/h/m ² wet reduction 0.07 wt %/h/m ²	Zinc loss above 600 °C				Loss of Mo was suppressed under some calcination conditions	0.13 - 0.26 wt %/h/m ² in dry reduction 0.020 wt %/h/m ² in wet reduction	no observable zinc loss		
Elemental Sulfur Formation	50 - 65 mol% of total S in dry regeneration 5% of S in wet regeneration	3 - 8 % of total sulfur				no elemental sulfur formation	1 - 3% dry and low steam concentration - 10% with high steam concentration			some elemental S was produced	20% of total sulfur	
Other Observations	no surface area loss up to 750 °C	initial loss of surface area (about 40%)	H ₂ S at breakthrough increases with temperature	limited loss of surface area			better performance at lower H ₂ /H ₂ S ratios	some sintering at 650 °C	loss of surface area and pore volume in cycling		COS completely removed	some COS remained

rates of these reactions are also very slow. The temperature dependence of the regeneration reactions are usually greater than that of the sulfidation reactions.⁽¹⁵⁾

Sulfate formation during regeneration is a major problem causing the consumption of valuable coal gas in an extra reductive regeneration step following the oxidative regeneration. At low regeneration temperatures and high O_2 and SO_2 partial pressures metal sulfates can form due to:

where M represents a metal. The second reaction is especially important for copper sulfate formation. There is also evidence of surface sulfate formation as in the case of alumina.⁽¹⁴⁾

Zinc sulfate starts decomposing around 600°C and copper sulfate does not decompose below 650°C.⁽¹⁸⁾ As a result, for complete elimination of sulfate formation, regeneration above 750°C will be necessary for the zinc ferrite and $CuO:Fe_2O_3:Al_2O_3$ sorbents. Addition of TiO_2 to ZnO seems to suppress sulfate formation. No evidence of sulfate formation is observed during the regeneration of $ZnO:TiO_2$ sorbents in a fixed-bed reactor with 10% air/90% N_2 regeneration gas mixture.⁽¹⁴⁾ Increased pressure promotes the formation of sulfates.

II.E. Composition of the Regeneration Off-gas

Since regeneration produces SO_2 , a downstream treatment facility for recovering the sulfur in a resalable form or for disposing of the sulfur in an environmentally acceptable way, should be an integral part of any desulfurization process. Process alternatives for accomplishing this include conversion to elemental sulfur, production of sulfuric acid, or conversion to a disposable

sulfate preferably by recycling the regeneration off-gas to the gasifier where the sulfur can be captured as calcium sulfate by dolomite or limestone used as an in-bed desulfurization sorbent.

If the steam to air ratio in the regeneration gas is taken to be 5-to-1 as suggested by METC the maximum recycle rate of SO_2 to the gasifier is limited to about 9 weight percent of the required steam flow to the gasifier.⁽¹⁷⁾ To provide some flexibility for control, the actual SO_2 recycle rate has to be lower than this value. Recovery of some sulfur as elemental sulfur during regeneration will help to decrease the SO_2 recycle. Decreased SO_2 formation might also retard the sulfate formation. Elemental sulfur production is also attractive economically; besides providing sales revenues, obtaining elemental sulfur in recoverable amounts will also decrease the energy requirements for sulfur removal.

Iron and vanadium containing sorbents yield appreciable amounts of elemental sulfur during regeneration under some conditions. It was reported that during dry regeneration of supported $\text{ZnO}:\text{V}_2\text{O}_5$ sorbents at 700°C as high as 50 - 65 mole % of all the sulfur was obtained as elemental sulfur. Elemental sulfur formation during wet regeneration was substantially lower amounting to about 5% of the total sulfur products.^(7, 23)

In contrast, dry regeneration of $\text{CuO}:\text{Fe}_2\text{O}_3:\text{Al}_2\text{O}_3$ sorbents yield very low amounts of sulfur. With increased steam in the regeneration gas mixture the elemental sulfur recovery increases. In regeneration at 650°C with 84% $\text{H}_2\text{O}/16\%$ air, the elemental sulfur yield amounted to 20 mole % of the total absorbed H_2S .^(7, 14) It was also observed that lowering the oxygen content of the mixture raised the amount of the elemental sulfur product. To increase the amount of elemental sulfur yield of iron containing sorbents, Flytzani-Stephanopoulos, et.al.⁽¹⁴⁾ introduced SO_2 into the regeneration gas. The elemental sulfur

produced at 600°C and 700°C; was, respectively, 40 and 72% of the theoretical value for 100% conversion of FeS to FeO.

II.F. Behavior Towards Other Impurities

Other sulfur products that may be present in the coal gas are in the order of abundance, carbonyl sulfide, carbon disulfide and thiophene. In tests performed at the METC showed that commercial zinc ferrite sorbents could lower COS from 500 ppm to less than 5 ppm, CS₂ from 1 ppm to about 0.1 ppm and thiophene from about 0.5 ppm to about 0.1 ppm.⁽⁹⁾

Other impurities that were tested include ammonia and chloride. Zinc ferrite appears to show no activity towards ammonia and very little sorption capacity for chloride. Only a certain zinc ferrite pellet containing some sodium almost completely eliminated the chloride in the sulfidation off-gas.⁽⁹⁾ Addition of CuO to zinc ferrite improved the behavior of the sorbent towards ammonia. A sorbent obtained by replacing 14% of ZnO in zinc ferrite by CuO was shown to be capable of converting over 50% of the ammonia in the coal gas to hydrogen and nitrogen.⁽²²⁾ It also removed the carbonyl sulfide completely while with zinc titanate some COS remained in the desulfurizer off-gas.

III. DESCRIPTION OF RESEARCH WORK

III.A. Objectives

From *Table 1* it can be seen that very few novel sorbents can satisfy the less-than-1 ppm sulfur requirement of the molten carbonate fuel cell power generation systems. These include the supported $\text{ZnO}:\text{V}_2\text{O}_5$ and $\text{CuO}:\text{MoO}_3$ sorbents, and the bulk 0.86 $\text{ZnO}:$ 0.14 $\text{CuO}:\text{Fe}_2\text{O}_3$ sorbent. The first two suffer from the existence of a large amount of inert support which results in a very low sulfur loading. In addition the $\text{CuO}:\text{MoO}_3$ sorbent lost some Mo and some surface area. Tests with the bulk 0.86 $\text{ZnO}:$ 0.14 $\text{CuO}:\text{Fe}_2\text{O}_3$ sorbent have shown that the H_2S level in the desulfurizer off-gas remained below 1 ppm for a considerable portion of desulfurization. Sulfur loading at breakthrough (100 ppmv H_2S) was found to be 0.14 g S/g sorbent which is about half the sulfur capture capacity of zinc ferrite.⁽²²⁾ From the reported results of the TGA experiments it appears that reduction of CuO to Cu occurs to some extent decreasing the H_2S removal efficiency of the sorbent. This might limit the ultimate sulfur capacity of this type of sorbents. Also during oxidative regeneration at 650°C, there was a considerable amount of sulfate formation (CuSO_4 and ZnSO_4). Although the Zn:Cu:Fe sorbents seem promising as a one-step desulfurization sorbent for molten carbonate fuel cell applications, there is still a great need for research to develop new and improved mixed oxide sorbents which can lower the sulfur content of the coal gas to less than 1 ppmv under practical conditions.

The initial interest in vanadium as a possible high temperature desulfurization sorbent arose from the fact that within the temperature range of interest it is the only metal which can thermodynamically accomplish essentially 100 percent desulfurization.⁽¹¹⁾ Unfortunately, the desulfurization kinetics of V_2O_5 is about an order of magnitude slower than that of ZnO.⁽²⁴⁾ This precludes the

use of vanadium oxide by itself as a hot gas desulfurization sorbent.

The superior sulfidation thermodynamics of vanadium was later disputed and some reported that it may even be inferior to zinc.⁽³⁾ There are contradictory experimental results in this area. However, recent work by Flytzani-Stephanopoulos, et. al.^(7, 23) has shown that sorbents formed by supporting a eutectic mixture of ZnO and V₂O₅ on alumina or zirconia exhibited a stable breakthrough conversion of about 0.65 over 5 cycles. The prebreakthrough H₂S levels were always less than 1 ppm. No surface area loss took place and the zinc is stabilized by vanadium in the alumina support suppressing the evaporative loss of metallic zinc. This makes regeneration at high temperatures up to 750°C possible and eliminates the sulfate formation problem encountered in low temperature regenerations. Although vanadium did not form any bulk vanadium sulfide, it was able to capture up to 0.20 mol H₂S/mol V₂O₅ through chemisorption which is substantially higher than that observed with titanium (0.0014 mol H₂S/mol TiO₂). This capacity, however, is impaired by the presence of high concentrations of H₂O in the coal gas. It was found that H₂O/H₂S ratios up to 10/1 might be allowed before a drastic inhibition of H₂S chemisorption by H₂O occurs.⁽⁷⁾ The reactions involved are summarized below:

Sulfidation at 700°C

Regeneration at 750°C

At the beginning of the desulfurization, a small amount of SO₂ was observed in

the exhaust gas as a result of the overall reaction:

This is a disadvantage of vanadium-based sorbents. In practice, this release of SO_2 at the beginning of the desulfurization stage may be prevented by some reductive regeneration following the oxidative regeneration, but the effects of prereduction on the desulfurization behavior of the sorbent should be studied.

Another advantage of the vanadium containing sorbents is the promotion of elemental sulfur formation especially under dry regeneration conditions through the catalytic decomposition of H_2S . Up to 50 - 65% of sulfur could be obtained as elemental sulfur.⁽⁷⁾ In fact vanadium sulfide either alone or in combination with iron and copper sulfides has been found to be a good catalyst for thermal decomposition of hydrogen sulfide.⁽²⁵⁾ The tests showed that the crystalline phases in vanadium sulfide-iron sulfide catalysts were V_2S_3 and Fe_7S_8 , but the vanadium and copper sulfides in the presence of H_2S reacted to form Cu_3VS_4 . The results indicated that the thio-anion VS_4^{3-} is a very good catalyst for the thermal decomposition of H_2S .

Considering the affinity of vanadium oxide catalysts towards carbon containing compounds, it may be expected that the incorporation of vanadium oxide into ZnO-based sorbents might improve the retention of carbonyl sulfide, carbon disulfide and thiophene. The above results show that if a sorbent with adequate physical properties can be prepared, vanadium-containing ZnO-based sorbents will have a very high degree of H_2S removal, no active metal loss even at high temperatures and will lead to substantial elemental sulfur formation.

Therefore it was believed that zinc- and vanadium-containing sorbents warranted further investigation. It was expected that the main disadvantage of

ZnO-V₂O₅ sorbents, their low overall sulfur capacity, can be improved by replacing the inert alumina support with iron oxide. This new sorbent may be prepared by several different ways as described in the following sections.

The main objective of this investigation has been to develop an optimum sorbent from a mixture of zinc oxide-iron oxide-vanadium oxide system for hot coal gas desulfurization; to evaluate its performance by fixed-bed experiments, supported by sorbent characterization at the various reaction extents; and to compare the performance of the novel sorbent with some representative sorbents like zinc ferrite and zinc titanate.

III.B. Plan of Study

The investigation is planned so that its results can be systematically compared with those in literature and also, can be used for the design and operation of industrial equipment. To elucidate the plan of study, the work undertaken will be categorized as follows:

- i. Sorbent preparation and characterization.
- ii. Sorbent evaluation in a fixed-bed microreactor.
- iii. Characterization of the spent sorbents by AA, XRD analysis and surface area and porosity measurements.

1. Sorbent Preparation

Zn-Fe-V-O sorbents were prepared by the impregnation of V₂O₅ on crushed zinc ferrite pellets obtained from United Catalysts, Inc. This was accomplished by using the incipient wetness technique and employing aqueous ammonium metavanadate, drying the resulting solid and calcining it. The main variables studied were the concentration of V₂O₅ in the sorbent; and the temperature of calcination.

A total of 8 test sorbents were prepared. Four batches were started with 100 g zinc ferrite which were then impregnated with a sufficient amount of aqueous ammonium metavanadate to give 1, 3, 4.8, and 15 mass per cent vanadium, using the incipient wetness technique and several impregnation steps as needed since the solubility of ammonium metavanadate is about 3% by mass at 75-80 °C. These were then divided into two, one half was calcined at 600 °C and the other at 750 °C under flowing air (40 cc/min at 20 °C and 1 atm) for 4 hours, thus giving a total of 8 test sorbents designated as ZF-V01-600, ZF-V01-750, ZF-V03-600, ZF-V03-750, ZF-V04.8-600, ZF-V04.8-750, ZF-V15-600, and ZF-V15-750. In these designations the numbers following V indicate the mass percentage of vanadium in the sorbent and the last three digits indicate the calcination temperature in °C. Some sorbents which were initially calcined at 873 K were subjected to a second calcination step at an elevated temperature. The sorbents prepared by this two-step calcination method exhibit different characteristics than those of the sorbents subjected to only one calcination step. The calcined sorbent was sieved and a sample was taken from the -20 +40 mesh size range.

The mass ratio of V to Zn in these sorbents are less than that required to form a eutectic mixture of ZnO and V₂O₅ (about 1.6 g V per g of Zn). The reason for this choice is that, in practice, it is better to have as little vanadium in the sorbent as possible because of the unfavorable effects of vanadium on the sorbent capacity and downstream consumption of the fuel gas.

2. Sorbent Characterization

The fresh sorbents prepared by the methods described above were characterized by atomic absorption spectroscopy for elemental analysis; X-ray diffraction for the identification of crystalline phases; and surface area, porosity and pore

volume measurements.

The prepared sorbent samples were dissolved in HCl and analyzed by atomic absorption to determine their actual composition. The results of these measurements are presented in *Section IV.A*. These measurements have indicated that some iron has been lost during sorbent preparation; the prepared sorbents had slightly higher Zn/Fe ratios than the original zinc ferrite sorbent. A dark blue solution eluted from the reactor in the first half hour of the calcination procedure; this may be an ammonium-iron complex. Increases in Zn/Fe ratios were also observed in the used sorbents. This is discussed in *Section IV. B*.

The surface area of sorbent ZF-V01-600 was determined both by single point and multi-point BET methods. Since the results with multi-point method and the single point method were very close ($2.92 \text{ m}^2/\text{g}$ and $2.83 \text{ m}^2/\text{g}$, respectively), it was decided that the single point measurements will be sufficient for the purpose of this research. The solid densities are measured by a helium pycnometer. Porosity and pore volume measurements were done using a Quantachrome mercury porosimeter. The X-Ray diffraction analysis of the samples were done at the Geological Sciences Department of the Old Dominion University.

3. Sorbent Evaluation

The sorbents prepared by the methods explained above were evaluated with respect to their sulfidation performance by the H_2S breakthrough curves obtained in a packed-bed microreactor setup and their regenerability behavior. The setup used is shown schematically in *Figure 1*. A quartz tube of 1 cm diameter was used as the reactor; the bed temperature was measured by chromel-alumel (K-type) thermocouples placed in quartz thermowells and located at the top and bottom of the sorbent bed. The reactor was placed in a vertical electric tubular furnace

FIGURE 1. Packed-Bed Microreactor Setup

equipped with a temperature controller and operated isothermally. The packed section had a diameter of 1.5 cm and a packed height of about 2 cm; a shallow sorbent bed was used to minimize the axial temperature gradient. During the experiments the temperature difference between the top and bottom of the bed was between 2 to 8°C. Reactant gases were obtained from Air Products and used without further purification; the gas flow rates were measured by calibrated rotameters. Water was introduced into the feed stream by bubbling nitrogen through distilled water in a 3-neck flask assembly and monitoring the water temperature. Sections of the setup coming in contact with H₂S are constructed from teflon or teflon-coated stainless steel. The gas lines after the introduction of water are heated by insulated heating tapes and the temperatures on the lines are measured by K-type thermocouples connected to a multi-channel digital readout. Gas compositions were measured by a Varian 3400 gas chromatograph equipped with flame photometric (FPD) and thermal conductivity (TCD) detectors. A teflon column, 8' long x 1/8 in O.D., and a glass column, 6' long x 1/4 in O.D., both packed with Chromosil 310 (Supelco, Inc.) were used in the analyses. Gas samples could be analyzed every 3.5 minutes to provide time-resolved composition. Data acquisition and analysis were done by Varian Star Integrator data acquisition system.

The main variables for sulfidation experiments were temperature and inlet H₂O concentration. The sulfidation gas composition was chosen according to the suggestions of the technical monitor. H₂O/H₂S ratio was found to affect the H₂S uptake by vanadium oxide; a ratio of about 10 is allowable before a drastic inhibition of H₂S adsorption occurs.⁽⁷⁾ Thus, H₂O content of the sulfidation gas was varied between 7 - 20% and the feed gas composition was balanced by adjusting the N₂ content.

Standard sulfidation experiments have been performed at 873 K with a feed gas composition of 1% H_2S , 20% H_2 , 7% H_2O , and 72% N_2 . The effects of sulfidation temperature and H_2O concentration of the sulfidation gas has been studied in the subsequent experiments.

Reactor dimensions, sorbent particle size and space velocity were kept constant at values cited in the literature so as to facilitate the comparison between the sorbents of this study with those in the literature. Usually a particle size of 20/35 mesh to 60/80 mesh and a space velocity of 600 - 2000 h^{-1} have been employed in previous studies to minimize mass transfer limitations. In this study, 20/40 mesh size range for the particle size has been employed. The volumetric flowrate of the sulfidation gas was 200 cc(at 20°C and 1 atm)/min and the reactor was loaded with about 3 grams of sorbent, giving a gas hourly space velocity of 4000 per hour.

The sulfidation experiments were performed on both the novel sorbents prepared in this study, and also, on zinc ferrite and zinc titanate obtained from UCI, Inc. Each sulfidation test was followed by a regeneration test and this procedure was repeated for five cycles.

The regeneration experiments were also performed in the packed-bed microreactor set-up, explained above, on sulfided samples. The regeneration gas was composed of O_2 and N_2 . Main operating variables are temperature, oxygen concentration in the feed gas (1 - 4% (mol)) and H_2O concentration in the feed gas (0 - 50% (mol)). H_2O in the gas reduces elemental S formation. O_2 content of the gas affects sulfate formation, higher values resulting from higher O_2 contents. However, in this study oxygen concentration of the regeneration gas was not varied; and no water is introduced into the regeneration gas to prevent reduction in the elemental sulfur formation. The particle size and bed

dimensions were kept the same as the values used during sulfidation; the space velocity was kept at 2000 per hour. The exit gas from regeneration runs was analyzed for H_2S and SO_2 by G. C. The sulfate formation was quantified by measuring the SO_2 released from sulfate when the O_2 in the regeneration gas is replaced by N_2 . Total H_2S and SO_2 released during regeneration was determined by absorbing the exit gases in 1 N iodine solution and titrating the resulting solution by 0.1 N sodium thiosulfate solution.⁽⁷⁾ Sulfur formation could not be quantified accurately; approximate values were obtained by scraping the sulfur formed at the reactor exit and weighing it.

Standard regeneration experiments have been performed at 973 K with a gas composition of 10% air and 90% N_2 . Effect of regeneration temperature was studied subsequently.

There is some controversy in literature on whether H_2S forms a sulfide with vanadium oxide or is chemisorbed on it.^(7, 28, 29) To clarify this point, some additional sulfidation/regeneration runs were performed where regeneration was preceded by N_2 purge at 700°C to desorb any reversibly chemisorbed H_2S .

The standard regeneration procedure was conducted as follows: After the sulfidation experiment, the reactor temperature was raised to 973 K under flowing nitrogen to desorb any H_2S chemisorbed on the sorbent; this procedure was terminated when the H_2S levels in the off-gas fell to about 20 ppmv at which time the regeneration gas was switched to the (10% air + 90% N_2) mixture at 973 K. This was continued until the SO_2 content of the off-gas was reduced to approximately 20 ppmv at which time air was turned off. The sorbent was treated with nitrogen at 973 K to dissociate any sulfate that might have been formed on the sorbent. This procedure was continued until the SO_2 content of the off-gas was reduced below 20 ppmv.

The structural and chemical characterization of the sulfided and regenerated sorbents was carried out on selected samples by the methods cited in *Section III.B.2*. Zinc loss was determined by atomic absorption measurements.

IV. RESULTS AND DISCUSSION

The experimental results are presented and discussed in this section.

IV. A. Sorbent Properties

The results obtained from the characterization of the fresh sorbents are presented in *Tables 2-5*.

TABLE 2. NOMINAL AND ACTUAL COMPOSITIONS OF FRESH SORBENTS

Sorbent	Nominal Composition, mass %	Actual Composition, mass %
ZF	Zn: 25.8; Fe: 44.0	Zn: 25.8; Fe: 44.0
ZF-V01-600	Zn: 25.3; Fe: 43.2; V: 1.00	Zn: 25.6; Fe: 41.9; V: 0.84
ZF-V01-750	Zn: 25.2; Fe: 43.2; V: 1.00	Zn: 26.2; Fe: 42.1; V: 0.77
ZF-V03-600	Zn: 24.4; Fe: 41.7; V: 3.00	Zn: 23.9; Fe: 40.5; V: 2.90
ZF-V03-750	Zn: 24.4; Fe: 41.7; V: 3.00	Zn: 24.1; Fe: 39.4; V: 2.56
ZF-V4.8-600	Zn: 23.6; Fe: 40.3; V: 4.79	Zn: 23.1; Fe: 37.8; V: 3.99
ZF-V4.8-750	Zn: 23.6; Fe: 40.3; V: 4.79	Zn: 25.5; Fe: 40.7; V: 3.96
ZF-V15-600	Zn: 19.3; Fe: 32.9; V: 15.0	Zn: 22.0; Fe: 31.7; V: 15.3

Table 2 tabulates the results obtained from the atomic absorption measurements and compares the actual composition with the nominal one. All the fresh sorbents had slightly higher Zn/Fe ratios than the original zinc ferrite sorbent(*Table 3*).

The loss of iron appears to increase with increasing calcination temperature and vanadium content. The vanadium mass percentage varies from 0.77 to 15.0. These give Zn/V ratios which are much larger than those used by Flytzani-Stephanopoulos et al.⁷ which were close to the eutectic composition.

TABLE 3. ZN/FE RATIO IN THE SORBENTS

Sorbent	Nominal Zn/Fe Ratio	Actual Zn/Fe Ratio
ZF-V01-600	0.585	0.61
ZF-V01-750	0.585	0.62
ZF-V03-600	0.585	0.59
ZF-V03-750	0.585	0.61
ZF-V4.8-600	0.585	0.61
ZF-V4.8-750	0.585	0.63
ZF-V15-600	0.585	0.69

The composition of fresh sorbents and the crystalline phases determined by X-Ray diffraction measurements are given in Table 4. Samples containing less than 4% vanadium did not show any vanadium compound. The main component in these samples is the synthetic Franklinite (ZnFe_2O_4). Fresh ZF-V4.8-600 sorbent contains ZnFeVO_4 and synthetic Magnetite (Fe_3O_4) in addition to the synthetic Franklinite. Sorbent ZF-V4.8-750 does not contain Magnetite but some V_2O_5 is possibly present. Sorbent ZF-V15-600 contains ZnFe_2O_4 and ZnFeVO_4 . In addition to these, sorbent ZF-V15-750 also appears to contain some Fe_2O_3 .

The surface areas of the fresh sorbents that are calcined at 600°C are almost independent of the vanadium percentage up to about 5% vanadium content and are slightly lower than that of the zinc ferrite (Table 5). The surface area of the

sorbent containing 15% vanadium is about 25% less than the sorbents with lower vanadium contents. On the other hand, the sorbents calcined at 750°C have considerably lower surface areas which decrease with the vanadium content.

TABLE 4. SORBENT COMPOSITIONS

Sorbent	Zn:Fe:V Ratio (mass)	Major Crystalline Phases Present
ZF-V01-600	25.6:41.9:0.84	
ZF-V01-750	26.2:42.1:0.77	
ZF-V03-600	23.9:40.5:2.90	ZnFe ₂ O ₄
ZF-V03-750	24.1:39.4:2.56	ZnFe ₂ O ₄
ZF-V4.8-600	23.1:37.8:3.99	ZnFe ₂ O ₄ , ZnFeVO ₄
ZF-V4.8-750	25.5:40.7:3.96	ZnFe ₂ O ₄ , V ₂ O ₅ , ZnFeVO ₄
ZF-V15-600	22.0:31.7:15.3	ZnFe ₂ O ₄ , ZnFeVO ₄
ZF-V15-750		ZnFe ₂ O ₄ , ZnFeVO ₄ , Fe ₂ O ₃
Zinc Ferrite	25.8:44.0:0.0	

The results of the porosity measurements on fresh sorbents show that the porosities of the prepared sorbents decrease with increasing vanadium content and calcination temperature (Table 5). The corresponding increase in the mean pore diameter indicate that small pores are lost by sintering at high temperature calcinations and that some small pores are plugged by V₂O₅. An interesting observation is the different sorbent properties obtained by two step calcination (calcination at 873 K followed by a second calcination step at a higher temperature). It can be seen from Table 5 that initial calcination at a lower temperature (873 K) imparts considerable stability against sintering at high

temperatures.

It was also observed that the sorbents calcined at the lower temperature are lighter in color, have a lower bulk density, and were more difficult to dissolve in HCl when preparing samples for atomic absorption analysis.

TABLE 5. PHYSICAL CHARACTERISTICS OF SORBENTS (* indicates two step calcination first at 600°C and then at the indicated temperature)

Sorbent	Helium Density (g/cm ³)	Surface Area (m ² /g)	Intruded Hg Volm. (cm ³ /g)	Mean Pore Rad. (μm)	Porosity (%)
ZF-V01-600	5.384	2.854			
ZF-V01-750	5.470	1.032			
ZF-V03-600	5.357	2.828			
ZF-V03-750	5.240	1.006			
ZF-V4.8-600	5.149	2.960	0.2328	0.1715	0.5452
ZF-V4.8-650*		2.968	0.2342	0.1743	0.5467
ZF-V4.8-700*		2.482			
ZF V4.8-750*		1.656			
ZF-V4.8-750	5.219	0.8271	0.0849	0.2055	0.3070
ZF-V15-600		1.934	0.1596	0.007 and 0.18	0.4188
ZF-V15-750		0.488			
Zinc Ferrite	5.140	3.316	0.2416	0.1583	0.5635

IV.B. Characterization of Used Sorbents

Used sorbents were characterized by the same methods used for fresh sorbents. The results are presented in *Tables 6 and 7*.

TABLE 6. COMPARISON OF THE COMPOSITIONS OF USED AND FRESH SORBENTS

Sorbent	Condition	Zn:Fe:V Ratio	Zn/Fe Ratio	Major Phases Present
ZF-V01-600	Fresh	28.8:43.5: 1.1	0.663	
ZF-V01-600	Reg. after 5th cycle $T_s=873$ K, $y_{H_2O}=0.07$	30.2:40.1: 2.9	0.754	
ZF-V4.8-600	Fresh	27.5:40.3: 4.5	0.682	ZnFeVO ₄ , ZnFe ₂ O ₄ , Magnetite, syn.
ZF-V4.8-600	Sulf. after 5th cycle $T_s=923$ K, $y_{H_2O}=0.07$	27.9:34.2: 4.7	0.816	Franklinite, syn., Magnetite, syn., V ₂ O ₅ , ZnFeVO ₄ , Fe ₃ S ₄ , Pyrrhotite
ZF-V4.8-600	Reg. after 5th cycle $T_s=873$ K, $y_{H_2O}=0.07$	27.8:39.0: 5.4	0.713	Franklinite, syn., V ₂ O ₅
ZF-V4.8-600	Reg. after 4th cycle $T_s=923$ K (cycles 1-3) 973 K (cyc 4) $y_{H_2O}=0.07$	36.0:30.7: 6.3	1.173	
ZF-V4.8-650	Reg. after 5th cycle $T_s=923$ K, $y_{H_2O}=0.07$	30.3:36.9: 5.3	0.821	
ZF-V4.8-650	Reg. after 5th cycle $T_s=923$ K, $y_{H_2O}=0.20$	29.1:38.3: 5.1	0.760	
ZF-V15-600	Fresh	22.0:31.7: 15.3	0.694	ZnFe ₂ O ₄ , ZnFeVO ₄
ZF-V15-600	Reg. after 5th cycle $T_s=923$ K, $y_{H_2O}=0.07$	29.3:21.5: 18.4	1.363	

Table 6 shows that all the used sorbents have higher Zn/Fe ratios than the fresh sorbents. Highest increases in the Zn/Fe ratios are seen at high sulfidation temperatures and in sorbents with high vanadium content. This observation is discussed in more detail in Section IV.C.2. The major crystalline phases observed in regenerated sorbents were generally the same as those observed

TABLE 7. COMPARISON OF THE PHYSICAL CHARACTERISTICS OF FRESH AND USED SORBENTS

Sorbent	Condition	Surf. Area (m ² /g)	Intrud. Volume (cm ³ /g)	Mean Pore Rad. (μm)	Porosity %
ZF-V01-600	Fresh	2.64			
ZF-V01-600	Reg. after 5th cycle T _s =873 K, y _{H2O} =0.07	0.655	0.1112	0.4539	0.3748
ZF-V4.8-600	Fresh	2.96	0.2328	0.1715	0.5452
ZF-V4.8-600	Sulf. after 3rd cycle T _s =873 K, y _{H2O} =0.07	2.47			
ZF-V4.8-600	Sulf. after 5th cycle T _s =873 K, y _{H2O} =0.07	1.72			
ZF-V4.8-600	Reg. after 5th cycle T _s =873 K, y _{H2O} =0.07	1.49	0.1731	0.2400	0.4713
ZF-V4.8-600	Reg. after 4th cycle T _s =923 K for cycles 1-3, 973 K for cycle 4, y _{H2O} =0.07	2.14			
ZF-V4.8-650	Fresh	2.968	0.2342	0.1743	0.5467
ZF-V4.8-650	Reg. after 5th cycle T _s =923 K, y _{H2O} =0.07	1.59	0.1545	0.2680	0.4431
ZF-V4.8-650	Reg. after 5th cycle T _s =923 K, y _{H2O} =0.20	1.35	0.1518	0.2721	0.4387
ZF-V15-600	Fresh	1.93	0.1596	0.007 & 0.18	0.4188
ZF-V15-600	Reg. after 5th cycle T _s =923 K, y _{H2O} =0.07	1.17	0.1540	0.2100	0.4101
ZF	Fresh	3.56	0.2416	0.1583	0.5635
ZF	Reg. after 5th cycle T _s =923 K, y _{H2O} =0.07	5.32	0.1582	0.02414	0.4581

in fresh sorbents. The only difference was that regenerated sorbents contained some V_2O_5 , while in fresh sorbents vanadium occurred only as $ZnFeVO_4$. The X-Ray diffraction analysis of a sulfided sample showed only pyrrhotites and Fe_7S_{10} as the sulfur containing crystals. No evidence of ZnS could be obtained indicating that sulfur compounds of zinc did not form crystalline phases during sulfidation. All sorbents containing vanadium undergo structural changes upon cycling. They lose surface area and pore volume through the loss of smaller pores. This is indicated by the increase in mean pore radius. Sorbents with high (15%) vanadium content retain their original porosity although the mean pore size increases significantly. Table 7 shows that the bimodal pore structure of fresh ZF-V15-600 sorbent is lost upon cycling. The mean pore size of the sorbent regenerated after 5 sulfidation cycles is larger than the mean pore size of the group of larger pores in the fresh sorbent. In contrast to the vanadium containing sorbents, the surface area of the original zinc ferrite sorbent increases upon regeneration. This is due to a drastic change in the mean pore size of the sorbent. The observation that the pore sizes in the zinc ferrite sorbent decrease considerably when the sorbent is subjected to repeated sulfidation-regeneration cycles, while the pore sizes of the vanadium-containing sorbents increase mildly, is difficult to explain with the available data. It might be due to the presence of different compounds with different physical properties. The physical characteristics of the sorbents calcined at 923 K by the two-step method are very similar to those of the sorbent calcined at 873 K.

IV.C. Fixed-Bed Reactor Tests

1. Standard Sulfidation Experiments

One sorbent that was calcined at 750°C (ZF-V01-750); four sorbents calcined

at 600°C (ZF-01-600, ZF-V03-600, ZF-V4.8-600, and ZF-V15-600); and zinc ferrite and zinc titanate were tested in the fixed-bed microreactor setup under standard sulfidation and regeneration conditions. As expected sorbent ZF-V01-750 showed a considerably lower sulfur capture capacity and was only tested for two cycles. The sorbents prepared by low temperature calcination and the original zinc ferrite sorbent were tested over five sulfidation-regeneration cycles. The breakthrough curves for these tests are shown in *Figures 2 - 6* and the breakthrough curves for different sorbents are compared for each of the five cycles in *Figures 7 - 11*. These figures show the H₂S breakthrough profiles as a function of a normalized time for each of these sorbents. The normalized time, t/t' , is the ratio of the actual run time, t , over the theoretical time, t' , that will be required for the complete conversion of ZnO and FeO to ZnS and FeS. When the final products in the sulfided sorbent are the stoichiometric ZnO and FeO, t/t' gives the fractional sorbent conversion. If another stoichiometry prevails, t/t' gives an approximate value for the sorbent conversion. In case of the zinc ferrite sorbents promoted by vanadium, it is assumed that vanadium does not form a sulfide, but that it chemisorbs hydrogen sulfide. Thus, t/t' for such sorbents gives an approximate value for sorbent conversion. The shapes of the breakthrough curves typically reflect the insignificance of diffusion limitations. All sorbents produced prebreakthrough H₂S levels below the detection limit of the fpd for 2.5 ml gas sample. Hydrogen sulfide levels over 1 ppmv were clearly detectable but 1 ppmv peak was difficult to separate from noise. These results indicate that the desulfurization levels obtained were below the equilibrium levels for zinc oxide. *Tables 8-11* summarize the results in terms of conversion at breakthrough and sorbent sulfur capacity.

Breakthrough Curves for ZF-V01-600

Inlet H₂S=1%; P=1 atm; T=873K; H₂O=7%

FIGURE 2. t₀ = 418 min

Breakthrough Curves for ZF-V03-600

Inlet H₂S=1%; P=1atm; T=873K; H₂O=7%

FIGURE 3. t₀ = 393 min

Breakthrough Curves for ZF-V4.8-600

Inlet H₂S=1%; P=1atm; T=873K; H₂O=7%

FIGURE 4. t* = 381 min

Breakthrough Curves for ZF-V15-600

Inlet H₂S=1%; P=1 atm; T=873K; H₂O=7%

FIGURE 5. t₀ = 314 min

Breakthrough Curves for Zinc Ferrite

Inlet H₂S=1%; P=1 atm; T=873K; H₂O=7%

FIGURE 6. t₀ = 427 min

Breakthrough Curves for Cycle 1

Inlet H₂S=1%; P=1 atm; T=873K; H₂O=7%

FIGURE 7.

Breakthrough Curves for Cycle 2

Inlet H₂S=1%; P=1 atm; T=873K; H₂O=7%

FIGURE 8.

Breakthrough Curves for Cycle 3

Inlet H₂S=1%; P=1atm; T=873K; H₂O=7%

FIGURE 9.

Breakthrough Curves for Cycle 4

Inlet H₂S=1%; P=1 atm; T=873K; H₂O=7%

FIGURE 10.

Breakthrough Curves for Cycle 5

Inlet H₂S=1%; P=1 atm; T=873K; H₂O=7%

FIGURE 11.

TABLE 8. CONVERSION AND SORBENT CAPACITY AT A BREAKTHROUGH OF 10 ppm H₂S FOR CYCLE 1.

Sorbent	Conversion, %	Sorbent Capacity, g S/g sorbent
Sulfidation Temperature = 873 K H ₂ O = 7%		
ZF-V01-600	87.3	0.319
ZF-V03-600	84.4	0.294
ZF-V4.8-600	74.0	0.244
ZF-V15-600	53.3	0.148
Zinc Ferrite	84.0	0.318
Zinc Titanate	66.2	0.157
Sulfidation Temperature = 923 K H ₂ O = 7%		
ZF-V4.8-600	85.3	0.281
ZF-V15-600	34.0	0.0944
Zinc Ferrite	58.4	0.221
ZF-V4.8-650	82.0	0.271
ZF-V15-650	35.9	0.100

Although sorbent ZF-V01-600 showed very good performance in the first cycle, its performance deteriorates rapidly as the cycle number increases. The breakthrough curves for the second and third cycles indicate an increasing diffusion limitation. Apparently loss of pores and surface area is taking place. Table 7 shows that the sorbent surface area decreases from 2.64 m²/g when fresh to 0.655 m²/g after the fifth cycle.

Sorbent ZF-V03-600 shows a superior performance in the first four cycles. Its conversion at breakthrough is about the same as that of zinc ferrite for the first cycle, but it has higher conversions than zinc ferrite in second

through fourth cycles. Sulfur capture capacity of ZF-V03-600 is slightly below that of zinc ferrite in the first cycle, but its capacity is higher than that of zinc ferrite in the second through fourth cycles and then about the same in the fifth cycle.

TABLE 9. CONVERSION AND SORBENT CAPACITY AT A BREAKTHROUGH OF 50 ppm H₂S FOR CYCLE 1

Sorbent	Conversion, %	Sorbent Capacity, g S/g sorbent
Sulfidation Temperature = 873 K H ₂ O = 7%		
ZF-V01-600	88.5	0.324
ZF-V03-600	91.7	0.320
ZF-V4.8-600	77.8	0.256
ZF-V15-600	56.2	0.156
Zinc Ferrite	85.0	0.322
Zinc Titanate	69.3	0.165
Sulfidation Temperature = 923 K H ₂ O = 7%		
ZF-V4.8-600	87.3	0.288
ZF-V15-600	35.5	0.099
Zinc Ferrite	61.7	0.234
ZF-V4.8-650	83.9	0.277
ZF-V15-650	37.8	0.105

Sorbent ZF-V4.8-600 shows a similar behavior but has somewhat lower conversions until the fourth cycle. Its superiority seems to be in the relatively stable behavior it exhibits for cycles 2 through 5. In the fifth cycle it shows superior performance. Sorbent ZF-V15-600 shows very stable

performance but consistently lower conversions. The low conversion is the result of low initial surface area and porosity due to the plugging of pores by vanadium oxide.

TABLE 10. CONVERSION AND SORBENT CAPACITY AT A BREAKTHROUGH OF 10 ppm H₂S FOR CYCLE 5

Sorbent	Conversion, %	Sorbent Capacity, g S/g sorbent
Sulfidation Temperature = 873 K H ₂ O = 7%		
ZF-V01-600	36.3	0.133
ZF-V03-600	57.2	0.200
ZF-V4.8-600	68.9	0.227
ZF-V15-600	53.7	0.149
Zinc Ferrite	57.3	0.217
Sulfidation Temperature = 923 K H ₂ O = 7%		
ZF-V4.8-600	38.4	0.127
ZF-V15-600	37.7	0.105
Zinc Ferrite	37.6	0.143
ZF-V4.8-650	58.6	0.193

The sulfur capture capacity of the vanadium-promoted zinc ferrite sorbents is considerably higher than the recommended zinc titanate sorbents (*Figure 7, and Tables 8 and 10*). This suggests that the addition of vanadium provides additional capacity by chemisorbing H₂S. This was confirmed by the H₂S desorption runs discussed in *Section IV.C.2*.

TABLE 11. CONVERSION AND SORBENT CAPACITY AT A BREAKTHROUGH OF 50 ppm H₂S FOR CYCLE 5

Sorbent	Conversion, %	Sorbent Capacity, g S/g sorbent
Sulfidation Temperature = 923 K H ₂ O = 7%		
ZF-V01-600	38.3	0.140
ZF-V03-600	60.0	0.210
ZF-V4.8-600	72.0	0.237
ZF-V15-600	54.9	0.152
Zinc Ferrite	60.7	0.230
Sulfidation Temperature = 923 K H ₂ O = 7%		
ZF-V4.8-600	39.3	0.130
ZF-V15-600	38.7	0.107
Zinc Ferrite	39.1	0.148
ZF-V4.8-650	60.0	0.198

2. Standard Regeneration Experiments

A standard regeneration procedure (*Section III.B.3*) was used between the standard sulfidation experiments discussed in *Section IV.A.1*. The results for zinc ferrite and ZF-V4.8-600 are presented in *Figures 12 and 13*. The regeneration curves for these sorbents are similar except that the amount of H₂S observed during the regeneration of ZF-V4.8-600 is about an order of magnitude larger than that observed with zinc ferrite. This indicates that the desorption of chemisorbed H₂S continues even after air is turned on.

To check the amount of residual sulfate, third regeneration cycles for ZF-V03-600 and zinc ferrite sorbent, and fourth regeneration cycle for ZF-V15-600 were followed by nitrogen purge at 973 K (*Figure 14*). For ZF-V03-600 and ZF-V15-

REGENERATION OF ZF

T_{reg}=973 K; Reg. gas=(N₂+Air)

Figure 12. Sulfidation Conditions:
H₂S=1%; H₂O=7%; T=873K; P=1 atm; cycle1
Y1= SO₂ in exit gas; Y2= H₂S in exit gas

Regeneration of ZF-V4.8-600

T_{reg}=973 K; Reg.gas=(N₂+Ar)

Figure 13. Sulfidation Conditions:
H₂S=1%; H₂O=7%; T=873K; P=1 atm; cycle2
Y1= SO₂ in exit gas; Y2= H₂S in exit gas

Effect of V Content on Sulfate Formation

Treg=973K; Reg. gas= N2

FIGURE 14. Sulfidation Conditions:
H2S=1%; H2O=7%; T=873K; P=1 atm

600, very small amounts of SO_2 was observed, while for zinc ferrite the SO_2 in the nitrogen purge off-gas is about six times larger. The fact that some of the residual sulfate was decomposed, might have contributed to the improvement in the sulfidation behavior of zinc ferrite in the subsequent cycles.

Figures 15, 16, and 17 show the effects of process variables on sulfate formation. These figures show that the regeneration temperature is the most important variable affecting the sulfate formation. Figure 15 shows that sulfate formation becomes significant for vanadium-containing sorbents at regeneration temperatures below 973 K. The sulfidation temperature does not seem to have an appreciable effect on the sulfate formation. Sulfate formation shows the same trend upon regeneration after sulfidation at 923K: No sulfate is formed on vanadium-promoted sorbents, while appreciable sulfate formation is detected on zinc ferrite. Figure 16 shows that the decomposition of the sulfate becomes slower at higher sulfidation temperatures in the case of zinc ferrite probably due to changes in the sorbent structure. Calcination temperature and the H_2O content of the fuel gas do not affect the sulfate formation significantly.

Nitrogen purge used before oxidative regeneration indicated that vanadium containing sorbents chemisorbed hydrogen sulfide. Figure 18 shows the H_2S desorption for a vanadium-containing sorbent during nitrogen purge. Nitrogen purge before the regeneration of the zinc ferrite sorbent did not produce any H_2S . Quantification of this chemisorbed hydrogen sulfide was attempted by passing the gasses through a trap containing iodine solution and titrating the unreacted iodine with sodium thiosulfate. Unfortunately this procedure gave inconsistent results and no reliable quantification of the chemisorbed H_2S could be obtained. Loss of water by evaporation was considered to be a possible cause but calculations showed that it did not explain the observed behavior.

Effect of Treg on Sulfate Formation

ZF-V4.8-650

FIGURE 15. Sulfidation Conditions:
H2S=1%; H2O=7%; T=923K; P=1 atm

Effect of Tsulf on Sulfate Formation

FIGURE 16.

Effect of Tcalc on Sulfate Formation

ZF-V4.8; Tsulf=923 K; Treg=973 K

FIGURE 17.

Regeneration of ZF-V03-600

Treg=973K; Reg. gas:N2

FIGURE 18. Sulfidation Conditions:
H2S=1%; H2O=7%; T=873K; P=1 atm; cycle1
Y1=SO2 in exit gas; Y2=H2S in exit gas

Although it could not be quantified accurately, significant amounts of elemental sulfur were collected after the regeneration of vanadium-containing sorbents. Elemental sulfur was collected on the reactor wall near the exit and in the fittings and on the thermowell. Collection and quantification of this sulfur was attempted and the available results are shown in *Table 12*. It should be noted that the values in the table are probably much lower than the actual conversion to elemental sulfur. For more meaningful results, modification of the reactor exit is necessary. This may be attempted in a subsequent study.

TABLE 12. ELEMENTAL SULFUR FORMATION

Sorbent	Condition	Sorb. Cap. g S/g sorb.	S Formed g S/g sorb.	% of tot. sulfur as S
ZF-V03-600	Reg. after 2nd cycle $T_s=923\text{K}, y_{\text{H}_2\text{O}}=0.07$	0.320	0.0315	9.8
ZF-V4.8-600	Reg. after 4th cycle $T_s=923\text{K}$ cyc. 1-3, 973K cyc. 4, $y_{\text{H}_2\text{O}}=0.07$	0.107	0.0154	14.4
ZF-V4.8-650	Reg. after 5th cycle $T_s=923\text{K}, y_{\text{H}_2\text{O}}=0.07$	0.185	0.0146	7.9

3. Active Metal Loss From Sorbents

Quantification of zinc loss during 5 sulfidation-regeneration cycles was done by comparing the atomic absorption analysis for the fresh and regenerated sorbents. Since no iron loss was expected, comparison of the zinc/iron ratios of the fresh and regenerated sorbents should give the fraction of zinc lost during 5 cycles of operation. This was expected to give more accurate results than extracting the deposits at the reactor exit. The results of these analyses are shown in *Table 13*.

TABLE 13. ATOMIC ABSORPTION ANALYSIS OF SORBENTS

Sorbent	Condition	Zn:Fe:V mass %	Zn/Fe wt fraction	Zn/V wt fraction
ZF-V01-600	Fresh	30.30:37.14:5.15	0.663	27.32
ZF-V01-600	Reg'd, 5th cycle $T_s=823$ K, $y_{H_2O}=0.07$	30.21:40.06:2.87	0.754	10.53
ZF-V4.8-600	Fresh	27.50:40.34:4.54	0.682	6.062
ZF-V4.8-600	Reg'd, 5th cycle $T_s=873$ K, $y_{H_2O}=0.07$	27.83:39.01:5.38	0.713	5.176
ZF-V4.8-600	Sulf'd, 5th cycle $T_s=873$ K, $y_{H_2O}=0.07$	27.86:34.15:4.73	0.816	5.887
ZF-V4.8-600	Reg'd, 5th cycle $T_s=923$ K, $y_{H_2O}=0.07$	36.02:30.71:6.30	1.173	5.714
ZF-V4.8-650	Reg'd, 5th cycle $T_s=923$ K, $y_{H_2O}=0.07$	30.32:36.94:5.29	0.821	5.728
ZF-V4.8-650	Reg'd, 5th cycle $T_s=923$ K, $y_{H_2O}=0.20$	29.11:38.28:5.06	0.760	5.750
ZF-V15-600	Fresh	21.98:31.69:15.3	0.694	1.437
ZF-V15-600	Reg'd, 5th cycle $T_s=923$ K, $y_{H_2O}=0.07$	29.28:21.48:18.4	1.363	1.592

The results presented in *Table 13* are rather unexpected. The Zn/Fe ratios increase upon cycling under every condition. Since the trend is the same for every case, the inaccuracies in the atomic absorption measurements, which were made by an established environmental laboratory, were ruled out as an explanation. To gain more insight, the fractional decreases in zinc and iron after 5 cycles of sulfidation and regeneration, the corresponding decrease to be expected in the sulfur capture capacity, and the actual decrease in the sulfur capacity calculated from the conversions obtained in microreactor studies are

presented in *Table 14*. The last column of the table contains the ratios of final surface areas to initial surface areas.

TABLE 14. DECREASE IN SORBENT CAPACITY FROM ZINC AND IRON LOSSES COMPARED TO THOSE CALCULATED FROM CONVERSION DATA

Sorbent	Zn_s/Zn_f	Fe_s/Fe_f	SorbCap _s /SorbCap _i from loss	SorbCap _s /SorbCap _i from conv	Area _s / Area _f
ZF-V01-600	0.385	0.339	0.356	0.416	0.230
ZF-V4.8-600	0.854	0.816	0.830	0.930	0.503
ZF-V4.8-650	0.945	0.785	0.843	0.791	0.536
ZF-V15-600	1.00	0.509	0.692	1.00	0.605

We observe from *Table 14* that iron losses are more severe than zinc losses, the decrease in sorbent capacity is closely related to zinc losses. The loss of surface area is also expected to affect the loss of sulfur capture capacity and these two effects cannot be isolated using the available data. The observed iron losses cannot be explained at this point. The observation that iron is lost during cycling needs to be confirmed by additional analyses. Another important observation is that zinc losses decrease with increasing vanadium content of the sorbent. In fact, the sorbent containing 15 wt % vanadium does not experience any zinc loss and its sulfur capacity does not decrease upon cycling. If this sorbent can be manufactured with modified pore size and structure, it will be a very promising sorbent for high temperature desulfurization.

4. Effect of Temperature on Sulfidation

Figures 19 - 21 show the results of the sulfidation experiments performed at

Breakthrough Curves for ZF-V4.8-600

Inlet H₂S=1%; P=1 atm; T=923K; H₂O=7%

FIGURE 19. t₀ = 378 min

Breakthrough Curves for ZF-V15-600

Inlet H₂S=1%; P=1 atm; T=923K; H₂O=7%

FIGURE 20. t=314 min

Breakthrough Curves for ZF

Inlet H₂S=1%; P=1 atm; T=923K; H₂O=7%

FIGURE 21. t=463.1min

923 K with the same feed gas composition used for the standard sulfidation runs; the sorbents were regenerated between cycles at the standard regeneration conditions. Conversions and sulfur capture capacities of the sorbents for 923 K sulfidation were given in *Tables 8 - 11* together with the results for the 873 K sulfidations.

Increase of sulfidation temperature from 873K to 923K increased the conversion in the first cycle of sulfidation of ZF-V4.8-600. In the subsequent cycles, conversion dropped continuously. This behavior may be due to active metal loss by vaporization or surface area loss due to sintering. An investigation of *Tables 6 and 7* indicate that the loss of active metal appears to play a more significant role. A replicate experiment has been performed to check the experimental reproducibility on the sulfidation of ZF-V4.8-600 at 923 K: Since the reproducibility was very good, sulfidation was carried out through 3 cycles; fourth cycle was performed at 973K (*Figure 22*). This latter cycle is also superimposed on *Figure 19* as 'Cycle 4R'. The sharp drop in conversion at 973 K may be mainly due to active metal loss.

ZF-V15-600 shows the same behavior as ZF-V4.8-600 at higher sulfidation temperature, that is, the conversion is consistently lower at each cycle. The interesting behavior of this sorbent is that the range of drop in the conversion is narrower than the other sorbents (*Figure 20*).

Zinc ferrite (*Figure 21*) shows behavior similar to those of the sorbents promoted by vanadium. The fifth cycle conversion is very close to that of ZF-V4.8-600, unlike the superior performance shown by the promoted sorbent at 873 K. This is mainly due to the fact that the adsorption of H_2S on vanadium at higher temperatures is expected to be lower.

Figure 22 presents the comparison of the performance of different sorbents

Effect of Temperature on Sulfidation

Inlet H₂S=1%; P=1 atm; H₂O=7%; Cycle 4

FIGURE 22. Calcination temperature=873K

at Cycle 4. Similar, significant decreases in sorbent conversions can be observed from this figure for all sorbents including zinc ferrite.

5 . Effect of Calcination Temperature on Sulfidation

The sorbents calcined at 873K have been further calcined under air for five hours at 923K to observe the effect of calcination temperature. These results are presented on *Figures 23 and 24*. *Figure 23* shows the behavior of ZF-V4.8-650' and ZF-V15-650' for sulfidation at 923K at cycle 1, also comparing with ZF-V4.8-600 and ZF-V15-600: There is no effect of calcination temperature in this temperature range on sulfidation behavior.

Figure 24 shows four cycles of sulfidation of ZF-V4.8-650' at 923K. Since no effect of calcination temperature was observed for cycle 1, it was decided to regenerate the sorbent at 923K which will be beneficial for industrial use. This decision was based on the fact that no sulfate formation was observed on the vanadium-promoted sorbents at 973K. However, regeneration at 923 K caused excessive sulfate formation, which may explain the sharp drop in the conversion at the second cycle. Therefore, subsequent regenerations were performed at 973K. This resulted in an increase in the stability of sorbent performance, however the conversion levels are still low, slightly higher than those observed for ZF-V4.8-600. The excellent stability of the sorbent for cycles 2-5 may be attributed to the structural stability of the sorbents activated by a two-step calcination technique which was discussed in *Section IV.B*.

A series of runs were made to compare the performances of sorbents prepared by single-step and two-step calcination. The results are presented for cycles 1 through 4 in *Figures 25 - 28*. These figures show that the sorbents calcined at 923 and 973 K by two-step calcination exhibit high conversions. All sorbents

Effect of Tcalc on Sulfidation

Inlet H₂S=1%; P=1 atm; T=923K; H₂O=7%

Cycle 1

FIGURE 23

Breakthrough Curves for ZF-V4.8-650

Inlet H₂S=1%; P=1 atm; T=923K; H₂O=7%

FIGURE 24. t=372 min
(two-step calcination)

Effect of Tcalc on Sulfidation

Inlet H₂S=1%; P=1 atm; T=923 K; H₂O=20%
ZF-V4.8

Figure 25. Cycle 1

Effect of Tcalc on Sulfidation INLET H₂S=1%; P=1 atm; T=923 K; H₂O=20% ZF-V4.8

FIGURE 26. Cycle 2

Effect of Tcalc on Sulfidation INLET H2S=1%; P=1 atm; T=923 K; H2O=20% ZF-V4.8

FIGURE 27. Cycle 3

Effect of Tcalc on Sulfidation Inlet H2S=1%; P=1 atm; T=923 K; H2O=20% ZF-V4.8

FIGURE 28. Cycle 4

have relatively stable performance throughout the 4 cycles. The most interesting observation is the behavior of sorbents calcined at 1023 K by one and two step calcination. The sorbent which was initially calcined at 1023 K in a single step showed much lower conversions than the sorbent first calcined at 873 K and then at 1023 K in two steps. This may be attributed to the structural stability imparted to the sorbent as a result of the initial low temperature calcination step.

6. Effect of the Partial Pressure of Water on Sulfidation

To test the effect of fuel gas water partial pressure on the performance of the sorbents, some selected sorbents were tested for several cycles using a simulated fuel gas containing 20 % water vapor. Individual breakthrough curves for vanadium-promoted sorbents ZF-V4.8-650', ZF-V4.8-700', ZF-V4.8-750', ZF-V15-650', all prepared using two-step calcination, ZF-4.8-750 prepared using one-step calcination, and commercial zinc ferrite and zinc titanate sorbents are given in *Figures 29 - 35* and the performances of these sorbents were compared at each cycle in *Figures 36 - 39*. Sorbents ZF-V15-650' (two-step calcination), ZF-V4.8-750 (one-step calcination) and zinc titanate show very good stability. In fact, their performance improve with cycling. The conversion of ZF-V4.8-750 appears to approach that of ZF-V4.8-750' as the number of cycles increase. Other sorbents experience a deterioration in performance upon cycling.

The zinc titanate sorbent exhibits the best conversion behavior. This performance is very similar to that during sulfidation with lower water content in the fuel gas. *Tables 15 - 18* show that because of the very high conversions obtained with this sorbent, its sulfur capture capacity after the fifth cycle is the highest for sulfidations at 923 K with a gas containing 20 % water vapor.

Breakthrough Curves for ZF-V4.8-650

Inlet H₂S=1%; P=1 atm; T=923K; H₂O=20%

FIGURE 29. t=376 min
(two-step calculation)

Breakthrough Curves for ZF-V4.8-700

Inlet H₂S=1%; P=1 atm; T=923K; H₂O=20%

FIGURE 30. t=380 min
(two-step calculation)

Breakthrough Curves for ZF-V4.8-750

Inlet H₂S=1%; P=1 atm; T=923K; H₂O=20%

FIGURE 31. $t_0 = 372$ min
(two-step calcination)

Breakthrough Curves for ZF-V15-650

Inlet H₂S=1%; P=1 atm; T=923K; H₂O=20%

FIGURE 32. $t^*=316$ min
(two-step calculation)

Breakthrough Curves for ZF-V4.8-750

Inlet H₂S=1%; P=1 atm; T=923K; H₂O=20%

FIGURE 33. $t_0=408$ min
(one-step calculation)

Breakthrough Curves for ZF

Inlet H₂S=1%; P=1 atm; T=923K; H₂O=20%

FIGURE 34. t=425 min

Breakthrough Curves for ZT

Inlet H₂S=1%; P=1 atm; T=923K; H₂O=20%

FIGURE 35. t=271 min

Breakthrough Curves for Cycle 1

Inlet H₂S=1%; P=1 atm; T=923 K; H₂O=20%

FIGURE 36.

Breakthrough Curves for Cycle 2

H₂S=1%; P=1 atm; T=923 K; H₂O=20%

FIGURE 37.

Breakthrough Curves for Cycle 3

H₂S=1%; P=1 atm; T=923 K; H₂O=20%

FIGURE 38.

Breakthrough Curves for Cycle 4

H₂S=1%; P=1 atm; T=923 K; H₂O=20%

FIGURE 39.

It shows a very stable behavior throughout the five sulfidation-regeneration cycles. A similar stable behavior was observed for the sorbent ZF-V15-650 prepared by two-step calcination. Its conversion and capacity also increased with cycling. The main reason it exhibited lower conversion and capacity than those of zinc titanate was because substantial amount of surface area and pore volume were lost during the preparation of the promoted sorbent.

TABLE 15. CONVERSION AND SORBENT CAPACITY AT A BREAKTHROUGH OF 10 ppm H₂S FOR CYCLE 1.

Sorbent	Conversion, %	Sorbent Capacity, g S/g sorbent
Sulfidation Temperature = 923 K H ₂ O = 7%		
ZF-V4.8-600	85.3	0.281
ZF-V15-600	34.0	0.0944
Zinc Ferrite	58.4	0.221
ZF-V4.8-650*	97.7	0.323
ZF-V15-650*	35.9	0.100
Sulfidation Temperature = 923 K H ₂ O = 20%		
ZF-V4.8-650*	81.5	0.269
ZF-V15-650*	42.7	0.119
ZF-V4.8-700*(C2)	78.3	0.259
ZF-V4.8-750*	61.0	0.201
ZF-V4.8-750	22.5	0.081
Zinc Ferrite	84.2	0.319
Zinc Titanate	78.5	0.187

TABLE 16. CONVERSION AND SORBENT CAPACITY AT A BREAKTHROUGH OF 50 ppm H₂S FOR CYCLE 1

Sorbent	Conversion, %	Sorbent Capacity, g S/g sorbent
Sulfidation Temperature = 923 K H ₂ O = 7%		
ZF-V04.8-600	87.3	0.288
ZF-V15-600	35.5	0.099
Zinc Ferrite	61.7	0.234
ZF-V4.8-650*	99.5	0.328
ZF-V15-650*	37.8	0.105
Sulfidation Temperature = 923 K H ₂ O = 20%		
ZF-V4.8-650*	83.5	0.276
ZF-V15-650*	47.4	0.132
ZF-V4.8-700* (C2)	80.7	0.267
ZF-V4.8-750*	64.2	0.212
ZF-V4.8-750	23.8	0.086
Zinc Ferrite	86.7	0.329
Zinc Titanate	81.1	0.193

The effect of H₂O in the fuel gas on the sulfidation behavior of various sorbents can be seen in *Figures 40 - 44 and Tables 15 - 18*. *Figures 40, 41, and 42* show that increased water content of the fuel gas decreases the conversion of ZF-V4.8-650*, but increases the conversions of zinc ferrite, zinc titanate, and ZF-V15-650* in the first cycle. The water content of the fuel gas does not seem to have an appreciable effect on sorbent conversion in the following cycles.

Effect of H₂O on Sulfidation

H₂S=1%, P=1 atm; T=923 K;

ZF-V4.8-660

FIGURE 40.

Effect of H2O on Sulfidation

Inlet H2S=1%; P=1 atm; T=923K;

ZF-V4.8-650

FIGURE 41.

Effect of H₂O on Sulfidation

Inlet H₂S=1%; P=1 atm; T=923K;
ZF

FIGURE 42.

Effect of H2O on Sulfidation

H₂S=1%; P=1 atm; T=923 K;
ZF-V15-650

FIGURE 43.

Effect of H2O on Sulfidation

H₂S=1%; P=1 atm; T=923;
ZT

FIGURE 44.

TABLE 17. CONVERSION AND SORBENT CAPACITY AT A BREAKTHROUGH OF 10 ppm H₂S FOR CYCLE 5

Sorbent	Conversion, %	Sorbent Capacity, g S/g sorbent
Sulfidation Temperature = 923 K H ₂ O = 7%		
ZF-V4.8-600	38.4	0.127
ZF-V15-600	37.7	0.105
Zinc Ferrite	37.6	0.143
ZF-V4.8-650*	54.9	0.181
Sulfidation Temperature = 923 K H ₂ O = 20%		
ZF-V4.8-650*	51.4	0.170
ZF-V15-650* (C4)	50.6	0.141
ZF-V4.8-700*	49.1	0.162
ZF-V4.8-750* (C4)	44.0	0.145
ZF-V4.8-750	35.6	0.128
Zinc Ferrite (C4)	42.6	0.161
Zinc Titanate (C4)	86.1	0.205

TABLE 18. CONVERSION AND SORBENT CAPACITY AT A BREAKTHROUGH OF 50 ppm H₂S FOR CYCLE 5

Sorbent	Conversion, %	Sorbent Capacity, g S/g sorbent
Sulfidation Temperature = 923 K H ₂ O = 7%		
ZF-V4.8-600	39.3	0.130
ZF-V15-600	38.7	0.107
Zinc Ferrite	39.1	0.148

ZF-V4.8-650°	56.2	0.185
Sulfidation Temperature = 923 K H ₂ O = 20%		
ZF-V4.8-650°	53.1	0.175
ZF-V15-650° (C4)	54.6	0.152
ZF-V4.8-700°	50.7	0.167
ZF-V4.8-750° (C4)	48.0	0.158
ZF-V4.8-750	36.9	0.132
Zinc Ferrite	48.0	0.182
Zinc Titanate (C4)	88.4	0.210

CONCLUSIONS

1. With all vanadium-promoted sorbents prebreakthrough H_2S levels below the equilibrium levels for zinc oxide have been attained. Prebreakthrough H_2S amounts were below the detection limit of the gas chromatograph using fpd for a sample size of 2.5 ml. Hydrogen sulfide levels over 1 ppmv could be detected with this instrument.
2. Some H_2S was chemisorbed by vanadium containing sorbents. This increased the sulfur capture capacity of the vanadium-promoted sorbents.
3. Sorbents containing vanadium produced elemental sulfur during regeneration. This could not be quantified accurately, but it was estimated that more than 15 mass % of the sulfur could be obtained in elemental form. The process conditions for maximum elemental sulfur production were not determined.
4. Vanadium-promoted sorbents containing 1 and 3 % vanadium had conversions similar to that of zinc ferrite, but had lower sulfur capture capacities after 5 cycles of sulfidation and regeneration.
5. The sorbent containing 4.8 % vanadium has the highest conversion and sulfur capture capacity of all the tested vanadium-promoted sorbents, and has higher conversion than zinc ferrite and higher capacity than zinc titanate after five 873 K-sulfidation - 973 K-regeneration cycles using low moisture (7 %) simulated fuel gas. When sulfided at 923 K, it shows behavior similar to other vanadium-promoted sorbents and zinc ferrite.
6. The sorbent containing 15 % vanadium showed the most stable performance through five 873 K-sulfidation - 973 K-regeneration cycles using low moisture simulated fuel gas, but its conversions were low due to its low surface area and porosity. For 923 K-sulfidation its conversion was at the same level as the other promoted sorbents and zinc ferrite.

7. The sorbent ZF-V4.8-650^{*}, which was prepared by two-step calcination, had the highest conversion after five 923 K-sulfidation - 973 K-regeneration cycles using low-moisture simulated fuel gas.
8. Calcination at high temperature stabilizes zinc in the vanadium-promoted sorbents and suppresses zinc loss during sulfidation. On the other hand, the surface area and porosity of the sorbent are greatly reduced.
9. If the sorbents are calcined first at low temperature and then at a higher temperature (two-step calcination), the sorbent retains the structure it has attained after the first calcination and therefore its surface area and porosity does not undergo any significant change during the second calcination step. The conversions of these sorbents did not decrease much upon cycling even at high sulfidation temperatures, because the second high temperature calcination step suppresses zinc loss during sulfidation.
10. Atomic absorption analyses of the fresh and used sorbents indicated that the Zn/Fe mass ratios increased when the vanadium-promoted sorbents were subjected to several sulfidation-regeneration cycles. Although some zinc was lost, it appears that more iron was lost in the process. Zinc loss seemed to have a more significant effect on the decrease of sorbent activity during cycling. These observations could not be explained with the available data.
11. If sorbents containing 15 mass % vanadium and calcined at temperatures above 923 K, can be prepared with high surface areas and porosities, these sorbents will have stabilities comparable to that of zinc titanate but with much higher sorbent capacities.
12. Sorbents containing 4.8 % by mass vanadium or higher did not indicate any appreciable sulfate formation when regenerated at 973 K while zinc ferrite

sorbent underwent some sulfate formation. Regeneration at lower temperatures caused sulfate formation in vanadium-promoted sorbents.

13. When subjected to sulfidation-reduction cycles, zinc ferrite sorbent experienced an increase in its surface area and a decrease in its porosity, while its pore size decreased significantly. On the other hand, all vanadium-containing sorbents lost surface area and pore volume, and in contrast to zinc ferrite, their pore size increased.
14. Increased water content of the fuel gas decreases the conversion of ZF-V4.8-650°, but increases the conversions of zinc ferrite, zinc titanate, and ZF-V15-650° in the first cycle. The water content of the fuel gas does not seem to have an appreciable effect on sorbent conversion in the subsequent cycles.

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