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QUARTERLY TECHNICAL PROGRESS REPORT 7
APRIL - JUNE, 1988

ENHANCED DURABILITY AND REACTIVITY FOR ZINC FERRITE DESULFURIZATION SORBENT

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Prepared for
U. S. Department of Energy
Morgantown Energy Technology Center
P. O. Box 880
3610 Collins Ferry Road
Morgantown, West Virginia 26507-0880

DOE Contract No. DE-AC21-86MC23172
AMAX Project No. 80270

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LEGAL NOTICE

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SUMMARY

AMAX Research & Development Center (AMAX R&D) has been investigating methods for improving the reactivity and durability of the zinc ferrite desulfurization sorbent. Zinc ferrite sorbents are intended for use in desulfurization of hot coal gas in integrated gasification combined cycle (IGCC) or molten carbonate fuel cell (MCFC) applications. The reactivity of the sorbent may be defined as its sulfur sorption capacity at the breakthrough point in a bench-scale, fixed-bed reactor. The durability may be defined as the ability of the sorbent to maintain its reactivity and other important physical characteristics such as size, strength, and specific surface area during 10 cycles of sulfidation and oxidation. Two base case sorbents, spherical pellets and cylindrical extrudes used in related METC sponsored projects, are being used to provide a basis for the comparison of physical characteristics and chemical reactivity.

During the seventh quarter of the project (April - June, 1988), cyclic bench-scale testing of sorbents prepared at AMAX R&D continued and the sulfidized sorbents were characterized. All cylindrical extrude and spherical pellet sorbent formulations from the screening test matrix had been prepared by the end of the reporting period. One additional cylindrical extrude sorbent was prepared using a very low-cost iron oxide feedstock. Characterization of this sorbent is in progress. Single particle kinetic studies continued at Louisiana State University.

Project status was reviewed at the Eighth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting held in Morgantown, West Virginia, during May.

INTRODUCTION

The U. S. Department of Energy (DOE), through the Morgantown Energy Technology Center (METC), has been investigating a number of advanced systems for producing electric power from large coal reserves available in the United States. The integrated gasification combined cycle (IGCC) concept has been identified as one of the most promising technologies for coal utilization. The goal of hot gas cleanup programs at METC is to develop contaminant control technologies that operate under conditions compatible with those of the gasifier and power generator (gas turbine or molten carbonate fuel cell).

Sulfur control at high temperature and pressure forms a major portion of the hot gas cleanup program at METC. Previous research has established that high temperature desulfurization can be accomplished using solid zinc ferrite sorbents to remove sulfur species from the coal gas to the 10 ppmv level or less, and the sorbent can be regenerated with air for reuse. The zinc ferrite sorbents experience chemical, physical, and thermal changes during sulfidation and regeneration. Deterioration of sorbent performance and physical characteristics is strongly influenced by the chemical composition of the sorbent and the method of preparation.

The objective of the present contract is to systematically investigate methods for enhancing the physical durability and chemical reactivity of the zinc ferrite desulfurization sorbent.

The program is divided into the following five tasks:

Task 1. Experimental Test Plan
Task 2. Sorbent Preparation and Characterization
Task 3. Bench-Scale Testing
Task 4. Bench-Scale Analysis
Task 5. Topical Report

Accomplishments for each of the major tasks are summarized in the following section.

ACCOMPLISHMENTS

TASK 1. EXPERIMENTAL TEST PLAN

No changes were made to the experimental test plan during the reporting period.

TASK 2. SORBENT PREPARATION AND CHARACTERIZATION

Sorbent Preparation

All of the sorbent formulations from the screening test matrix have been prepared. Sorbent formulations P22 and E2 were selected as the final two sorbents for bench-scale testing. These two sorbents were fired in batches of sufficient size for the multi-cycle testing and were identified as P22A and E2A.

An additional sorbent was prepared using a low-cost Ruthner-process iron oxide, which is produced during recovery of acid from steel pickling liquors. This type of iron oxide typically contains chloride as the primary contaminant and is available for about $0.05 per pound. For comparison, attempts were made to prepare a sorbent using the same formulation as sorbent E7A, with only the substitution of Ruthner iron oxide for pigment-grade iron oxide. The Ruthner iron oxide contains particles which are typically about 1 micron or less in size versus the 0.3 micron size of the pigment-grade iron oxide. Due to some difficulties in extruding this mixture, the bentonite content was increased to 5 percent from 2 percent. Upon further plugging in the extrusion chamber, the sorbent was successfully prepared using a 3/16-inch diameter die (pipe) and a rod to press a small quantity of the mixture into extrudes. The sorbent was fired at 1,500^{o}F for 4 hours.

Sorbent Characterization

Additional characterizations were performed on sorbents which had been prepared earlier. Tables 1 and 2 summarize the formulations, induration conditions, and physical properties of the sorbents which were prepared from the screening test matrix. Characterizations of the P22A and E2A sorbents selected for bench-scale testing were in progress at the end of the reporting period.

Based on discussions with the COTR during a meeting at AMAX R&D, some of the units for reporting physical properties were changed. For example, loss on attrition values were converted to "attrition resistance", with values potentially ranging from 0 to 100 percent. Crush strength of extrudes are being converted to units of "pounds/mm (length)" from the "pounds" units previously used. The crush strength values for

Table 1. Zinc Ferrite Spherical Pellet Characteristics

		Pellet Formulation				Induration Conditions		Physical Properties					
									Crush Strength, lb				
Sorbent Sample Number	Run No.	Fe_2O_3 Grade	ZnO/Fe_2O_3	% Bentonite	% Starch	Temp., °F	Time, Hours	Bulk Density, kg/l	x	s	Attrition Resistance %	BET Surface Area, m^2/g	TGA Testing
1094-59	Base	Pigment	1.0	5	2	1,825	3.00	1.014	5.1	2.9	45.5	1.01	*
P1	2	Pigment	0.8	2	0	1,500	0.25	0.876	4.6	1.8	34.9		
P2						1,500	4.00	0.912	3.8	1.5	23.3		
P3						1,700	2.00	0.916	4.8	1.5	39.8		
P4						1,700	2.00	0.860	5.7	2.8	46.0		
P5						1,900	0.25	0.952	6.6	3.7	48.5	3.95	*
P6						1,900	4.00	1.529	40.3	10.7	89.8	1.28	*
P6A						1,900	4.00	1.488	22.0	8.2	89.0	1.68	
P7	3	Catalyst	1.0	2	0	1,500	0.25	0.999	9.3	4.4	57.2		
P8						1,500	4.00	0.952	6.8	2.9	59.3		
P9						1,700	2.00	1.013	10.0	4.8	66.3		
P10						1,700	2.00	1.048	10.1	4.1	68.4	2.43	*
P11						1,900	0.25	1.036	10.5	4.1	67.6	2.47	*
P11A						1,900	0.25	1.141	16.6	6.0	80.5	2.63	
P12						1,900	4.00	1.273	21.5	10.2	75.5	1.38	*
P13	5	Catalyst	0.8	2	2	1,500	0.25	1.028	14.5	3.3	83.8		
P14						1,500	4.00	1.034	17.6	5.5	81.3		
P15						1,700	2.00	1.075	18.2	5.5	86.2		
P16						1,900	0.25	1.196	27.3	5.4	89.3	1.55	*
P17						1,900	4.00	1.339	32.8	5.3	91.6	1.43	*
P18	19	Catalyst	1.0	10	0	1,500	0.25	0.956	10.2	1.8	63.5		
P19						1,500	4.00	0.955	11.3	2.5	66.5		
P20						1,700	2.00	0.952	11.6	2.6	68.0		
P21						1,900	0.25	0.955	12.3	3.4	70.3	2.46	*
P22						1,900	4.00	1.132	20.8	6.6	77.2	2.10	*
P22A						1,900	4.00						
P23	21	Catalyst	0.8	10	2	1,500	0.25	0.914	5.7	2.3	57.6		
P24						1,500	4.00	0.902	7.1	2.5	61.0		
P25						1,700	2.00	0.922	10.4	1.9	65.0		
P26						1,900	0.25	0.956	15.0	3.5	74.5	2.05	*
P27						1,900	4.00	1.111	21.2	4.8	80.1	1.91	*
P27A						1,900	4.00	1.143	22.0	8.5	80.9	1.21	
P28	8	Pigment	1.0	2	2	1,500	0.25	0.900					
P29						1,500	4.00	0.918	3.7	1.4			
P30						1,700	2.00	0.906	3.9	0.8			
P31						1,900	0.25	0.972	6.5	3.0		2.57	*
P32						1,900	4.00	1.270	19.4	6.9			
P32A						1,900	4.00	1.276	20.5	6.4	74.9	0.77	*

Table 1. Zinc Ferrite Spherical Pellet Characteristics
(Continued)

Sorbent Sample Number	Pellet Formulation					Induration Conditions		Physical Properties				BET Surface Area, m^2/g	TGA Testing
	Run No.	Fe_2O_3 Grade	ZnO/Fe_2O_3	% Bentonite	% Starch	Temp., °F	Time, Hours	Bulk Density, kg/l	Crush Strength, lb x	Crush Strength, lb s	Attrition Resistance %		
P33	10	Pigment	0.8	5	0	1,500	0.25	0.878					
P34						1,500	4.00	0.834	4.3	1.0			
P35						1,700	2.00	0.877	5.2	1.6			
P36						1,900	0.25	0.993	10.0	3.6	50.1		
P37						1,900	4.00	1.456	34.8	9.7	89.2		
P37A						1,900	4.00	1.279	22.1	6.6	90.7	1.76	*
P38	16	Pigment	1.0	5	2	1,500	0.25	0.926					
P39						1,500	4.00	0.940	4.4	2.0			
P40						1,700	2.00	0.928	3.9	1.7			
P41						1,900	0.25	1.020	9.1	3.4	60.5		
P42						1,900	4.00	1.383	31.2	5.9	85.4		
P42A						1,900	4.00	1.240	17.0	3.0	79.1	1.07	*
P43	11	Catalyst	1.0	5	0	1,500	0.25	0.930	5.8	1.6			
P44						1,500	4.00	0.939	5.1	1.9			
P45						1,700	2.00	0.979	6.9	3.0			
P46						1,900	0.25	0.988	6.8	3.0			
P47						1,900	4.00	1.234	17.7	4.1	78.0	1.40	*
P48	13	Catalyst	0.8	5	2	1,500	0.25	0.889	7.3	3.5			
P49						1,500	4.00	0.882	5.7	2.7			
P50						1,700	2.00	0.920	9.0	4.5			
P51						1,900	0.25	0.997	13.4	6.6	67.3	1.76	
P52						1,900	4.00	1.142	22.3	6.8	74.5	1.63	*
P53	18	Pigment	0.8	10	0	1,500	0.25	0.860	3.5	1.7			
P54						1,500	4.00	0.846	5.1	2.0			
P55						1,700	2.00	0.858	5.6	2.0			
P56						1,900	0.25	0.860	5.8	1.6			
P57						1,900	4.00	1.275	45.3	8.5	84.9	1.67	*
P58	24	Pigment	1.0	10	2	1,500	0.25	0.712	0.6	0.6			
P59						1,500	4.00	0.733	0.8	0.9			
P60						1,700	2.00	0.751	1.8	0.7	20.4		
P61						1,900	0.25	0.729	2.2	1.8	15.5		
P62						1,900	4.00	0.947	12.2	4.4	50.8	1.64	*

Notes: x = Average of 25 single pellet crush strength determinations.
s = Standard deviation.
An "A" designation in the sorbent sample number indicates preparation of a larger sample for cyclic testing.

Table 2. Zinc Ferrite Cylindrical Extrude Characteristics

	Pellet Formulation					Induration Conditions		Physical Properties					
Sorbent Sample Number	Run No.	Fe_2O_3 Grade	ZnO/Fe_2O_3	% Bentonite	% Methocel	Temp., °F	Time, Hours	Bulk Density, kg/l	Crush Strength, lb x	Crush Strength, lb s	Attrition Resistance %	BET Surface Area, m^2/g	TGA Testing
T-2465	Base	Catalyst	1.0	2	0			1.306	30.2	6.3	88.8	3.30	*
E1	1	Catalyst	0.8	2	0	1,500	0.25	1.199	29.4	7.0	90.2	5.12	*
E2						1,500	4.00	1.120	42.5	8.5	92.3	4.39	*
E2A						1,500	4.00						
E3						1,700	2.00	1.159	39.1	8.0	88.1		
E4						1,900	0.25	1.172	46.2	8.0	91.8	3.59	
E5						1,900	4.00	1.355	>50		94.3		
E6	4	Pigment	1.0	2	0	1,500	0.25	1.130	24.6	4.6	83.5		
E7						1,500	4.00	1.154	26.0	6.1	81.8	5.77	*
E7A						1,500	4.00	1.250	24.4	7.1	87.5	5.62	
E8						1,700	2.00	1.147	24.2	6.3	85.9		
E9						1,900	0.25	1.354	46.8	11.7	93.4	2.74	*
E10						1,900	4.00	1.501	>50		95.1		
E11	7	Catalyst	1.0	2	0.5	1,500	0.25	1.215	31.8	8.5	87.8	4.39	*
E12						1,500	4.00	1.196	33.3	6.5	86.7	4.36	*
E13						1,700	2.00	1.148	37.7	6.6	84.5	3.37	*
E13A						1,700	2.00	1.260	33.2	7.2	85.4	4.06	
E14						1,900	0.25	1.272	>50		91.7		
E15						1,900	4.00	1.623	>50		93.2	1.42	*
E16	9	Catalyst	0.8	5	0	1,500	0.25	1.269	>50		93.9	4.78	*
E17						1,500	4.00	1.238	>50		90.6		
E18						1,700	2.00	1.231	>50		89.2		
E19						1,900	0.25	1.367	>50		91.5	2.51	
E20						1,900	4.00	1.743	>50		94.3		
E21	15	Catalyst	1.0	5	0.5	1,500	0.25	1.195	≈50		90.1	4.62	*
E22						1,500	4.00	1.207	36.8	7.6	88.3		
E23						1,700	2.00	1.220	>50		89.8		
E24						1,900	0.25	1.300	>50		92.6	2.93	*
E24A						1,900	0.25	1.328	41.3	12.0	91.7	4.15	
E25						1,900	4.00	1.676	>50		94.7		
E26	14	Pigment	0.8	5	0.5	1,500	0.25	1.070	43.5	8.9	90.7		
E27						1,500	4.00	1.082	46.2	9.4	91.1		
E28						1,700	2.00	1.110	44.8	8.2	91.0		
E28A						1,700	2.00	1.115	29.7	7.3	89.3	4.99	*
E29						1,900	0.25	1.254	>50		94.0		
E30						1,900	4.00	1.888	>50		96.1		
E31	6	Pigment	0.8	2	0.5	1,500	0.25	1.168	26.1	9.7	86.1	6.31	*
E32						1,500	4.00	1.174	20.5	8.4	86.0		
E32A						1,500	4.00	1.191	27.9	7.1	8464	6.33	*
E33						1,700	2.00	1.123	25.8	8.0	87.5		
E34						1,900	0.25	1.234	38.2	11.3	91.0		
E35						1,900	4.00	1.686	>50		97.1	1.42	*
E36	12	Pigment	1.0	5	0	1,500	0.25	1.092	39.8	12.0	93.1	5.76	*
E37						1,500	4.00	1.138	40.7	7.4	93.3		
E38						1,700	2.00	1.174	44.7	9.6	94.3	4.12	*
E39						1,900	0.25	1.314	50.9		96.7		
E40						1,900	4.00	2.039	>50		97.8	0.85	*

Notes: x = Average of 25 single extrude crush strength determinations.
s = Standard deviation.
An "A" designation in the sorbent sample number indicates preparation of a larger batch for cyclic testing.

the cylindrical extrudes selected for bench-scale testing (Table 4) have been converted. Crush strength values for the remaining extrudes prepared under the screening test matrix (Table 2) are currently being converted.

Porosity determinations were made on the sorbents which were selected for bench-scale testing. Tables 3 and 4 summarize the porosity and other characteristics of these sorbents.

The Ruthner iron oxide used to prepare the sorbent sample described above contained about 0.49 percent chloride. After washing in water at pH 11 and then filtering, the chloride content was reduced to less than 70 ppm. According to the supplier, chloride should be easily removed upon heating as well. Further chemical analysis will determine how well the chlorides can be removed by heating. The level of other contaminants will also be determined. The sorbent prepared using the Ruthner iron oxide exhibited a bulk density of about 0.77 kg/l and a crush strength of about 35 pounds. A sample of this sorbent (called E7R) was forwarded to LSU for single particle kinetic studies using the TGA.

TASK 3. BENCH-SCALE TESTING

Bench-Scale Test Results

Bench-scale testing was completed using the E24A, E28A, and P37A sorbents. Cyclic testing was in progress using the E32A cylindrical extrude sorbent at the end of the quarter. A 1.0 percent hydrogen sulfide gas concentration is being used at a test temperature of 550°C for sulfidation. Tables 3 and 4 summarize the sorbent characteristics and the sulfidation response of each sorbent evaluated so far during the cyclic test program. Sulfur loadings are based on the calculated pounds of sulfur picked up by the sorbent (based on gas flow rate and analysis) per 100 pounds of initial sorbent weight.

Sorbents P22A and E2A were readied for bench-scale testing. These represent the final two sorbents to be tested under the base contract. A total of 13 sorbents will have been tested after these multi-cycle tests are completed.

Alternate Regeneration Procedure Testing

A report describing the two-stage regeneration procedures and test results was submitted during the reporting period.[1] The laboratory tests demonstrated the feasibility of the two-stage regeneration procedure which first converts the sulfided sorbent to sulfate form, followed by conversion to oxide at higher temperatures. Physical integrity of the sorbent was maintained during the sulfidation to saturation, first-stage regeneration, and second-stage regeneration procedures.

Table 3. Summary of Spherical Pellet Sorbent Performance

Sorbent Formulation						
Sorbent Sample Number	1094-59	P11A	P6A	P27A	P37A	P22A
Preparation Run Number	—	3	2	21	10	19
Iron Oxide Grade	Pigment	Catalyst	Pigment	Catalyst	Pigment	Catalyst
ZnO/Fe_2O_3 Ratio	1.0	1.0	0.8	0.8	0.8	1.8
Bentonite, %	5	2	2	10	5	10
Kaolin, %	1.5	—	—	—	—	—
Starch, %	2	0	0	2	0	0
Na_2CO_3, %	0.2	—	—	—	—	—
MoS_2, %	0.2	—	—	—	—	—
Induration Conditions						
Temperature, °F	1825	1900	1900	1900	1900	1900
Time, hours	3	0.25	0.25	4	4	4
Physical Properties						
Bulk Density, kg/l	1.014	1.141	1.488	1.143	1.389	
Crush Strength, lb	5.1	16.6	22.0	22.0	22.1	
Attrition Resistance, %	45.4	80.5	89.0	80.9	90.7	
Surface Area, m^2/g	1.01	2.63	1.68	1.21	1.76	
Porosity, %	59.2	63.8	52.1	56.2	52.3	
Pore Volume, cm^3/g	0.277	0.319	0.207	0.270	0.212	
Average Pore Radius, A	0.549	0.243	0.246	0.446	0.241	
Cyclic Test Number	5	7	9	11	14	17
Desulfurization Performance in Bench-Scale Reactor Sulfur Sorption Capacity, g S sorbed/100 g fresh sorbent						
a) At 200 ppm H_2S Breakthrough:						
1st Cycle	1.3	25.2	16.1	13.3	1.7	
2nd Cycle	1.5	20.2	14.3	16.0	2.6	
3rd Cycle	3.4	11.0*	13.0	12.7	2.4	
4th Cycle	1.4	34.2	10.4	9.8	2.1	
5th Cycle	1.4	33.0	8.5	10.4	2.2	
6th Cycle	1.2	24.8	6.8	7.5	3.3	
7th Cycle	1.4	24.0	7.7	7.2	2.0	
8th Cycle	0.8	19.5	7.0	7.0	3.3	
9th Cycle	0.8	20.3	7.6	7.9	1.9	
10th Cycle	1.3	21.0	8.0	7.7	2.8	
Average	1.2	24.7	9.9	10.0	2.4	
b) At Saturation, Actual	34.0	32.6	27.2	29.8	25.1	
c) At Saturation, Theoretical	37.3	39.1	39.1	35.9	37.9	
Desulfurization Performance in TGA Sulfur Sorption Capacity During First Cycle at t = 20 minutes, g S sorbed/100 g fresh sorbent	19.2	28.2	20.8	22.0	17.8	25.3
Reactivity Change, Increase or Decrease in Reactivity During 2nd Cycle, %	+4	-16	-14	-11	-27	-11

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* Test cycle suspended early due to reactor system plugging.

Table 4. Summary of Cylindrical Extrude Sorbent Performance

Sorbent Formulation							
Sorbent Sample Number	T-2465	E13A	E7A	E24A	E28A	E32A	E2A
Run Number	--	7	4	15	14	6	1
Iron Oxide Grade	Catalyst	Catalyst	Pigment	Catalyst	Pigment	Pigment	Catalyst
ZnO/Fe_2O_3 Ratio	1.0	1.0	1.0	1.0	0.8	0.8	0.8
Bentonite, %	2	2	2	5	5	2	2
Methocel, %	0	0.5	0	0.5	0.5	0.5	0
Induration Conditions							
Temperature, °F		1700	1500	1900	1700	1500	1500
Time, hours		2	4	0.5	2	4	4
Physical Properties							
Bulk Density, kg/l	1.306	1.260	1.250	1.328	1.115	1.191	
Crush Strength, lb/mm	3.5	4.4	2.5	5.3	3.3	3.0	
Attrition Resistance, %	88.8	85.4	87.5	91.7	89.3	84.6	
Surface Area, m^2/g	3.30	4.06	5.62	4.15	4.99	6.33	
Porosity, %	58.2	56.2	58.0	56.7	56.4		
Pore Volume, cm^3/g	0.256	0.239	0.265	0.249	0.250		
Average Pore Radius, A	0.155	0.118	0.094	0.120	0.100		
Cyclic Test Number	4	8	10	12	13	15	16
Desulfurization Performance							
Sulfur Sorption Capacity, g S sorbed/100 g fresh sorbent							
a) At 200 ppm H_2S Breakthrough:							
1st Cycle	13.7	17.6	25.6	16.2	9.3	8.8	
2nd Cycle	28.6	15.3	14.9	14.7	5.5	12.6	
3rd Cycle	26.3	17.7	11.5	14.0	5.6	9.6	
4th Cycle	24.0	17.1	10.8	12.2	6.0	9.6	
5th Cycle	22.2	15.3	12.4	11.3	6.2	8.9	
6th Cycle	22.6	20.3	10.4	11.0	5.7	9.0	
7th Cycle	22.2	16.1	8.8	10.1	5.9	9.5	
8th Cycle	20.2	15.8	8.8	9.6	5.8	8.4	
9th Cycle	20.4	16.6	9.5	9.5	5.9	9.5	
10th Cycle	22.3	25.3	9.2	9.8	5.8	15.2	
Average	22.3	17.7	12.2	11.8	6.2	10.1	
b) At Saturation, Actual	34.3	36.9	35.5	37.7	32.1		
c) At Saturation, Theoretical	39.1	39.1	39.1	37.9	37.9	39.1	
Desulfurization Performance in TGA							
Sulfur Sorption Capacity During First Cycle at t = 30 minutes, g S sorbed/100 g fresh sorbent	22.9	20.9	18.2	17.7	16.0	21.1	
Single Particle TGA Reactivity Change, Increase or Decrease in Reactivity During 2nd Cycle, %	-11	-24	-19	-49	-20	-9	

Single Particle Kinetic Studies at LSU

The single particle kinetic studies performed in the TGA apparatus at LSU continued. LSU requested that some additional sorbents which had already been prepared and indurated at AMAX R&D be forwarded for TGA analysis in order to better establish the comparative effects of the sorbent preparation conditions. Additional sorbents representing the remaining samples from the screening test matrix were also forwarded to LSU for single particle kinetic studies.

Data analysis was performed to establish techniques for comparing the reactivity maintenance of sorbents during the second sulfidation cycle. The selection of elapsed time at which to compare the results with first cycle results was the focus of the effort. Selection of a time early during the sulfidation step results in significant data scatter due to the very high initial reaction rates. On the other hand, selection of a time late during the sulfidation step provides information related more to sulfur sorption capacity than to reactivity. A balance between these factors was obtained by selection of standard times of 20 minutes for the spherical pellets and 30 minutes for the cylindrical extrudes.

Tables 5 and 7 summarize the available single particle kinetic data (reactivity) during the first sulfidation cycle for spherical pellets and cylindrical extrudes, respectively. Tables 6 and 8 summarize the second sulfidation cycle data (reactivity maintenance) for the same sorbents. LSU interpreted the results of available single particle kinetic studies early in the quarter. Some of these results and more recent interpretations are reviewed below. The interpretations are subject to change based on evaluation of the more recently obtained data.

$ZnO:Fe_2O_3$ Ratio

Stoichiometric equivalents of ZnO and Fe_2O_3 appear to provide generally better reactivity than the 0.8 ratio for spherical pellets. More of the high-reactivity pellets (Table 5) contain the stoichiometric mixture of zinc and iron oxides. Of those exhibiting low reactivity, more pellets contain the 0.8 $ZnO:Fe_2O_3$ ratio. Extrude reactivity dependence on the $ZnO:Fe_2O_3$ ratio is not as clear.

The reactivity maintenance during the second sulfidation cycle supports the conclusion of better performance from the stoichiometric zinc and iron oxide mixture for spherical pellets. Reactivity maintenance results for the cylindrical extrudes were not conclusive.

Table 5. Comparison of Pellet Reactivity

Sorbent	Reactivity*	$Zn:Fe_2$ Ratio	Fe_2O_3 Grade	% Bentonite	% Starch	Induration	
						Temperature, °C	Time, Hours
P10	0.297	1.0	C	2	0	1,700	2.00
P5	0.290	0.8	P	2	0	1,900	0.25
P21	0.284	1.0	C	10	0	1,900	0.25
P11	0.282	1.0	C	2	0	1,900	0.25
P12	0.257	1.0	C	2	0	1,900	4.00
P22	0.253	1.0	C	10	0	1,900	4.00
P26	0.247	0.8	C	10	2	1,900	0.25
P52	0.241	0.8	C	5	2	1,900	4.00
P62	0.241	1.0	P	10	2	1,900	4.00
P31	0.240	1.0	P	2	2	1,900	0.25
P47	0.222	1.0	C	5	0	1,900	4.00
P27	0.220	0.8	C	10	2	1,900	4.00
P6	0.208	0.8	P	2	0	1,900	4.00
1094-59	0.192	1.0	C	5	1.7	1,825	3.00
P57	0.190	0.8	P	10	0	1,900	4.00
P16	0.179	0.8	C	2	2	1,900	0.25
P37A	0.178	0.8	P	5	0	1,900	4.00
P32A	0.176	1.0	P	2	2	1,900	4.00
P17	0.171	0.8	C	2	2	1,900	4.00
P42A	0.167	1.0	P	5	2	1,900	4.00

---

* Sulfur sorption capacity (weight of S sorbed/initial sorbent weight) at time = 20 minutes.

C = Catalyst-grade iron oxide.
P = Pigment-grade iron oxide.

Table 6. Comparison of Pellet Reactivity Maintenance

Sorbent	Reactivity Maintenance*	Zn:Fe_2 Ratio	Fe_2O_3 Grade	% Bentonite	% Starch	Induration Temperature, °C	Induration Time, Hours
1094-59	1.04	1.0	C	5	1.7	1,825	3.00
P62	0.99	1.0	P	10	2	1,900	4.00
P52	0.92	0.8	C	5	2	1,900	4.00
P26	0.91	0.8	C	10	2	1,900	0.25
P31	0.90	1.0	P	2	2	1,900	0.25
P22	0.89	1.0	C	10	0	1,900	4.00
P27	0.89	0.8	C	10	2	1,900	4.00
P42A	0.89	1.0	P	5	2	1,900	4.00
P21	0.88	1.0	C	10	0	1,900	0.25
P6	0.86	0.8	P	2	0	1,900	4.00
P10	0.84	1.0	C	2	0	1,700	2.00
P11	0.84	1.0	C	2	0	1,900	0.25
P16	0.84	0.8	C	2	2	1,900	0.25
P12	0.83	1.0	C	2	0	1,900	4.00
P47	0.83	1.0	C	5	0	1,900	4.00
P32A	0.82	1.0	P	2	2	1,900	4.00
P57	0.81	0.8	P	10	0	1,900	4.00
P17	0.79	0.8	C	2	2	1,900	4.00
P5	0.79	0.8	P	2	0	1,900	0.25
P37A	0.73	0.8	P	5	0	1,900	4.00

---

* Ratio of 2nd cycle sulfur sorption capacity to 1st cycle sulfur sorption capacity at time = 20 minutes.

C = Catalyst-grade iron oxide.
P = Pigment-grade iron oxide.

Table 7. Comparison of Extrude Reactivity

						Induration	
Sorbent	Reactivity*	$Zn:Fe_2$ Ratio	Fe_2O_3 Grade	% Bentonite	% Methocel	Temperature, °C	Time, Hours
T-2465	0.229	1.0	C	2	0		
E32A	0.211	0.8	P	2	0.5	1,500	4.00
E2	0.209	0.8	C	2	0	1,500	4.00
E13	0.209	1.0	C	2	0.5	1,700	2.00
E1	0.207	0.8	C	2	0	1,500	0.25
E12	0.207	1.0	C	2	0.5	1,500	4.00
E11	0.194	1.0	C	2	0.5	1,500	0.25
E21	0.193	1.0	C	5	0.5	1,500	4.00
E31	0.192	0.8	P	2	0.5	1,500	0.25
E7	0.182	1.0	P	2	0	1,500	4.00
E24	0.177	1.0	C	5	0.5	1,900	0.25
E28A	0.160	0.8	P	5	0.5	1,700	2.00
E9	0.156	1.0	P	2	0	1,900	0.25
E36	0.154	1.0	P	5	0	1,500	0.25
E38	0.153	1.0	P	5	0	1,700	2.00
E16	0.144	0.8	C	5	0	1,500	0.25
E15	0.082	1.0	C	2	0.5	1,900	4.00

* Sulfur sorption capacity (weight of S sorbed/initial sorbent weight) at time = 30 minutes.

R = Ruthner iron oxide.
C = Catalyst-grade iron oxide.
P = Pigment-grade iron oxide.

Table 8. Comparison of Extrude Reactivity Maintenance

Sorbent	Reactivity Maintenance*	Zn:Fe$_2$ Ratio	Fe$_2$O$_3$ Grade	% Bentonite	% Methocel	Induration Temperature, °C	Induration Time, Hours
E12	0.92	1.0	C	2	0.5	1,500	4.00
E32A	0.91	0.8	P	2	0.5	1,500	4.00
T-2465	0.89	1.0	C	2	0		
E31	0.89	0.8	P	2	0.5	1,500	0.25
E21	0.88	1.0	C	5	0.5	1,500	4.00
E11	0.85	1.0	C	2	0.5	1,500	0.25
E2	0.84	0.8	C	2	0	1,500	4.00
E1	0.83	0.8	C	2	0	1,500	0.25
E7	0.81	1.0	P	2	0	1,500	4.00
E28A	0.80	0.8	P	5	0.5	1,700	2.00
E16	0.78	0.8	C	5	0	1,500	0.25
E13	0.76	1.0	C	2	0.5	1,700	2.00
E15	0.75	1.0	C	2	0.5	1,900	4.00
E16	0.78	0.8	C	5	0	1,500	0.25
E38	0.67	1.0	P	5	0	1,700	2.00
E9	0.66	1.0	P	2	0	1,900	0.25
E36	0.65	1.0	P	5	0	1,500	0.25
E24	0.51	1.0	C	5	0.5	1,900	0.25

* Ratio of 2nd cycle sulfur sorption capacity to 1st cycle sulfur sorption capacity at time = 30 minutes.

R = Ruthner iron oxide.
C = Catalyst-grade iron oxide.
P = pigment-grade iron oxide.

Iron Oxide Grade

The catalyst-grade iron oxide provides generally better reactivity than does pigment-grade iron oxide. More of the higher-reactivity pellets (Table 5) and extrudes (Table 7) were prepared using catalyst-grade iron oxide. Catalyst-grade iron oxide also provides generally better reactivity maintenance.

Bentonite Content

The effects of the bentonite content on reactivity and reactivity maintenance for the spherical pellets were mixed. For extrudes, the 2-percent bentonite-content sorbents provided the highest reactivity and reactivity maintenance.

Organic Binder

Spherical pellets prepared without starch appear to exhibit the highest first-cycle reactivity (Table 5). However, the reactivity maintenance was generally better for pellets prepared using starch (Table 6). More of the lower-reactivity and lower reactivity-maintenance cylindrical extrude sorbents were prepared without Methocel additions.

Induration Conditions

In general, less severe induration conditions resulted in greater sorbent reactivity. These effects are more clear for the extrudes than for the pellets, since a wider range of conditions has been selected for the extrudes examined so far.

Effect of Regeneration Temperature

The effects of regeneration temperature on reactivity maintenance were determined for selected sorbents. Table 9 summarizes the results which showed that second-cycle sulfidation performance (reactivity maintenance) was improved when using lower regeneration temperatures.

Table 9. Effect of Regeneration Temperature

	Reactivity Maintenance[a]		
	700°C	650°C	600°C
Sorbent E2 (at t = 30')	0.84	0.93	1.00
Sorbent P21 (at t = 20')	0.88	0.90	0.93

---

[a] Reactivity maintenance is the ratio of sulfur sorption capacity during Cycle 2 to Cycle 1 at an elapsed time of 20 or 30 minutes.

TASK 4. BENCH-SCALE TEST ANALYSIS

Physical properties and chemical analyses of sorbents from bench-scale tests completed during the reporting period are shown in Table 10. In some cases, a sulfur content gradient was found to exist vertically through the fixed bed. Apparently, some of the sorbents were not completely sulfided in the upper portions of the bed. Although the final sulfidation cycle is continued until the exit gas hydrogen sulfide content remains constant at a value of about 1 volume percent, a continued slow pickup of sulfur in the upper portions of the bed continues. Future analysis of the data will focus on the sulfur content in the bottom portion of the bed rather than the average sulfur content as an indicator of sorbent sulfur sorption capacity at saturation. Since the sulfidation gas is introduced into the bottom of the bed, sorbent in the lower regions of the reactor would be expected to be fully saturated with sulfur.

Of the new sorbents evaluated so far, P11A pellets and E13A extrudes have provided the greatest degree of sulfur sorption capacity at breakthrough during the 10 cycles of sulfidation/oxidation testing. Both of these sorbent formulations were prepared using catalyst-grade iron oxide, a ZnO/Fe_2O_3 ratio of 1.0, and a 2 percent bentonite binder addition level. An average calculated sulfur sorption capacity of 24.7 pounds sulfur per 100 pounds fresh sorbent at 200 ppm H_2S breakthrough was obtained using the P11A sorbent. Sorbent E13A exhibited a calculated average sulfur sorption capacity of 17.7 pounds sulfur per 100 pounds fresh sorbent at breakthrough during the 10 cycles of testing.

Other sorbents prepared using the lower-cost pigment-grade iron oxide have exhibited somewhat lower sulfur sorption capacity at breakthrough but have performed very well in terms of the sulfur sorption capacity at saturation. For example, the P6A, E7A, and E32A sorbents were prepared using pigment-grade iron oxide and exhibited average sulfur sorption capacities at breakthrough of about 10 to 12 pounds sulfur per 100 pounds fresh sorbent during the 10 sulfidation cycles. The corresponding sulfur sorption capacities at saturation for these sorbents prepared using pigment-grade iron oxide were 27.1, 35.4, and 37.4 pounds sulfur per 100 pounds fresh sorbent (based on the measured sulfur content in the bottom portion of the fixed bed), respectively. For comparison, the sulfur sorption capacities at saturation of the P11A and E13A sorbents which were prepared using catalyst-grade iron oxide were 32.6 and 36.9 pounds per 100 pounds fresh sorbent, respectively (also based on the measured sulfur content in the bottom portion of the fixed bed).

Table 10. Physical Properties and Chemical Analyses of Fresh and Sulfided Sorbents

	P27A (Test 11, Reactor R)		P37A (Test 14, Reactor L)		E24A (Test 12, Reactor L)		E28A (Test 13, Reactor R)	
	Fresh Sorbent	Sulfided Sorbent	Fresh Sorbent	Sulfided Sorbent	Fresh Sorbent	Sulfided Sorbent	Fresh Sorbent	Sulfided Sorbent
Physical Properties								
Crush Strength, lb	22.0	33.6	22.1	34.7				
Crush Strength, lb/mm					5.3	5.3	3.3	4.5
Attrition Resistance, %	80.9	83.0	90.7	96.8	91.7	89.9	89.3	93.9
Bulk Density, kg/l	1.143	1.252	1.279	1.504	1.328	1.489	1.229	1.364
Surface Area, m^2/g	1.21	1.45	1.76	2.25	4.15	2.70	4.99	6.79
% <20 Mesh	--	0.46	--	0.08	--	0.31	--	0.20
Chemical Analyses								
Zinc, %	20.0		22.1		25.1		22.4	
Top		20.0		20.3		22.7		20.7
Middle		20.0		20.8		22.8		20.4
Bottom		19.5		20.3		22.4		20.5
Iron, %	41.2		39.2		42.7		38.3	
Top		39.9		38.5		39.3		37.5
Middle		40.0		39.2		39.2		36.8
Bottom		41.1		40.5		37.1		36.3
Sulfur, %	<0.01		0.02		0.06		0.02	
Top		26.8		19.9		32.8		27.2
Middle		25.8		22.4		33.3		29.1
Bottom		26.3		24.5		34.1		29.0

The sulfur sorption capacity results for those sorbents which have undergone bench-scale testing are summarized in Table 11. These results indicate that, in general, cylindrical extrude shapes achieved a somewhat greater sulfur sorption capacity at saturation compared to spherical pellet shapes. The results also illustrated that the pigment-grade iron oxide formulations resulted in only a slightly lower sulfur sorption capacity at saturation compared to the catalyst-grade formulations. Pigment-grade formulations resulted in sulfur sorption capacities at saturation ranging from about 80 to 88 percent of theoretical. The catalyst-grade formulations resulted in sulfur sorption capacities at saturation ranging from about 83 to 94 percent of theoretical.

Table 11. Sulfur Sorption Capacity as a Function of Iron Oxide Grade

	Sulfur Sorption Capacity at Saturation, pound/ 100 pounds Sorbent		Percent of Theoretical Capacity Achieved
	Theoretical	Observed	
Pigment-Grade Fe_2O_3			
Spheres	38.2	30.6	80.1
Extrudes	38.5	33.8	87.8
Catalyst-Grade Fe_2O_3			
Spheres	37.5	31.2	83.2
Extrudes	38.7	36.3	93.8

Note: The theoretical sulfur sorption capacities are based on the composition of the sorbents tested and assume that the zinc and iron oxides are pure and are converted to ZnS and FeS upon sulfidation.

As a result of the good performance of some of the pigment-grade iron oxide formulations at breakthrough and at saturation and because of reduced sorbent materials costs, the pigment-grade iron oxide formulations can be considered as good economic and technical choices for commercial operation.

The grading system for sorbent performance was modified to better reflect the reactivity and durability factors which constitute the basis for evaluation. Fifty percent of the total sorbent rating is based on reactivity parameters, while the remaining 50 percent of the total is based on physical properties which contribute to durability. Table 12 summarizes the general categories to be considered during sorbent performance evaluation.

Table 12. Zinc Ferrite Sorbent Performance Evaluation Criteria

Sorbent Rating Criteria	Weighing Factor, %
Chemical Reactivity Factors	
A. Sulfur Sorption Capacity at 200 ppm H_2S Breakthrough	
1. Average of 10 Cycles	10
2. Increase (or Decrease) During 10 Cycles	10
Subtotal	20
B. Sulfur Sorption Capacity at Saturation	10
C. Surface Area	
1. Fresh Sorbent	5
2. Sulfided Sorbent	5
Subtotal	10
D. Porosity	10
Total	50
Physical Durability Factors	
A. Crush Strength	
1. Fresh Sorbent	10
2. Sulfided Sorbent	10
Subtotal	20
B. Attrition Resistance	
1. Fresh Sorbent	10
2. Sulfided Sorbent	10
Subtotal	20
C. % <20 Mesh Fines Produced During 10 Cycles of Testing	10
Total	50

The sorbent grading system continues to be modified in order to establish criteria for porosity determinations. Initial evaluation of the total porosity, total pore volume, and average pore radius showed no trend with sorbent reactivity as measured in the TGA and bench-scale reactors. However, some initial correlations were noted between reactivity and the porosity contained within selected pore size ranges. In particular, pores with diameters greater than about 0.2 micron appear to contain active desulfurization sites, while smaller pores do not appear to contribute significantly to desulfurization. The reasons for this are under investigation. Samples of fresh and sulfided sorbents were forwarded to the University of Rochester for additional porosity characterization under another DOE/METC contract.

Reports describing the mineralogy of fresh and sulfided P27A, P37A, E24A, and E28A sorbents were prepared and are attached as Appendix A. Each fresh sorbent was found to contain mostly franklinite (zinc ferrite) by X-ray diffraction analysis. Hematite was observed as a distinct phase for two of the three sorbents which were prepared using a stoichiometric zinc deficiency. Sulfided sorbents which were sampled from the bottom portion of the reactor bed contained from 8 to 25 percent franklinite. Sulfided P27A and E24A samples taken from near the top of the reactor contained a similar range of franklinite content. Sulfided P37A and E28A samples taken from near the top of the reactor exhibited greater franklinite content than samples of the same sorbents which were taken near the bottom of the reactor verifying incomplete sulfidation at the top of the reactor in these cases. A sample of the P37A sorbent was removed from the top of the reactor bed following the 9th oxidation cycle (just prior to beginning the sulfidation to saturation step). The sample was shown to exhibit virtually the same X-ray pattern as the fresh sorbent. Similar samples are to be taken after the 9th cycle during the remaining bench-scale tests.

PAPERS AND PRESENTATIONS

The program status and accomplishments were presented to the Eighth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting held in Morgantown, West Virginia, on May 10-12, 1988.[2]

REFERENCES

1. Jha, M. C. and Berggren, M. H., "Two-Stage Regeneration of Zinc Ferrite Desulfurization Sorbent", AMAX Research & Development Center, DOE Contract No. DE-AC21-86MC23172, June 28, 1988.

2. Jha, M. C. and Berggren, M. H., "Enhanced Durability and Reactivity for Zinc Ferrite Desulfurization Sorbent", AMAX Research & Development Center, Prepared for the Eighth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, Morgantown, West Virginia, DOE Contract No. DE-AC21-86MC23172, May 10-12, 1988.

APPENDIX A

MINERALOGY REPORTS

AMAX Research & Development Center

5950 McIntyre Street • Golden, Colorado 80403-7499
(303) 273-7200

Subject: X-Ray Diffraction Analysis of Six Zinc Ferrite Sorbents (80270)

May 12, 1988

To: Mark Berggren

From: Ron Corbett

The six samples received for analysis consisted of three from each of two types or groups: E24A (cylindrical) and P27A (spherical). Individual samples are designated as follows:

E24A	P27A
12-10-L-RD FEED	11-10-R-RD FEED
12-10-L-RD TOP	11-10-R-RD TOP
12-10-L-RD BOTTOM	11-10-R-RD BOTTOM

The E24A FEED is brown, and the P27A FEED is reddish-brown. The other four samples are black.

Representative portions of each sample were ground to fine powders and scanned on the x-ray diffractometer for phase identification. Numerical estimates were made for the amounts of the phases identified, based on peak intensities and comparisons with previous scans. These estimates follow, in tabular form. Without adequate standards, the numbers should not be interpreted in too strict a sense.

R. K. Corbett

Ron K. Corbett

/lc

cc: T. B. Cox
M. C. Jha
Project File

MET NO. 329

X-RAY DIFFRACTION ANALYSIS
OF
ZINC FERRITE SORBENTS

PHASE AND ESTIMATED WEIGHT PERCENT

	SAMPLE	FRANKLINITE ($ZnFe_2O_4$)	SPHALERITE (β-ZnS)	WURTZITE (α-ZnS)	PYRRHOTITE($Fe_{1-x}S$) + TROILITE(FeS)	HEMATITE (Fe_2O_3)	TOTAL UNIDENTIFIED
1.	12-10-L-RD FEED	98+	--	--	--	--	<2
2.	12-10-L-RD TOP	8	40	22	30	--	tr (<1)
3.	12-10-L-RD BOTTOM	8	40	22	30	--	tr (<1)
4.	11-10-R-RD FEED	92	--	--	--	7	tr ($\leq$1)
5.	11-10-R-RD TOP	25	38	10	27	--	tr (<1)
6.	11-10-R-RD BOTTOM	25	38	10	27	--	tr (<1)

AMAX Research & Development Center

5950 McIntyre Street • Golden, Colorado 80403-7499
(303) 273-7200

Subject: X-Ray Diffraction Analysis of Seven Zinc Ferrite Sorbent Samples (80270)

June 28, 1988

To: Mark Berggren

From: Ron Corbett

Of the seven samples submitted, three are from group or type E28A (cylindrical) and four are from group or type P37A (spherical). Individual sample designations and colors are as follows:

Sample	Color
E28A	
13-10-R-RD Feed	Brown
13-10-R-RD Top	Black
13-10-R-RD Bottom	Black
P37A	
14-10-L-RD Feed	Brown
14-9-L-OX Top of Reactor (regen. sorbent)	Reddish Brown
14-10-L-RD Very Top	Black
14-10-L-RD Very Bottom	Black

Diffractometer scans for phase identification were run on fine powders produced from representative portions of each sample. Peak intensities on the resulting patterns were used to make numerical abundance estimates for the phases identified, after comparison with previous scans on similar material. The estimates are subject to error, particularly without preparation of standard mixtures. They are presented in tabular form on an attached page.

R.K. Corbett

R.K. Corbett

RKC:jb

Enclosure

cc: T.B. Cox
M.C. Jha
Project File
Met No. 384

AMAX MINERALS & ENERGY

X-Ray Diffraction Analysis of Zinc Ferrite Sorbents

PHASE AND ESTIMATED WEIGHT PERCENT

	Sample	Franklinite ($ZnFe_2O_4$)	Sphalerite (β-ZnS)	Wurtzite (α-ZnS)	Pyrrhotite ($Fe_{1-X}S$) + Troilite (FeS)	Hematite (Fe_2O_3)	Total Unidentified
1.	13-10-R-RD Feed	95	-	-	-	5	tr (<1)
2.	13-10-R-RD Top	18	45	15	22	-	tr (<1)
3.	13-10-R-RD Bottom	12	42	15	30	-	tr (≤1)
4.	14-10-L-RD Feed	98+	-	-	-	-	< 2
5.	14-9-L-OX Top of Reactor	98+	-	-	-	-	< 2
6.	14-10-L-RD Very Top	30	42	12	16	-	tr (<1)
7.	14-10-L-RD Very Bottom	20	40	13	27	-	tr (<1)

END

DATE FILMED

9/01/92