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Absorption of Hydrogen Sulfide by Zinc Ferrite in the Temperature Range 315 to 538°C (600 to 1,000°F)

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BACKGROUND AND OBJECTIVE

The high-temperature, regenerable, desulfurization sorbents under development at METC for use in advanced power systems incorporating coal gasification have been designed to operate at temperatures upwards of about 538°C (1,000°F). This temperature has been thought to be optimal, taking into account such factors as higher sorbent reactivity, increased thermodynamic efficiency, and regeneration temperature.

Recent revision of total system considerations indicates that, in certain circumstances, it may be desirable to operate these sorbents at lower temperatures because of materials considerations. Therefore, a small laboratory investigation of the desulfurization performance of zinc ferrite, one of the sorbents under development, was conducted in the temperature range 315 to 538°C (600 to 1,000°). A previous study (Grindley 1982) had indicated a dramatic decline of zinc ferrite's desulfurization performance at 427°C (800°F) compared to that at 538°C (1,000°F).

A number of sulfidation tests were performed using a low-pressure, fixed-bed reactor and simulated gas containing hydrogen sulfide. Hydrogen sulfide breakthrough times were determined and sorbent properties, including sorbent sulfur loading, mineral properties, and porosity, were measured. An attempt was made to apply

a fixed-bed simulation model to the data. These points are summarized:

Background

- Performance of regenerable hot-gas desulfurization sorbents below 538°C relatively neglected.
- Decline in rate of desulfurization known but not sufficiently quantified.

Objective

- Conduct sulfidation tests in a small fixed-bed reactor at 315 to 538°C.
- Determine hydrogen sulfide breakthrough times.
- Measure sorbent porosity by mercury porosimetry and nitrogen adsorption.
- Determine effect of sorbent reduction (i.e., $\text{ZnFe}_2\text{O}_4 \rightarrow \text{ZnO} + \text{Fe}_3\text{O}_4$) on reactivity.
- Estimate effect of sorbent pore size and crystallite size on reactivity.

PROJECT DESCRIPTION

Hot Gas Desulfurization Sorbents

The zinc ferrite sorbent studied was manufactured by United Catalysts, Inc., and designated L-2465. A zinc titanate sorbent, L-3024, also included in the study for comparison, was made by the same company. Details of the sorbents are given in Table 1.

Table 1. Fresh Sorbent Characteristics

	United Catalysts, Inc. L-2465 Zinc Ferrite	United Catalysts, Inc. L-3024 Zinc Titanate
Form	5 mm Extrudates	5 mm Extrudates
Composition	ZnO/Fe ₂ O ₃	2 ZnO/TiO ₂
Bentonite Binder (wt%)	2	3
Calcination Conditions (Hr @ °C)	2 @ 815°	2 @ 871°
Bulk Density (g/cm ³)	1.57	1.26
Crush Strength (N/mm)	24.0	35.8
B.E.T. Surface Area (m ² /g)	3.2	3.1
Median Pore Diameter, Volume (nm)	292.0	437.5
Mercury Porosity for Pores >12 nm (%)	54.5 ⁺	63.6 [#]
Nitrogen Porosity for Pores <60 nm (%)	2.6 [*]	2.3 [*]
Helium Skeletal Density (g/cm ³)	5.3 g/cm ³ *	5.2 g/cm ³ *

⁺ Mercury porosity calculated using total pore volume reported by United Catalysts, Inc., and METC helium density.

[#] Mercury porosity calculated using total pore volume reported by Coors Analytical Laboratory and METC helium density.

^{*} Analysis performed at METC. All other data provided by United Catalyst, Inc.

Laboratory Test Unit

The test unit is the same as that used in previous studies (Grindley 1990, 1991). The process flow diagram is shown in Figure 1. The sorbent was placed in a 150-cm (60-in) long, 5-cm (2-in) diameter fused-silica reactor located within a 3-zone, clamshell, electric furnace. The reactor is shown in greater detail in Figure 2. The sorbent, in the form of extrudates, was supported by a perforated, fused-silica disc. Temperatures along the centerline of the reactor were

measured by thermocouples, located inside a metal thermowell.

Gases and water are supplied through rotameters. The manifolded mixture was preheated before entering the reactor. Hot gases from the reactor were cooled by teflon condensers. The system was maintained at a positive pressure of 172 kPag (25 psig). In the sulfidation mode, gases were passed upwards through the reactor. Process conditions were recorded

MS4002175W

Figure 1. Hot Gas Desulfurization Lab-Scale Unit Process Flow Diagram Fixed Bed Operation

MS4001865W

Figure 2. Reactor Details

by an automatic data acquisition and control system.

Test Unit Operation

Five sulfidation tests, 72A, 73, 74, 75, and 76, were performed on zinc ferrite and one test, 68, on zinc titanate. The tests were continued until a breakthrough point of 100 ppmv of hydrogen sulfide was reached. Nominal test conditions are detailed in Table 2. The sulfidation gas composition was typical of that from an air-blown, fluidized-bed gasifier, except for hydrogen sulfide, which was considerably higher, in order to produce an accelerated effect.

In Tests 74, 75, and 76, the sorbent was first reduced for 4 hours at 538°C (1,000°F) in the absence of hydrogen sulfide, followed by sulfidation at the prescribed test temperatures. The reduction converted the zinc ferrite into zinc oxide and magnetite ($\text{ZnFe}_2\text{O}_4 \rightarrow \text{ZnO} + \text{Fe}_3\text{O}_4$). At the end of each test, the sorbent was removed from the reactor, by vacuuming, in four sections for analysis.

EXPERIMENTAL RESULTS

Hydrogen Sulfide Breakthrough

Hydrogen sulfide breakthrough plots are shown in Figures 3 and 4. The hydrogen sulfide concentrations were measured by Gastec detector tubes, accurate to about 25 percent. Figure 3 illustrates the large effect of prereduction of zinc ferrite on the breakthrough plot at 427°C (800°F). Because sorbent reduction is rapid at 538°C (1,000°F), the breakthrough plot for Test 72A is the same as if the sorbent had been prereduced, and reduction accompanies sulfidation in this case. The plot for Test 73 at 427°C (800°F) shows a dramatic decline in breakthrough time to 1 hour from 7.5 hours in Test 72A. In Test 74, however, also at 427°C

(800°F), but in which the sorbent has been prereduced at 538°C (1,000°F), the breakthrough time is somewhat greater than 5 hours, which represents a much more modest decline. The breakthrough time for zinc titanate in Test 68 at 538°C (1,000°F) is about 1.5 hours.

Figure 4 compares breakthrough times for prereduced zinc ferrite at 427°C (800°F), 371°C (700°F), and 315°C (600°F), which are contrasted with the breakthrough time for unreduced zinc ferrite at 427°C (800°F).

The decline of breakthrough time with temperature is faster than if linear. Whereas the decline for Test 72A to Test 74 (Figure 3) is from 7.5 to 5 hours, further decreases in temperature of 56°C (100°F) result in a breakthrough time of 1 hour in Test 76 and less than 0.5 hour in Test 75. The breakthrough plots are corroborated by the sorbent sulfur loadings given in Table 3. These were measured by LECO analyzer for samples at four levels in the sorbent bed. The sorbents from the various tests were analyzed by X-ray diffraction using a RIGAKU diffractometer at West Virginia University. The total integrated intensities, which are proportional to the concentrations of crystalline phases, are given in Table 4 for the predominant mineral constituents, franklinite, sphalerite, and zincite.

Of special interest is the small amount of zincite in the sorbent from Test 73, which was the only sorbent not to undergo prereduction at 538°C (1,000°F). This same phenomenon was observed in a previous investigation (Grindley 1988) in which reductive regeneration to eliminate residual sulfate was studied.

Crystallite sizes for the three mineral species were also obtained from the X-ray diffraction analyses. These are given in Table 5 where available, averaged over the sorbent bed. The crystallite size for franklinite in Test 73 is

Table 2. Nominal Test Conditions

Temperature, °C	315 - 538
Pressure, kPa(g)	172.3
Sulfidation Gas Composition, Volume %	
Nitrogen	45.6
Carbon Dioxide	5.1
Carbon Monoxide	18.3
Hydrogen	11.9
Hydrogen Sulfide	1.0
Steam	18.1
Space Velocity, hr ⁻¹	2000
Bed Height, cm	20.3
Reduction Conditions when Applicable	4 Hours @ 538°C

Gas composition during reduction was sulfidation gas composition without hydrogen sulfide.

Tests HGD-073 & HGD-074 Gas Chromatograph Readings
Tests HGD-068 & HGD-072A Detector Tube Readings

Figure 3. Hydrogen Sulfide Concentration in Exit Gas Stream
Zinc Ferrite and Zinc Titanate

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Tests HGD-073 & HGD-074 Gas Chromatograph Readings
Tests HGD-075 & HGD-076 Detector Tube Readings

Figure 4. Hydrogen Sulfide Concentration in Exit Gas Stream: Zinc Ferrite

Table 3. Sorbent Sulfur Loading

Weight %
After Sulfidation

TEST NUMBER Test Temperature Time on Stream Sorbent	Without Reduction			With Reduction		
	HGD-068 538°C 4 Hours Zinc Titanate	HGD-072A 538°C 7.5 Hours	HGD-073 427°C 1 Hour	HGD-074 427°C 5 Hours Zinc Ferrite	HGD-075 315°C 0.5 Hour	HGD-076 371°C 1 Hour
Top	3.41	2.17	0.16	0.96	0.28	0.32
Top Middle	12.40	9.83	0.46	4.77	0.70	0.76
Bottom Middle	14.70	19.90	1.18	9.66	0.98	2.01
Bottom	19.20	28.50	3.80	18.30	1.37	4.55

Analysis by ASTM D4239-83 on LECO SC32 instrument.

Table 4. X-Ray Diffraction Analysis, % Total Integrated Intensity

**United Catalysts, Inc., L-2465 Zinc Ferrite
After Sulfidation**

TEST NUMBER Test Temperature	<u>Without Reduction</u>		<u>With Reduction</u>		
	HGD-072A 538°C	HGD-073 427°C	HGD-074 427°C	HGD-075 315°C	HGD-076 371°C
TOP OF BED					
Franklinite $\text{ZnFe}_2\text{O}_4 + \text{Fe}_3\text{O}_4$	76.8	96.2	77.0	83.8	74.4
Sphalerite, $\beta\text{ZnS} + \text{FeS}$	3.0	0.6	1.8	0.0	0.0
Zincite, ZnO	15.1	0.8	16.9	16.2	25.6
BOTTOM OF BED					
Franklinite	34.9	92.7	63.0	85.3	82.4
Sphalerite	40.3	2.9	21.9	0.0	8.9
Zincite	5.0	1.2	4.0	14.7	8.7

% Total integrated intensity is proportional to the concentration of the crystalline phase.

much larger than that for Test 74, where pre-reduction occurred. This is probably a factor in explaining the lower sorbent reactivity in Test 73.

Sorbent Porosity

The sorbent porosity was measured using a Micromeritics Mercury Porosimeter and a Micromeritics Digisorb BET Surface Area Analyzer. The former is applicable to pore diameters greater than about 12 nm, whereas the latter applies to pore diameters less than about 60 nm, where it is considered to be more accurate. The porosity values for large pores together with average pore diameters are given in Table 6. Those for small pores are given in Table 7.

For the top of the sorbent bed in Table 6, there appears to be a slightly greater porosity in Tests 74, 75, and 76 where prereduction occurred, than in Test 73 where it did not. Also noticeable is a marked decrease in porosity and average pore diameter with sulfidation, which is greater at the bottom of the bed. Similar results can be seen in Table 7 for small pores. Selected sorbent porosities are plotted in Figures 5, 6, and 7.

Figure 5 illustrates the large impact of sulfidation on porosity in Test 72A. The bottom of the bed is much more heavily sulfided than the top. In Figure 6, porosities at the top of the bed for Tests 72A and 73 are compared. There is an outstandingly lower porosity for small pores in the case of Test 73 where sorbent prereduction

Table 5. X-Ray Diffraction Analysis

**United Catalysts, Inc., L-2465 Zinc Ferrite
After Sulfidation**

TEST NUMBER Test Temperature	<u>Without Reduction</u>		<u>With Reduction</u>		
	HGD-072A 538°C	HGD-073 427°C	HGD-074 427°C	HGD-075 315°C	HGD-076 371°C
CRYSTALLINE SIZE, nm					
Franklinite $\text{ZnFe}_2\text{O}_4 + \text{Fe}_3\text{O}_4$	73.2	136.7	87.5	NA	NA
Sphalerite, $\beta\text{ZnS} + \text{FeS}$	30.1	ND	14.8	NA	NA
Zincite, ZnO	28.5	ND	35.2	NA	NA
TOTAL INTEGRATED INTENSITY, %					
Franklinite	59.9	94.9	73.4	80.0	79.7
Sphalerite	14.8	1.3	9.6	ND	3.4
Zincite	10.2	0.9	9.9	20.0	14.0

ND = None Detected. NA = Not Analyzed. Fresh zinc ferrite sorbent crystallite size as reported by United Catalysts: > 200 nm. All values are average for the entire bed. Total integrated intensity is proportional to the concentration of the crystalline phase.

did not occur. Figure 7 shows the smaller porosity of both large and small pores for Test 73 compared to Test 74, both at the same temperature but with sorbent prereduction only for Test 74.

Dynamic Simulation Model

The fixed-bed reactor model used to fit the experimental data was similar to that developed by Louisiana State University, assuming a shrinking unreacted core regime (Focht 1986; Wang 1988). In this case, the principal reaction resistances are diffusion within the sorbent pellets and mass transfer at the pellet exteriors. The rate of the intrinsic reaction between H_2S

and the interior solid surfaces is assumed to be very rapid. These conditions appear to hold for Test 72A, as evidenced by the electron microscope, x-ray sulfur map for a pellet which is about three-quarters reacted (Figure 8). The sulfur map for Test 74 at a lower temperature (Figure 9) indicates a less sharp unreacted core. The x-ray maps were obtained by a JEOL-840A Scanning Electron Microscope interfaced to a Noran Instruments 8502 Switcher System equipped with a Noran Instruments Micro-Z Energy Dispersive Spectrometer. An attempt was made to fit the experimental hydrogen sulfide breakthrough plot by employing a $T^{1.8}$ temperature dependence of the effective diffusivity in the sorbent pores and an $\exp(-E/RT)$ dependence of

Table 6. Mercury Intrusion

United Catalysts, Inc., L-2465
Zinc Ferrite
After Sulfidation

TEST NUMBER Test Temperature	<u>Without Reduction</u>		<u>With Reduction</u>		
	HGD-072A 538°C	HGD-073 427°C	HGD-074 427°C	HGD-075 315°C	HGD-076 371°C
LARGE PORE POROSITY, %					
Top	52.5	52.6	54.3	54.8	52.9
Top Middle	52.5	53.5	49.9	54.5	53.2
Bottom Middle	38.4	52.2	46.3	53.5	49.4
Bottom	33.6	50.3	39.4	53.1	53.6
MEDIAN PORE DIAMETER (Volume), nm					
Top	312.6	295.5	310.8	312.0	283.8
Top Middle	308.8	298.9	282.3	288.2	290.0
Bottom Middle	265.5	274.5	267.0	283.4	264.4
Bottom	255.0	261.0	244.1	268.7	272.7

Porosity for pores < 20 nm. Analyses performed at METC except for HGD-076 performed by Micrometrics. Fresh sorbent porosity 54.5%; median pore diameter 292 nm.

the intrinsic reaction rate constant. It was hoped that the latter would account for the departure from the unreacted core regime. As can be seen, the fit is fairly good (Figure 10). The principal parameters employed in the model are listed in Table 8, and comparison is made with a previous simulation done by Harrison for a similar test (Wang 1988).

CONCLUSIONS

Below about 538°C (1,000°F), there is a rapid fall in the rate of reduction of zinc ferrite (i.e., $\text{ZnFe}_2\text{O}_4 \rightarrow \text{Fe}_3\text{O}_4 + \text{ZnO}$) in coal-derived gas. This has a large effect on the rate of sulfidation, which also falls rapidly. Therefore,

for operation at temperatures lower than 538°C (1,000°F), zinc ferrite should first be prereduced. This is easily accomplished at 538°C (1,000°F) by immersion for a short time in a flow of clean coal-derived gas. Such treatment would also eliminate any residual sulfate in the sorbent from a previous oxidative regeneration. These major findings are summarized below:

- Reduction of zinc ferrite (i.e., $\text{ZnFe}_2\text{O}_4 \rightarrow \text{Fe}_3\text{O}_4 + \text{ZnO}$) is necessary for good desulfurization.
- Reduction caused formation of zinc oxide and magnetite of smaller crystallite size than original zinc ferrite.
- Reduction of zinc ferrite caused a significant increase in small pore porosity.

Table 7. Nitrogen Adsorption Percent

United Catalysts, Inc., L-2465
Zinc Ferrite
After Sulfidation

	<u>Without Reduction</u>		<u>With Reduction</u>		
TEST NUMBER	HGD-072A	HGD-073	HGD-074	HGD-075	HGD-076
Test Temperature	538°C	427°C	427°C	315°C	371°C
Top	3.15	2.60	3.02	3.01	3.18
Top Middle	2.59	2.80	3.31	3.36	2.97
Bottom Middle	2.06	3.01	2.51	3.29	3.13
Bottom	1.98	2.94	2.21	3.31	2.91

Porosity for pores < 60 nm. Analyses performed at METC. Fresh sorbent porosity 2.6%.

ACKNOWLEDGEMENT

- Zinc ferrite can be used below 538°C (1,000°F) if an initial reduction is carried out.

We acknowledge with thanks the contributions of J. A. Poston, who provided the x-ray sorbent cross-sectional sulfur maps, and E. J. Boyle, who modeled the breakthrough plots.

Table 8. Model Parameters

HGD-072A:	
Bed Length (cm)	17.8
Bed Radius (cm)	2.85
Bed Mass (g)	629
Particle Diameter (cm)	0.476
Skeletal Particle Density (g/cc)	5.3
Bulk Density (g/cc)	1.39
Gas Velocity (cm/s)	12.8
Inlet Pressure (psig)	24
Temperature (K)	818
All Runs:	
De, effective diffusivity (cm ² /hr)	90 (Harrison: 400)
k, intrinsic reaction rate (cm ² /mol-hr)	3 x 10 ⁷ (Harrison: 3 x 10 ⁷)
ka, mass transfer (cm/hr)	55800 (Harrison: 22400)
E intrinsic/R (K)	17900
De temp dependence	(T/884.26) ^{1.78}

Average Pore Diameter by Mercury Intrusion
 Fresh 2920 nm; HGD-072A Top 3126 nm; HGD-072A Bottom 2550 nm

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Figure 5. POROSITY vs. PORE DIAMETER
Sulfided L-2465 Zinc Ferrite Sorbent
Test No. HGD-072a 538°C

Median Pore Diameter by Mercury Intrusion;
 HGD-072A 312.6 nm; HGD-073 295.5 nm

HGD-072A 538°C
 HGD-073 427°C

M94001758WME

Figure 6. POROSITY vs. PORE DIAMETER
Sulfided L-2465 Zinc Ferrite Sorbent
Top of Bed

Figure 7. POROSITY vs. PORE DIAMETER
Sulfided L-2465 Zinc Ferrite Sorbent
Top of Bed

Figure 8. Zinc Ferrite Test 72A
Sulfur Map

Figure 9. Zinc Ferrite Test 74
Sulfur Map

Figure 10. Breakthrough Curves

REFERENCES

Focht, et al., 1986, *Structural Property Changes in Metal Oxide Hot Coal Gas Desulfurization Sorbents*, Report No. DOE/MC/21166-2163, National Technical Information Service, Springfield, Virginia.

Grindley, T., 1982, Development and Testing of Regenerable Hot Coal Gas Desulfurization Sorbents, in *Proceedings of the Second Annual Contractors Meeting on Contaminant Control in Hot Coal Derived Gas Streams*, Report No. DOE/METC/82-47, National Technical Information Service, Springfield, Virginia.

Grindley, T., 1988, Sidestream Zinc Ferrite Regeneration Tests: Laboratory-Scale Study of Reductive Regeneration of Zinc Ferrite Sorbents, in *Proceedings of the Eighth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting*, Report No. DOE/METC-88/6092, National Technical Information Service, Springfield, Virginia.

Grindley, T., 1990, Effect of Chlorine on Hot Gas Desulfurization Sorbents, in *Proceedings of the Tenth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting*, Report No. DOE/METC-90/6115, National Technical Information Service, Springfield, Virginia.

Grindley, T., 1991, Lab-Scale Sorbent Development, in *Proceedings of the Eleventh Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting*, Report No. DOE/METC/91-6123, National Technical Information Service, Springfield, Virginia.

Wang, et al., 1988, *Dynamic Simulation Models for High-Temperature Desulfurization Processes*, Report No. DOE/MC/23089-2601, National Technical Information Service, Springfield, Virginia.