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**Enhanced Durability and Reactivity for
Zinc Ferrite Desulfurization Sorbent
Volume I
Bench-Scale Testing and Analysis**

Final Report

**M.H. Berggren
M.C. Jha**

October 1989

Work Performed Under Contract No.: DE-AC21-86MC23172

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

**By
AMAX Research and Development Center
Golden, Colorado**

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October 1989

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The authors would like to thank Mr. Suresh Jain of METC, the Contracting Officer's Technical Representative (COTR), for technical guidance provided throughout the program.

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The AMAX R&D project team members contributed greatly to the project success. Tony Blandon set up much of the laboratory procedures and equipment and utilized his skills in preparing the numerous sorbent formulations. Mike O'Sullivan was responsible for much of the sorbent characterization, bench-scale testing, and data collection. Linda Baltich provided valuable input in the preparation of the experimental plan and in the design and installation of the data acquisition system.

Significant effort was also put forth by several other AMAX R&D employees. In particular, we would like to recognize Jeff Boyd for contributing to the establishment of gas analysis techniques and their implementation, Ron Corbett and Jerry Odekirk for providing mineralogical support for the program, and Wendy Kennedy for preparing and assembling reports and presentations.

EXECUTIVE SUMMARY

AMAX Research & Development Center (AMAX R&D) investigated methods for enhancing the reactivity and durability of zinc ferrite desulfurization sorbents. 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. For this program, the reactivity of the sorbent may be defined as its sulfur sorption capacity at the breakthrough point and at saturation in a bench-scale, fixed-bed reactor. Durability may be defined as the ability of the sorbent to maintain important physical characteristics such as size, strength, and specific surface area during 10 cycles of sulfidation and oxidation.

Two base case sorbents, a spherical pellet and a cylindrical extrude used in related METC-sponsored projects, were used to provide a basis for the aimed enhancement in durability and reactivity. Sorbent performance was judged on the basis of physical properties, single particle kinetic studies based on thermogravimetric (TGA) techniques, and multi-cycle bench-scale testing of sorbents. A sorbent grading system was utilized to quantify the characteristics of the new sorbents prepared during the program. Significant enhancements in both reactivity and durability were achieved for the spherical pellet shape over the base case formulation. Overall improvements to reactivity and durability were also made to the cylindrical extrude shape.

The primary variables which were investigated during the program included iron oxide type, zinc oxide:iron oxide ratio, inorganic binder concentration, organic binder concentration, and induration conditions. The effects of some variables were small or inconclusive. Based on TGA studies and bench-scale tests, induration conditions were found to be very significant. The main effects of the variables are summarized briefly below.

- Catalyst-grade iron oxide was found to provide generally superior desulfurization performance. However, selected lower-cost pigment-grade iron oxide formulations also resulted in good overall desulfurization performance and physical durability.
- An alternative iron oxide powder, a very low-cost Ruthner process product, was found to provide very good reactivity during preliminary tests. Additional tests demonstrated that Ruthner process iron oxide can be formulated into reactive, durable, and very low-cost zinc ferrite sorbent.
- Zinc ferrite sorbents formulated using a $\text{ZnO}:\text{Fe}_2\text{O}_3$ stoichiometric molar ratio of 1.0 provided somewhat better desulfurization response than those sorbents formulated using a 0.8 ratio.

- Sulfur sorption capacity at a hydrogen sulfide gas breakthrough concentration of 200 ppm was greater for sorbents prepared using lower bentonite inorganic binder concentrations.
- The addition of an organic binder resulted in overall poorer sulfidation performance at breakthrough. However, sulfur sorption capacity at sulfur saturation was slightly improved for sorbent formulations which incorporated an organic binder.
- For any given sorbent formulation, more severe induration conditions (higher temperatures and longer times) resulted in improved sorbent durability and lower sorbent reactivity.

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
PROGRAM BACKGROUND	2
TASK 1. EXPERIMENTAL TEST PLAN	3
ZINC OXIDE:IRON OXIDE RATIO	3
IRON OXIDE GRADE	4
ORGANIC AND INORGANIC BINDER TYPES AND CONCENTRATIONS	5
SORBENT SHAPE	5
INDURATION CONDITIONS	6
SINGLE PARTICLE KINETIC STUDIES	6
SELECTION OF SORBENTS FOR BENCH-SCALE TESTING	6
BENCH-SCALE TESTING	6
BENCH-SCALE TEST ANALYSIS	7
TASK 2. SORBENT PREPARATION AND CHARACTERIZATION	8
SORBENT PREPARATION	8
Raw Materials	8
Spherical Pellet Sorbent Preparation	15
Cylindrical Extrude Sorbent Preparation	16
Sorbent Drying	17
Sorbent Induration	17
Sorbent Preparation Using Ruthner Process Iron Oxide	18
SORBENT CHARACTERIZATION	18
Bulk Density	19
Crush Strength	19
Attrition Resistance	21
Surface Area	23
Porosity	25
Mineralogy	25
Sorbent Prepared Using Ruthner Process Iron Oxide	25
TASK 3. BENCH-SCALE TESTING	26
BENCH-SCALE REACTOR SYSTEM	26
TEST CONDITIONS	28
BENCH-SCALE TEST RESULTS	29
Sulfur Sorption Capacity at Breakthrough	32
Sulfur Sorption Capacity at Saturation	37
Sorbent Regeneration	37
Chemical Analysis of Fresh and Sulfided Sorbents	38
SINGLE PARTICLE KINETIC STUDIES	38
Test Procedures and Conditions	40
ZnO:Fe ₂ O ₃ Ratio	44

TABLE OF CONTENTS (Continued)

	<u>Page</u>
Iron Oxide Grade	44
Bentonite Content	44
Organic Binder	47
Induration Conditions	47
Surface Area and Porosity	47
Effect of Regeneration Temperature	48
ALTERNATE REGENERATION PROCEDURE TESTING	49
 TASK 4. BENCH-SCALE TEST ANALYSIS	 51
CORRELATION OF TGA WITH BENCH-SCALE TEST RESULTS	51
CHEMICAL ANALYSES	51
PHYSICAL PROPERTIES	52
EFFECT OF SORBENT SHAPE	53
EFFECT OF IRON OXIDE GRADE	55
EFFECT OF ZnO:Fe ₂ O ₃ RATIO	56
EFFECT OF BENTONITE CONTENT	56
EFFECT OF ORGANIC BINDER	57
EFFECT OF INDURATION CONDITIONS	60
EFFECT OF POROSITY	61
EFFECT OF SURFACE AREA	65
SORBENT MINERALOGY	67
SORBENT GRADING SYSTEM	71
EFFECT OF SULFIDATION TEMPERATURE	75
EFFECT OF SULFIDATION GAS FLOW RATE	75
 TASK 5. TOPICAL REPORT	 77
 TASK 6. ADDITIONAL SORBENT TESTING	 78
SORBENT PREPARATION AND CHARACTERIZATION	78
Cylindrical Extrudes	78
Spherical Pellets	85
Chlorine Removal	88
BENCH-SCALE TESTING	90
Bench-Scale Test Results	90
Single Particle Kinetic Studies at LSU	94
BENCH-SCALE TEST ANALYSIS	96
Correlation of TGA with Bench-Scale Test Results	96
Chemical Analyses	96
Physical Properties	96
Effect of Sorbent Shape	98
Effect of Iron Oxide Grade	98
Sorbent Porosity	100
Sorbent Mineralogy	100
Sorbent Grading	101
PREPARATION OF A 1-CUBIC-FOOT SORBENT SAMPLE	101

TABLE OF CONTENTS
(Continued)

	<u>Page</u>
SORBENT PREPARATION SPECIFICATIONS	104
SELECTION OF SORBENT RAW MATERIALS	104
SORBENT MATERIALS COSTS	105
SORBENT PREPARATION EQUIPMENT	106
SORBENT QUALITY CONTROL	107
CONCLUSIONS	108
RECOMMENDATIONS	110
REFERENCES	111
APPENDIX A	
MULTI-CYCLE TEST OPERATION NOTES AND OBSERVATIONS . .	112
APPENDIX B	
TWO-STAGE SORBENT REGENERATION	117
APPENDIX C	
MINERALOGY REPORTS	155
APPENDIX D	
SORBENT RAW MATERIALS	182

LIST OF TABLES

		<u>Page</u>
Table 1.	Statistical Screening Design Test Matrix . .	4
Table 2.	Zinc Ferrite Spherical Pellet Characteristics	9
Table 3.	Zinc Ferrite Cylindrical Extrude Characteristics	12
Table 4.	Size Analysis of Zinc Ferrite Sorbent Raw Materials	14
Table 5.	Sorbent Raw Materials and Costs	14
Table 6.	Chemical Analysis of Zinc Ferrite Sorbent Raw Materials	15
Table 7.	Sorbent Induration Conditions	17
Table 8.	Crush Strength Determinations of Spherical Pellet Sorbent P27A	20
Table 9.	Surface Areas of Iron Oxide and Zinc Oxide Powders	25
Table 10.	Sulfidation Gas Composition	29
Table 11.	Physical Characteristics of Spherical Pellet Sorbents Selected for Bench-Scale Testing . .	30
Table 12.	Physical Characteristics of Cylindrical Extrude Sorbents Selected for Bench-Scale Testing	31
Table 13.	Spherical Pellet Sorbent Sulfidation Performance	35
Table 14.	Cylindrical Extrude Sorbent Sulfidation Performance	36
Table 15.	Chemical Analysis of Fresh and Sulfided Spherical Pellet Sorbents	39
Table 16.	Chemical Analysis of Fresh and Sulfided Cylindrical Extrude Sorbents	39
Table 17.	Comparison of Pellet Reactivity	42
Table 18.	Comparison of Extrude Reactivity	43

LIST OF TABLES
(Continued)

	<u>Page</u>
Table 19. Comparison of Pellet Reactivity Maintenance .	45
Table 20. Comparison of Extrude Reactivity Maintenance	46
Table 21. Effect of Regeneration Temperature	49
Table 22. Physical Properties and Chemical Analysis of Fresh and Sulfided Sorbents	54
Table 23. Effect of Iron Oxide Grade on Sulfur Sorption Capacity	55
Table 24. Effect of ZnO:Fe ₂ O ₃ Ratio and Iron Oxide Grade on Sulfur Sorption Capacity	56
Table 25. Effect of ZnO:Fe ₂ O ₃ Ratio and Iron Oxide Grade on Sorbent Durability	57
Table 26. Effect of Bentonite Content on Sulfur Sorption Capacity	57
Table 27. Effect of Bentonite Content on Sorbent Durability	58
Table 28. Effect of Organic Binder Addition on Sulfur Sorption Capacity	59
Table 29. Effect of Organic Binder Addition on Sorbent Durability	59
Table 30. Effect of Induration Conditions on Sulfur Sorption Capacity (Cylindrical Extrude Sorbents)	60
Table 31. Effect of Induration Conditions on Sorbent Durability (Cylindrical Extrude Sorbents) . .	61
Table 32. Porosity of Fresh and Sulfided Sorbents . . .	64
Table 33. X-Ray Diffraction Analysis of Zinc Ferrite Spherical Pellet Sorbents	68
Table 34. X-Ray Diffraction Analysis of Zinc Ferrite Cylindrical Extrude Sorbents	69
Table 35. Zinc Ferrite Sorbent Grading System Criteria	72

LIST OF TABLES
(Continued)

	<u>Page</u>
Table 36. Zinc Ferrite Spherical Pellet Sorbent Performance	73
Table 37. Zinc Ferrite Cylindrical Extrude Sorbent Performance	74
Table 38. Summary of Sorbent Performance	76
Table 39. Zinc Ferrite Cylindrical Extrude Characteristics (Ruthner Process Iron Oxide Formulations)	80
Table 40. Effect of Starch and Fiber Additions on Cylindrical Extrude Sorbent Properties	84
Table 41. Zinc Ferrite Spherical Pellet Characteristics (Ruthner Process Iron Oxide Formulations)	86
Table 42. Effect of Starch and Fiber Additions on Spherical Pellet Sorbent Properties	89
Table 43. Chlorine Content of Ruthner Process Iron Oxide Powder and Indurated Sorbents	90
Table 44. Physical Characteristics of Sorbents Formulated Using Ruthner Process Iron Oxide	91
Table 45. Performance of Sorbents Prepared Using Ruthner Process Iron Oxide	93
Table 46. Chemical Analysis of Zinc Ferrite Sorbents Formulated Using Ruthner Iron Oxide	94
Table 47. Physical Characteristics of Fresh and Sulfided Sorbents	97
Table 48. Effect of Iron Oxide Grade on Sorbent Properties	99
Table 49. Porosity of Fresh and Sulfided Sorbents Prepared Using Ruthner Process Iron Oxide	101
Table 50. Ruthner Process Iron Oxide Formulation Sorbent Performance	102
Table 51. Characteristics of a 1-Cubic-Foot Sample of Sorbent E44A	103

LIST OF TABLES
(Continued)

	<u>Page</u>
Table 52. Sorbent Preparation Materials Performance and Costs	106

LIST OF FIGURES

		<u>Page</u>
Figure 1.	Spherical pellet crush strength as a function of sorbent bulk density.	21
Figure 2.	Attrition resistance as a function of sorbent bulk density.	22
Figure 3.	Attrition resistance as a function of spherical pellet sorbent crush strength. . .	23
Figure 4.	Attrition resistance as a function of cylindrical extrude sorbent crush strength.	24
Figure 5.	Sorbent surface area as a function of bulk density.	24
Figure 6.	Bench-scale reactor system.	27
Figure 7.	H ₂ S exit gas concentration during spherical pellet sorbent sulfidation.	33
Figure 8.	H ₂ S exit gas concentration during cylindrical extrude sorbent sulfidation.	33
Figure 9.	Sulfur sorption capacity at H ₂ S breakthrough for spherical pellet sorbents.	34
Figure 10.	Sulfur sorption capacity at H ₂ S breakthrough for cylindrical extrude sorbents.	34
Figure 11.	SO ₂ concentration during regeneration (UCI T-2465 sorbent).	38
Figure 12.	Typical TGA response for 1-1/2 cycle test. .	41
Figure 13.	Sulfur sorption capacity as a function of sorbent reactivity.	52
Figure 14.	Sulfur sorption capacity as a function of sorbent porosity.	62
Figure 15.	Sorbent reactivity as a function of porosity.	63
Figure 16.	Correlation of calculated porosity and measured porosity.	63

LIST OF FIGURES
(Continued)

	<u>Page</u>
Figure 17. Sulfur sorption capacity as a function of fresh sorbent surface area.	65
Figure 18. Sulfur sorption capacity as a function of sulfided sorbent surface area.	66

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.¹ The zinc ferrite sorbents experience chemical, physical, and thermal changes during sulfidation and regeneration. Deterioration of sorbent sulfidation performance and physical characteristics is strongly influenced by the chemical composition of the sorbent and the method of preparation.²

In order to minimize the cost of high temperature desulfurization, it is necessary to develop low cost sorbents with long useful life. This program at AMAX R&D, under DOE/METC Contract No. DE-AC21-86MC23172, was aimed at systematically investigating methods for enhancing the physical durability and chemical reactivity of the zinc ferrite desulfurization sorbent.

The base program was 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

In addition, the contract provided an option to perform additional testing under Task 6.

This final report presents the results of the base program and contract option. It is a two volume report. The second volume presents detailed results of single particle kinetic studies performed at Louisiana State University under a subcontract.

PROGRAM BACKGROUND

Zinc ferrite was identified as an effective coal gas desulfurization sorbent during previous work at METC and AMAX R&D.^{1,2} The investigations showed that hydrogen sulfide could be removed to a few ppm level in the exit gas in a fixed-bed reactor until a breakthrough occurs. The following reaction describes the desulfurization process.

Sorbent can be regenerated according to the following reaction.

A mixture of steam and air is used in practice to avoid excessive heat generation and sintering of the sorbent bed during regeneration.

The goal of the program was to identify and investigate preparation methods which could be used to produce sorbents which exhibit enhanced reactivity and durability. Both of these characteristics have an effect on the economics of the high-temperature desulfurization process. For the present program, sorbent reactivity has been defined in terms of:

- Sulfur sorption capacity during single particle kinetic studies in a thermogravimetric analyzer (TGA).
- Sulfur sorption capacity at H_2S breakthrough in a bench-scale reactor.
- Sulfur sorption capacity at near saturation.

Sorbent durability has been defined in terms of physical characteristics such as crush strength, size, and attrition resistance for both fresh and sulfided sorbent.

Based on past experience, it was projected that a comparative evaluation of reactivity and durability could be made by bench-scale testing of sorbents during 10 cycles.

A zinc ferrite sorbent (Sample T-2465) produced by United Catalysts Incorporated (UCI) and used in the process development unit test program at KRW Energy Systems was designated as the cylindrical extrude base case sorbent for the program. Another spherical pellet sorbent produced for METC by AMAX R&D was designated as the spherical pellet base case sorbent for the program. These base case sorbents were selected to provide a basis for comparing performance of new sorbents produced during the present program.

TASK 1. EXPERIMENTAL TEST PLAN

An experimental test plan was developed to select the test variables and their ranges and to establish the responses to be measured. Some of the selected test ranges were modified during the course of the program based on the preliminary results. The overall experimental approach is discussed in this section.

Test variables which were selected for investigation during the program include the following.

- Iron Oxide Grade
- ZnO:Fe₂O₃ Ratio
- Bentonite Addition Level
- Organic Binder Addition
- Sorbent Shape

Different induration temperatures and times were utilized following a standard sorbent drying procedure.

The dependent responses measured during the program include the following.

- Bulk Density
- Crush Strength
- Attrition Resistance
- Surface Area
- Porosity
- Reactivity

A statistical screening design test matrix for sorbent preparation variables was prepared. Due to the large number of variables, a partial factorial design was utilized. Table 1 summarizes the sorbent preparation variables and their levels.

The values in Table 1 represented the best estimates based on previous sorbent preparation activities at AMAX R&D² and on preliminary tests conducted during this program. The primary variables and selection of their levels are discussed below.

ZINC OXIDE:IRON OXIDE RATIO

Iron oxide:zinc oxide mole ratios of 0.8 and 1.0 were utilized in order to establish whether a zinc deficiency might improve long-term performance by potentially preventing zinc migration to the sorbent surfaces. Previous work had shown that in some cases, a coating of zinc on the sorbent surfaces reduced desulfurization reactivity.² This occurred primarily in sorbents which were formulated using a stoichiometric excess of zinc oxide.

Table 1. Statistical Screening Design Test Matrix

Run No.	Iron Oxide Grade	ZnO/Fe ₂ O ₃ Ratio	Bentonite Addition Level, %	Organic Binder Addition, %	Sorbent Shape
1	Catalyst	0.8	2	0.0	Extrudes
2	Pigment	0.8	2	0.0	Pellets
3	Catalyst	1.0	2	0.0	Pellets
4	Pigment	1.0	2	0.0	Extrudes
5	Catalyst	0.8	2	2.0	Pellets
6	Pigment	0.8	2	0.5	Extrudes
7	Catalyst	1.0	2	0.5	Extrudes
8	Pigment	1.0	2	2.0	Pellets
9	Catalyst	0.8	5	0.0	Extrudes
10	Pigment	0.8	5	0.0	Pellets
11	Catalyst	1.0	5	0.0	Pellets
12	Pigment	1.0	5	0.0	Extrudes
13	Catalyst	0.8	5	2.0	Pellets
14	Pigment	0.8	5	0.5	Extrudes
15	Catalyst	1.0	5	0.5	Extrudes
16	Pigment	1.0	5	2.0	Pellets
17	Catalyst	0.8	10	0.0	Extrudes
18	Pigment	0.8	10	0.0	Pellets
19	Catalyst	1.0	10	0.0	Pellets
20	Pigment	1.0	10	0.0	Extrudes
21	Catalyst	0.8	10	2.0	Pellets
22	Pigment	0.8	10	0.5	Extrudes
23	Catalyst	1.0	10	0.5	Extrudes
24	Pigment	1.0	10	2.0	Pellets

IRON OXIDE GRADE

Iron oxide has been shown to be effective for the removal of hydrogen sulfide gas at high temperatures. One limitation in the use of iron oxide for the desulfurization of coal gas is that the H₂S concentration level cannot be reduced to a few ppm level required for applications such as molten carbonate fuel cells.²

During previous work at AMAX R&D, several grades of iron oxide were identified. The different grades range in cost from about \$0.05 to about \$2.00 per pound. The sorbents produced using the different grades of iron oxide exhibited very different reactivities. The differences in reactivity were thought to be attributed to particle size, specific surface area, and process conditions used in their production. A low-cost mineral grade iron oxide exhibited poor reactivity and was not recommended for further investigation.² The two different iron oxide grades selected for the program (catalyst and pigment) were utilized to establish the effects on sorbent sulfur sorption capacity at H₂S breakthrough and at saturation.

The pigment-grade iron oxide selected for the program contains a few percent manganese. Earlier work performed at LSU indicated that manganese oxide is a good desulfurizing agent.³ A manganese oxide based sorbent was also investigated by U. S. Steel Corporation.⁴ For the purposes of this program, the manganese content of the pigment-grade iron oxide was considered to be a substitute for a portion of the iron.

ORGANIC AND INORGANIC BINDER TYPES AND CONCENTRATIONS

An organic binder, Methocel, was used by United Catalysts Inc. (UCI) as an extruding aid in producing zinc ferrite extrudes used in earlier work at METC. While the surface area of these sorbents was high and the initial reactivity was good, the sorbents tended to disintegrate to fines and the porosity was reduced during repeated cyclic testing. The Methocel burned away during induration, leaving a porous structure, but there was no permanent bond to keep the structure intact when chemical and structural changes took place during sulfidation and regeneration.

The use of inorganic binders such as bentonite overcomes this problem and results in a durable sorbent, as shown by work performed during a previous contract at AMAX R&D.² Based on those results, METC recommended that UCI use a 2 percent bentonite addition as the binder in the production of zinc ferrite cylindrical extrudes to be tested at KRW Energy Systems. The same sorbent (T-2465) was also designated as the base case cylindrical extrude sorbent for this program. The use of a low amount of bentonite is intended to provide additional strength while maintaining a high level of reactive zinc and iron oxides. For the present program, additional quantities of bentonite (up to 10 percent) were investigated to determine the effects on sorbent durability and reactivity.

A combination of inorganic and organic binders was investigated in previous work at AMAX R&D.² Test results suggested that this is a valid approach. This program examined the use of an inorganic binder (bentonite) both with and without an organic binder (Methocel for cylindrical extrudes and corn starch for spherical pellets).

SORBENT SHAPE

Both cylindrical extrude and spherical pellet shapes have been used in past work at AMAX R&D.² United Catalysts has prepared sorbents by the extrusion method, which is standard in the preparation of many catalysts for the petrochemical industry. AMAX preferred to use a disk pelletizer, which is widely used to produce strong iron ore pellets for the steel industry. Spherical pellets may be preferable from a handling point of view and may produce a more uniform gas flow pattern

in desulfurization/regeneration reactors. Both sorbent shapes were investigated during the present program.

INDURATION CONDITIONS

Agglomerates produced using either the pelletization or extrusion methods require induration at high temperature to impart a combination of strength and porosity. The important parameters are temperature and time. Temperatures ranging from 1,500 to 1,900°F (815 to 1,038°C) for times periods of 15 minutes to 4 hours were selected for investigation.

SINGLE PARTICLE KINETIC STUDIES

Sorbent reactivity and reactivity maintenance measurements were performed using a thermogravimetric analyzer (TGA). Selected sorbents were forwarded to the Department of Chemical Engineering at Louisiana State University (LSU) for these tests. The TGA procedure selected for the program consisted of an initial reduction step performed in the absence of H₂S, sulfidation at 1,022°F (550°C), regeneration at 1,292°F (700°C), and a second sulfidation step at 1,022°F.

The degree of sulfidation observed at some given elapsed time was used to provide an index of reactivity (from the first sulfidation cycle) and reactivity maintenance (from the difference in sulfidation performance observed during the second sulfidation cycle). Rankings of the sorbent reactivity and reactivity maintenance were used to establish the effects of sorbent preparation variables on sulfidation performance.

SELECTION OF SORBENTS FOR BENCH-SCALE TESTING

Those sorbents which exhibited the best overall characteristics in terms of reactivity (measured by TGA) and physical properties were selected for multi-cycle bench-scale testing in the 2-inch diameter reactors at the AMAX R&D facilities.

Fifteen sorbents were to be selected for multi-cycle bench-scale testing. However, a contract modification was later issued to substitute bench-scale investigation of an alternate sorbent regeneration procedure for two of the sorbent tests. As such, 13 sorbents (including the two base case sorbents) were selected for the standard bench-scale tests under the base contract. The investigation of alternate regeneration procedures is discussed elsewhere.

BENCH-SCALE TESTING

The procedure selected for bench-scale testing consisted of cyclic sulfidation and regeneration steps. Sulfidation was

carried out to a 200 ppm H₂S breakthrough value (inlet value being 10,000 ppm) during 9 test cycles at 1,022°F (550°C). A standard regeneration procedure was used between sulfidation cycles to convert the sulfided sorbents back to oxide form with the concurrent release of SO₂ gas. Regeneration was carried out at temperatures between 1,292 and 1,382°F (700 and 750°C). During the 10th and final sulfidation step, the sulfidation was continued until near saturation (when the reactor exit gas H₂S concentration approached that of the inlet gas). The test series were completed following the 10th sulfidation step.

BENCH-SCALE TEST ANALYSIS

Samples of fresh and sulfided sorbents were analyzed for chemical and physical properties. Effects of the sorbent preparation conditions on sorbent reactivity and durability were then determined. A sorbent grading system was established to quantify overall sorbent performance in terms of chemical reactivity and physical durability factors.

TASK 2. SORBENT PREPARATION AND CHARACTERIZATION

Spherical pellet and cylindrical extrude formulations were prepared according to the screening test matrix shown in Table 1. As discussed in the following sections, some deletions to the test matrix were required as a result of difficulties in preparing certain cylindrical extrude sorbents. Tables 2 and 3 summarize the sorbent preparation conditions and the characterizations which were performed. The preparation run numbers and conditions shown in Table 1 correspond to those shown in Tables 2 and 3.

SORBENT PREPARATION

Sorbents for the research program were formulated using two shapes, spherical pellets and cylindrical extrudes. Except for the two base case sorbents shown in Tables 2 and 3, all of the spherical pellet formulations prepared for the program began with the letter P (example, P11). All cylindrical extrude formulations prepared for the program began with the letter E (example, E13). Those sorbents which were selected for multi-cycle bench-scale testing and which were then indurated in larger batches contain an "A" designation following the sorbent number (example, P11A).

The characteristics of raw materials used in the program and the processing of the blended dry powders into finished sorbent shapes are described below.

Raw Materials

The dry powder materials used in the program were of sufficiently small particle size to be utilized without further size reduction. The particle size distributions of the sorbent raw materials are shown in Table 4. Particle size distributions were determined with a SediGraph using particle sedimentation techniques. The pigment-grade iron oxide was observed to contain a small quantity of magnetic material. The catalyst-grade iron oxide also contained some magnetic material, but in lower concentration.

Except for catalyst-grade iron oxide, the different sorbent preparation components and their projected costs (based on 1988/1989 Chemical Marketing Reporter or vendor quotes, FOB point of origin) are summarized in Table 5. The cost for the catalyst-grade iron oxide is based on the purchase of smaller lots. Commercial prices and availability will depend on actual market conditions according to its producer, United Catalysts Inc.

Chemical analyses of the major sorbent feed materials were performed. The zinc oxide contained less than 0.3 percent

Table 2. Zinc Ferrite Spherical Pellet Characteristics

Sorbent Sample Number	Pellet Formulation					Induration Conditions		Physical Properties			BET	Porosity,	TGA
	Run No.	Fe ₂ O ₃ Grade	ZnO/ Fe ₂ O ₃	% Bentonite	% Starch	Temperature, °F	Time, Hours	Bulk Density, kg/l	Crush Strength, lb	Attrition Resistance, %	Surface Area, m ² /g	% (Pores >0.012 μm)	Testing
1094-59	Base	Pigment	1.0	5	2	1,825	3.00	1.014	5.1	45.5	1.01	59.2	*
P1	2	Pigment	0.8	2	0	1,500	0.25	0.876	4.6	34.9			
P2						1,500	4.00	0.912	3.8	23.3			
P3						1,700	2.00	0.916	4.8	39.8			
P4						1,700	2.00	0.860	5.7	46.0			
P5						1,900	0.25	0.952	6.6	48.5	3.95		*
P6						1,900	4.00	1.529	40.3	89.8	1.28		*
P6A						1,900	4.00	1.488	22.0	89.0	1.68	52.1	
P7	3	Catalyst	1.0	2	0	1,500	0.25	0.999	9.3	57.2			
P8						1,500	4.00	0.952	6.8	59.3			
P9						1,700	2.00	1.013	10.0	66.3			
P10						1,700	2.00	1.048	10.1	68.4	2.43		*
P11						1,900	0.25	1.036	10.5	67.6	2.47		*
P11A						1,900	0.25	1.141	16.6	80.5	2.63	63.8	
P12						1,900	4.00	1.273	21.5	75.5	1.38		*
P13	5	Catalyst	0.8	2	2	1,500	0.25	1.028	14.5	83.8			
P14						1,500	4.00	1.034	17.6	81.3			
P15						1,700	2.00	1.075	18.2	86.2			
P16						1,900	0.25	1.196	27.3	89.3	1.55		*
P17						1,900	4.00	1.339	32.8	91.6	1.43		*
P18	9	Catalyst	1.0	10	0	1,500	0.25	0.956	10.2	63.5			
P19						1,500	4.00	0.955	11.3	66.5			
P20						1,700	2.00	0.952	11.6	68.0			
P21						1,900	0.25	0.955	12.3	70.3	2.46		*
P22						1,900	4.00	1.132	20.8	77.2	2.10		*
P22A						1,900	4.00	1.146	19.4	82.4	1.95	59.6	

Table 2. Zinc ferrite Spherical Pellet Characteristics
(Continued)

Sorbent Sample Number	Pellet Formulation					Induration Conditions		Physical Properties			BET	Porosity,	TGA Testing
	Run No.	Fe ₂ O ₃ Grade	ZnO/ Fe ₂ O ₃	% Bentonite	% Starch	Temperature, °F	Time, Hours	Bulk Density, kg/l	Crush Strength, lb	Attrition Resistance, %	Surface Area, m ² /g	% (Pores >0.012 μm)	
P23	21	Catalyst	0.8	10	2	1,500	0.25	0.914	5.7	57.6			
P24						1,500	4.00	0.902	7.1	61.0			
P25						1,700	2.00	0.922	10.4	65.0			
P26						1,900	0.25	0.956	15.0	74.5	2.05		*
P27						1,900	4.00	1.111	21.2	80.1	1.91		*
P27A						1,900	4.00	1.143	22.0	80.9	1.21	56.2	
P28	8	Pigment	1.0	2	2	1,500	0.25	0.900					
P29						1,500	4.00	0.918	5.7				
P30						1,700	2.00	0.906	3.9				
P31						1,900	0.25	0.972	5.5		2.57		*
P32						1,900	4.00	1.270	19.4				
P32A						1,900	4.00	1.276	20.5	74.9	0.77	52.3	*
P33	10	Pigment	0.8	5	0	1,500	0.25	0.878					
P34						1,500	4.00	0.834	4.3				
P35						1,700	2.00	0.877	5.2				
P36						1,900	0.25	0.993	10.0	50.1			
P37						1,900	4.00	1.456	34.8	89.2			
P37A						1,900	4.00	1.279	22.1	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				
P40						1,700	2.00	0.928	3.9				
P41						1,900	0.25	1.020	9.1	60.5			
P42						1,900	4.00	1.383	31.2	85.4			
P42A						1,900	4.00	1.240	17.0	79.1	1.07		*

Table 2. Zinc Ferrite Spherical Pellet Characteristics
(Continued)

Sorbent Sample Number	Pellet Formulation					Induration Conditions		Physical Properties			BET	Porosity,	TGA
	Run No.	Fe ₂ O ₃ Grade	ZnO/ Fe ₂ O ₃	% Bentonite	% Starch	Temperature, °F	Time, Hours	Bulk Density, kg/l	Crush Strength, lb	Attrition Resistance, %	Surface Area, m ² /g	% (Pores >0.012 μm)	Testing
P43	11	Catalyst	1.0	5	0	1,500	0.25	0.930	5.8				
P44						1,500	4.00	0.939	5.1				
P45						1,700	2.00	0.979	6.9				
P46						1,900	0.25	0.988	6.8				
P47						1,900	4.00	1.234	17.7	78.0	1.40		*
P48	13	Catalyst	0.8	5	2	1,500	0.25	0.889	7.3				
P49						1,500	4.00	0.882	5.7				
P50						1,700	2.00	0.920	9.0				
P51						1,900	0.25	0.997	13.4	67.3	1.76		
P52						1,900	4.00	1.142	22.3	74.5	1.63		*
P53	18	Pigment	0.8	10	0	1,500	0.25	0.860	3.5				
P54						1,500	4.00	0.846	5.1				
P55						1,700	2.00	0.858	5.6				
P56						1,900	0.25	0.860	5.8				
P57						1,900	4.00	1.275	45.3	84.9	1.67		*
P58	24	Pigment	1.0	10	2	1,500	0.25	0.712	0.6				
P59						1,500	4.00	0.733	0.8				
P60						1,700	2.00	0.751	1.8	20.4			
P61						1,900	0.25	0.729	2.2	15.5			
P62						1,900	4.00	0.947	12.2	50.8	1.64		*

Note: An "A" designation in the sorbent sample number indicates preparation of a larger sample for cyclic testing.

Table 3. Zinc Ferrite Cylindrical Extrude Characteristics

Sorbent Sample Number	Extrude Formulation					Induration Conditions		Physical Properties				BET	Porosity,	TGA
	Run No.	Fe ₂ O ₃ Grade	ZnO/ Fe ₂ O ₃	% Bentonite	% Methocel	Temp., °F	Time, Hours	Bulk Density, kg/l	Crush Strength, lb/mm	Length, mm	Attrition Resistance %	Surface Area, m ² /g	% (Pores >0.012 μm)	Testing
T-2465	Base	Catalyst	1.0	2	0	1,550	2.00	1.306	3.5	8.6	88.8	3.30	58.2	*
E1	1	Catalyst	0.8	2	0	1,500	0.25	1.199	2.6	11.1	90.2	5.12		*
E2						1,500	4.00	1.120	3.6	11.8	92.3	4.39		*
E2A						1,500	4.00	1.220	3.7	10.1	93.3	4.38	58.5	
E3						1,700	2.00	1.159	3.3	11.8	88.1			
E4						1,900	0.25	1.172	3.9	12.0	91.8	3.59		
E5						1,900	4.00	1.355	>5		94.3			
E6	4	Pigment	1.0	2	0	1,500	0.25	1.130	2.1	11.8	83.5			
E7						1,500	4.00	1.154	2.2	11.2	81.8	5.77		*
E7A						1,500	4.00	1.250	2.5	9.6	87.5	5.62	58.0	
E8						1,700	2.00	1.147	2.5	9.6	85.9			
E9						1,900	0.25	1.354	4.8	9.7	93.4	2.74		*
E10						1,900	4.00	1.501	>5		95.1			
E11	7	Catalyst	1.0	2	0.5	1,500	0.25	1.215	3.3	9.5	87.8	4.39		*
E12						1,500	4.00	1.196	3.2	10.4	86.7	4.36		*
E13						1,700	2.00	1.148	3.5	10.7	84.5	3.37		*
E13A						1,700	2.00	1.260	3.3	10.1	85.4	4.06	56.2	
E14						1,900	0.25	1.272	>5		91.7			
E15						1,900	4.00	1.623	>5		93.2	1.42		*
E16	9	Catalyst	0.8	5	0	1,500	0.25	1.269	>5		93.9	4.78		*
E17						1,500	4.00	1.238	>5		90.6			
E18						1,700	2.00	1.231	>5		89.2			
E19						1,900	0.25	1.367	>5		91.5	2.51		
E20						1,900	4.00	1.743	>5		94.3			

Table 3. Zinc Ferrite Cylindrical Extrude Characteristics
(Continued)

Sorbent Sample Number	Extrude Formulation					Induration Conditions		Physical Properties				BET	Porosity, % (Pores >0.012 μ m)	TGA Testing
	Run No.	Fe ₂ O ₃ Grade	ZnO/ Fe ₂ O ₃	% Bentonite	% Methocel	Temp., °F	Time, Hours	Bulk Density, kg/l	Crush Strength, lb/mm	Length, mm	Attrition Resistance %	Surface Area, m ² /g		
E21	15	Catalyst	1.0	5	0.5	1,500	0.25	1.195	≈5		90.1	4.62		*
E22						1,500	4.00	1.207	3.2	11.1	88.3			
E23						1,700	2.00	1.220	>5		89.8			
E24						1,900	0.25	1.300	>5		92.6	2.93		*
E24A						1,900	0.25	1.328	5.3	7.8	91.7	4.15	56.7	
E25						1,900	4.00	1.676	>5		94.7			
E26	14	Pigment	0.8	5	0.5	1,500	0.25	1.070	3.9	11.3	90.7			
E27						1,500	4.00	1.082	4.2	11.0	91.1			
E28						1,700	2.00	1.110	3.8	11.8	91.0			
E28A						1,700	2.00	1.115	3.3	9.0	89.3	4.99	56.4	*
E29						1,900	0.25	1.254	>5		94.0			
E30						1,900	4.00	1.888	>5		96.1			
E31	6	Pigment	0.8	2	0.5	1,500	0.25	1.168	2.8	9.3	86.1	6.31		*
E32						1,500	4.00	1.174	2.2	9.4	86.0			
E32A						1,500	4.00	1.191	3.1	9.2	84.6	6.33	59.1	*
E33						1,700	2.00	1.123	2.9	8.9	87.5			
E34						1,900	0.25	1.234	4.1	9.4	91.0			
E35						1,900	4.00	1.686	>5		97.1	1.42		*
E36	12	Pigment	1.0	5	0	1,500	0.25	1.092	3.9	10.2	93.1	5.76		*
E37						1,500	4.00	1.138	4.6	8.8	93.3			
E38						1,700	2.00	1.174	4.3	10.4	94.3	4.12		*
E39						1,900	0.25	1.314	>5		96.7			
E40						1,900	4.00	2.039	>5		97.8	0.85		*

Note: An "A" designation in the sorbent sample number indicates preparation of a larger batch for cyclic testing.

Table 4. Size Analysis of Zinc Ferrite Sorbent Raw Materials

Particle Size, μm	Cumulative Weight Percent Passing Indicated Size			
	Catalyst Grade	Pigment Grade	ZnO	Bentonite
	<u>Fe₂O₃</u>	<u>Fe₂O₃</u>		
50				98
40	99	99		90
30	98	98		78
20	97	97		59
10	94	96		38
5	91	93	99	26
2	84	81	94	14
1	53	69	87	8
0.5	11	32	40	3

Table 5. Sorbent Raw Materials and Costs

<u>Component</u>	<u>Cost, \$/lb</u>
Zinc Oxide (ASARCO AZO-77)	0.95
Iron Oxide	
Pigment Grade (Mobay Chemicals, Bayferrox 645T)	0.76
Catalyst Grade (United Catalysts Inc.)	Up to 2.00
Bentonite (From Western United States)	0.02
Organic Binder	
Corn Starch	0.30
Dow Methocel K15MS	3.50

total contaminants, primarily as silicon and aluminum compounds. Analyses of the other materials are shown in Table 6.

Table 6. Chemical Analysis of Zinc
Ferrite Sorbent Raw Materials

<u>Element*</u>	<u>Pigment-Grade Fe₂O₃, %</u>	<u>Catalyst-Grade Fe₂O₃, %</u>	<u>Bentonite, %</u>
Fe	54.8	60.5	2.84
Zn	0.005	0.013	0.043
Si	0.955	0.045	27.7
Al	1.32	0.203	9.56
Na	0.134	0.067	1.97
K	0.058	0.012	0.440
Mn	3.25	0.020	0.019
Ca	0.015	0.010	0.67
Cd	0.011	0.012	0.0008
Cr	0.046	0.026	0.0007
Cu	0.050	0.009	<0.0002
Mg	0.037	0.030	1.18
Mo	0.015	0.006	0.005
Ni	0.030	0.010	<0.0007
P	0.0545	0.018	0.034
Pb	0.012	0.012	0.011
Sr	0.010	0.0002	0.026
Ti	0.012	0.005	0.089
V	0.013	0.009	0.0010

* Balance, oxygen.

Spherical Pellet Sorbent Preparation

The dry powders used for the sorbent formulations were blended in specified concentrations using a mix-muller. Twenty to twenty-five pounds of dry material were typically prepared for each batch. A 14-inch diameter Dravo disk pelletizer was then utilized to prepare the spherical pellet forms. Dry powder feed was introduced slowly by hand with a scoop, along with an intermittent water addition as a fine spray during pelletization. The disk pelletizer was modified to increase the diameter to 20 inches during the remainder of the program. This increased the production rate enough to allow for continuous spraying of water while solids were introduced. Disk angle and speed were adjusted as necessary for the different formulations to provide the desired 1/4-inch diameter pellets. Typical settings were 45 degrees disk angle and 13 to 15 rpm disk speed.

Development of suitable small seed material was important to the steady state production of properly size pellets. A uniform particle growth rate was achieved, and the properly-sized pellets were effectively discharged from the disk at a uniform rate during semi-continuous bench-scale production. The moisture content of green spherical pellet sorbents was typically 16 to 19 weight percent.

Spherical pellet sorbents manufactured using pigment-grade iron oxide typically exhibited a smoother surface texture than those manufactured using catalyst-grade iron oxide. This might be attributed to the smaller particle size of the pigment-grade iron oxide.

Cylindrical Extrude Sorbent Preparation

Dry powder mixtures were prepared in the mix-muller in the same manner used for preparation of spherical pellets. The dry powder mixtures were then blended with water using a Hobart kneader/mixer prior to introduction into a bench-scale single-screw extruder. A plate containing six 3/16-inch diameter holes was installed at the discharge of the extruder. A variable speed cutting device was installed at the exit from the plate. Extrude lengths between 1/4- and 3/4-inch were typically produced. The extrusion chamber was fitted with a water cooling jacket to avoid heat buildup from the high pressures exerted by the extruder.

While the feed to the extruder typically contained 24 to 27 weight percent moisture, the green extrudates typically contained 16 to 18 weight percent moisture. Some of the moisture was squeezed from the sorbents during the high-pressure extrusion procedure. Some additional moisture was lost due to dehydration in the collection pans as a result of the dry atmosphere and the elevated temperature of the product.

The pigment-grade iron oxide formulations tended to stick in the extruder more than the catalyst-grade iron oxide formulations. This may have been due to the greater magnetic content of the pigment-grade iron oxide or to the finer particle size.

The Methocel organic binder content used for cylindrical extrude production was changed from the level of 2.0 percent originally specified. A level of 0.5 percent Methocel was used after preliminary tests showed that the higher level of binder resulted in a thick paste which could not be successfully extruded.

Extrude formulations containing 10 percent bentonite were also very difficult to produce due to sticking and plugging in the extrusion chamber. After adjusting the moisture content of

the feed mixture, the material continued to plug the extruder. The sorbent compositions containing 10 percent bentonite could not be produced in sufficient quantity for testing and were deleted from the test matrix.

Sorbent Drying

Both spherical pellet and cylindrical extrude shapes were dried in a large forced air oven overnight at a temperature of about 230°F (110°C). Measurements of the crush strength and attrition resistance were not taken on the green or dried sorbents. However, the sorbents exhibited sufficient durability to allow for transferring from pans to ceramic trays for subsequent induration.

Sorbent Induration

Dried sorbent batches produced using the techniques described above were divided into subsamples for induration at different temperatures and times. Typically, about half of the dried sorbent was stored so that a sufficient quantity could be indurated later for multi-cycle bench-scale testing if desired. The subsamples, typically containing about 1 pound of sorbent, were placed into ceramic trays. The sorbents were then introduced into a preheated furnace (containing an air atmosphere) and were held for the desired time. The induration conditions are summarized in Table 7. After indurating for the specified times, the sorbents were removed from the furnace and cooled. Induration conditions for larger batches of sorbent (to be used in multi-cycle bench-scale testing) were selected after performing characterizations on the smaller indurated subsamples.

Table 7. Sorbent Induration Conditions

<u>Temperature,</u> <u>°F</u>	<u>Time,</u> <u>Hours</u>
1,500	0.25
1,500	4.00
1,700	2.00
1,900	0.25
1,900	4.00

The sorbent induration conditions were selected to represent a range which was expected to produce differences in physical properties and reactivity. This was in part based on the responses obtained on the base case spherical pellet and cylindrical extrude sorbents. The base case AMAX 1094-59 spherical pellet sorbent was indurated at a temperature of

1,825°F for a period of 3 hours. The base case UCI T-2465 cylindrical extrude sorbent was indurated at a temperature of 1,550°F for a period of 2 hours. In general, less severe induration conditions were expected to result in greater sorbent reactivity but lower strength.

Sorbent Preparation Using Ruthner Process Iron Oxide

One additional sorbent was prepared using a low-cost Ruthner process iron oxide. This type of iron oxide is available for about \$0.05 per pound and typically contains chloride as the primary contaminant. The Ruthner (or Dravo-Ruthner) process is used to regenerate waste hydrochloric acid pickling liquors. Pickling liquors containing hydrochloric acid and iron chloride are fed to a spray roaster. Reaction products are HCl, which is recovered in an absorber system, and iron oxide.⁵ The Ruthner iron oxide particle size is about 99 percent passing 400 mesh (37 microns).

For comparison, attempts were made to prepare a sorbent using the same formulation as Sorbent E7A (see Table 3) with only the substitution of Ruthner process iron oxide for pigment-grade iron oxide. After encountering 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 prepared using a 3/16-inch diameter pipe and a rod to press a small quantity of the mixture into extrudes. The sorbent was fired at 1,500°F for 4 hours.

The as-is Ruthner iron oxide 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. An additional test was performed to determine the degree of chlorine removal via heat treatment. For this test, the Ruthner iron oxide was heated to 1,500°F and held for 4 hours (similar to induration conditions which have been used to fire formed sorbent shapes). The resulting product contained 200 ppm chlorine. These results indicate that effective chlorine removal could be achieved during a washing step and during sorbent firing at high temperature.

Ruthner process iron oxide was investigated in greater detail during a contract option. Results are reported under "Task 6. Additional Sorbent Testing".

SORBENT CHARACTERIZATION

Indurated sorbents were subjected to characterizations after cooling. Bulk density and crush strength determinations were performed on all indurated sorbents. Attrition resistance determinations were performed on all indurated cylindrical

extrude sorbents. Attrition resistance was determined initially on all indurated spherical pellet sorbents; however, after establishing preliminary trends, only those spherical pellet sorbents which exhibited crush strength values of greater than 10 pounds were subjected to attrition resistance determinations. Tables 2 and 3 summarize the sorbent preparation conditions and characterizations. The following sections discuss the characterization techniques and results.

Bulk Density

The smaller indurated subsamples were weighed into 250-milliliter graduated cylinders to determine bulk density. The cylinders were gently tapped to ensure uniform packing. The larger indurated samples prepared for bench-scale testing were weighed into 1-liter graduated cylinders. These cylinders more closely represented the 2-inch diameter bench-scale reactor dimensions. Any differences in bulk density between the smaller indurated subsamples and the larger indurated batches (designated with an "A" in Tables 2 and 3) are probably due to the different cylinder sizes or slightly different induration intensity resulting from the difference in mass introduced into the furnace.

The results in Tables 2 and 3 show that the sorbents which were indurated at lower temperatures and for shorter time periods generally exhibited lower bulk density. The spherical pellet shape typically exhibited lower overall bulk density than the cylindrical extrude shape. Bulk density values for spherical pellets ranged from 0.71 to 1.53 kg/l. Bulk density values for cylindrical extrudes ranged from 1.07 to 2.04 kg/l.

As discussed in Volume 2 of this report, the density of single sorbent particles was measured during the course of TGA analysis. These single pellet densities values were found to trend well with the measured bulk density values.

Crush Strength

A Chatillon compression and tension strength tester was used for spherical pellet and cylindrical extrude crush strength determinations. The instrument has a maximum measurement capability of 50 pounds. The measurement technique was based on ASTM Standard Method D4179-82, "Single Pellet Crush Strength of Formed Catalyst Shapes". Most values shown in Tables 2 and 3 represent the average of at least 25 individual sorbent particle determinations.

The crush strength procedure consisted of measuring the value at which individual sorbent particles broke apart as force was uniformly increased. The instrument surfaces between which the sorbent particles were placed were cleaned between

each determination. The instrument indicator needle was set to lock at the highest applied pressure in order to provide accurate values which could be recorded and averaged.

The crush strength values of spherical pellet sorbents (about 1/4-inch diameter) were recorded as-is. Consideration was given to reporting spherical pellet crush strength on the basis of "pounds/mm (diameter)". To evaluate the suitability of these units, a test was performed using relatively large and relatively small spherical pellets which were taken from the same sorbent batch. Sorbent P27A (Table 2, Preparation Run No. 21, 1,900°F/4 hours) was selected since this sorbent exhibited fairly high crush strength and it was fired for a 4-hour period, which ensures complete heat treatment throughout both larger and smaller pellets. Twenty small and twenty large spherical pellets were subjected to diameter and crush strength measurements. The results were averaged in terms of "pounds" and "pounds/mm (diameter)" values. As shown in Table 8, the larger-diameter pellets did exhibit greater average crush strength values expressed in "pounds" units. However, the larger-diameter pellets exhibited lower average crush strength values in terms of "pounds/mm (diameter)". As a result of these measurements, all crush strength determinations for the spherical pellets were recorded as "pounds". These values should be valid for making comparisons between different sorbent batches because the spherical pellets were screened to a narrow size range (near 1/4 inch) prior to introduction into the fixed-bed reactor.

Table 8. Crush Strength Determinations
of Spherical Pellet Sorbent P27A

	Average Sorbent Diameter, mm	<u>Crush Strength</u>	
		<u>lb</u>	<u>lb/mm (Diameter)</u>
Small Pellets	4.3	23.0	5.4
Large Pellets	7.4	29.6	4.1

Cylindrical extrude sorbent crush strength measurements were taken along a radial orientation. Determinations along an axial orientation were not performed due to irregularities on the cut extrude surfaces. Measurement along a radial orientation provides for a line of contact between the sorbent and the compression surfaces. Spherical pellet determinations essentially provided only point contact on the compression surfaces. As such, the cylindrical extrude values were recorded on the basis of "pounds/millimeter (length)". This format is compatible with that used at METC and elsewhere for cylindrical extrude determinations. Note that in Table 3,

many of the values exceeded the 50-pound measurement capability of the instrument (which corresponds to 5 pounds/millimeter for an extrude 10 millimeters in length).

Crush strength determinations for spherical pellets correlated with bulk density determinations. Figure 1 shows spherical pellet crush strength as a function of bulk density. The linear fit based on regression of the data provided a coefficient of determination (r^2) of 0.80 (within a range of 0 to 1, with a value of 1.00 representing a perfect fit). No significant correlation between cylindrical extrude crush strength and bulk density was observed. However, many of the sorbents which exhibited higher values of bulk density also exhibited crush strength values which exceeded the measurement capabilities of the compression tester.

Figure 1. Spherical pellet crush strength as a function of sorbent bulk density.

Attrition Resistance

Attrition measurements were based on ASTM Standard Method D4058-81, "Attrition and Abrasion of Catalysts and Catalyst Carriers". A 10-inch diameter by 6-inch long cylindrical drum containing a single radial baffle was fabricated to conform to

the ASTM design. The method calls for testing of 100 grams of representative material from which the minus 20-mesh particles have been removed. The drum is rotated for 1,800 revolutions at a speed of 60 ± 5 rpm. The weight percentage of material greater than 20 mesh remaining after the test was expressed as the "Attrition Resistance" value shown in Tables 2 and 3. The same procedure was applied to both the spherical pellet and cylindrical extrude shapes.

Attrition resistance correlated with bulk density for both sorbent shapes. As shown in Figure 2, the cylindrical extrudes typically exhibited greater values of attrition resistance than spherical pellets. Attrition resistance of cylindrical extrudes was greater than 80 percent in all cases. A slight increase in cylindrical extrude attrition resistance occurred with increasing bulk density. Spherical pellet sorbent attrition resistance values approached those of the cylindrical extrudes at bulk density values greater than about 1.20 kg/l. However, spherical pellet attrition resistance dropped rapidly (to as low as about 16 percent) as bulk density values dropped below 1.20 kg/l.

Figure 2. Attrition resistance as a function of sorbent bulk density.

Figure 3 shows the relationship between attrition resistance and crush strength for spherical pellets. This figure indicates that a constant value range of attrition resistance (above about 85 percent) occurs for crush strength values greater than about 25 pounds. Figure 4 shows the attrition resistance of cylindrical extrudes as a function of crush strength. A weaker relationship was found for this sorbent shape.

Surface Area

BET surface area analyses were performed on selected sorbent samples using a Quantasorb system. Figure 5 shows the trend between bulk density and surface area values. In general, greater bulk density led to lower surface area. Surface areas for cylindrical extrudes were observed to fall within a band of values greater than those for the spherical pellets.

Figure 3. Attrition resistance as a function of spherical pellet sorbent crush strength.

Figure 4. Attrition resistance as a function of cylindrical extrude sorbent crush strength.

Figure 5. Sorbent surface area as a function of bulk density.

Surface area determinations were also performed on the zinc oxide and various iron oxide powders used for sorbent preparation. Table 9 summarizes the results.

Table 9. Surface Areas of Iron
Oxide and Zinc Oxide Powders

<u>Compound</u>	<u>Source</u>	<u>Surface Area, m²/g</u>
Fe ₂ O ₃	UCI Catalyst Grade	6.65
Fe ₂ O ₃	Mobay Pigment Grade	9.75
Fe ₂ O ₃	Arus-Andritz-Ruthner	2.21
ZnO	ASARCO	7.59

Porosity

Mercury intrusion porosimetry was performed on the sorbents which were selected for multi-cycle bench-scale testing. Cumulative porosity contained in pores greater than 0.012 micron was obtained with applied pressures up to 15,000 psi. Results of the porosity determinations and of relationships between sorbent porosity and reactivity are discussed in the "Task 4. Bench-Scale Test Analysis" section of the report.

Mineralogy

At the minimum, X-ray diffraction analyses were performed on each of the sorbents which were selected for multi-cycle bench-scale testing. Optical and scanning electron microscopy characterizations were also carried out on selected sorbents. Results of these characterizations are discussed in the context of the effects on reactivity and durability in the "Task 4. Bench-Scale Test Analysis" section of the report.

Sorbent Prepared Using Ruthner Process Iron Oxide

The surface area of the E7R sorbent prepared using the Ruthner process iron oxide (containing 0.49 percent chloride) was 2.59 m²/g. The product exhibited a bulk density of about 0.77 kg/l and a crush strength of about 35 pounds. Due to the small quantity of available sample, the bulk density determination was performed in a small graduated cylinder. As a result, the value of 0.77 kg/l is probably lower than would have been obtained in the standard 250-ml graduated cylinder normally used for these measurements. 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 testing consisted of two different techniques, single particle kinetic studies using thermogravimetric analysis (TGA) and multi-cycle testing using 2-inch diameter fixed-bed reactors. The TGA work was performed under the direction of Professor Douglas Harrison of the Chemical Engineering Department at Louisiana State University. Multi-cycle bench-scale testing was performed at the AMAX R&D laboratories.

Sorbent reactivity and durability are dependent on the sulfidation and regeneration conditions used during testing. However, the goal of the program was to perform a comparative evaluation of sorbent samples prepared under different conditions by subjecting them to a set of standard sulfidation and regeneration test conditions. The conditions were selected based on past experience of METC and AMAX R&D.

A preliminary evaluation of many candidate sorbent samples was performed in single particle kinetic studies by LSU. Thirteen sorbents (including the base case spherical pellet and cylindrical extrude sorbents) were then selected for multi-cycle bench-scale testing on the basis of the single particle kinetic studies and physical characterizations. The single particle kinetic study results are included in Volume 2 of this report. Results from the LSU work are highlighted in a later section of Volume 1.

BENCH-SCALE REACTOR SYSTEM

Figure 6 shows a diagram of the bench-scale reactor system used for the program. Two identical reactors were operated simultaneously. The 2-inch inside diameter by 36-inch long atmospheric pressure, fixed-bed reactors were fabricated using 446 stainless steel. The thermowells were fabricated using 304 stainless steel. This bench-scale reactor system (which was used in past AMAX R&D work) was disassembled, inspected, cleaned, modified, and reassembled. New valves and fittings were installed on the gas inlet and exit lines. Other modifications included:

- Installation of smaller-diameter thermowells to minimize channeling of the reaction gases. The new thermowells (which entered the reactors from the top flange) were fitted with three thermocouples each to measure the temperature near the top, middle, and bottom of the sorbent bed.
- Installation of new larger-diameter preheaters to minimize potential plugging with carbon deposits.

- Installation of a microcomputer to collect, display, and record important test data such as temperatures, pressure drop, and gas compositions.

Figure 6. Bench-scale reactor system.

A gas mixing manifold was used to prepare the desired dry gas composition. Individual gases were metered through needle valves and rotameters. From the manifold, the gas passed into an electric preheater. Water was added to the preheater at a specified rate to attain the desired steam content in the simulated coal gas. H_2S was introduced from a gas cylinder to the preheated, steam-containing gas at a point downstream from the preheater.

The sorbent bed (approximately 18 inches tall) rested on a layer of alumina chips, which in turn rested on a spacer and support containing glass wool. This provided a uniform gas distribution and placement of the sorbent column within the furnace heating zones. During sulfidation, the simulated coal gas entered the bottom of the reactor and the cleaned, low-

sulfur gas exited from the top of the reactor. During regeneration, oxidizing gas (a mixture of steam and air) entered the top of the reactor and SO₂-rich gas exited from the bottom of the reactor. Additional air was introduced in an afterburner to ensure that any H₂S or elemental sulfur formed during regeneration would be converted to SO₂. This procedure helped to reduce plugging in the exit gas piping.

Exit gases from sulfidation and regeneration were directed to a wet scrubber containing caustic and bleach. Alarms for H₂S and combustible gases were installed in the work area.

The reactors were enclosed in three-zone split-tube furnaces. Temperature controllers were used to maintain the desired temperatures during sulfidation and regeneration. Thermocouples were connected to the microcomputer for display and recording. One of the furnaces originally installed was 4 inches in diameter. The other furnace was 2.5 inches in diameter. The 2.5-inch diameter furnace provided a close fit to the reactor pipe. Based on early testing, it was observed that the larger diameter furnace resulted in a greater temperature profile across the radius of the sorbent bed. Because of this, the larger furnace was replaced with a 3-inch diameter, 3-zone furnace which was available at AMAX R&D. This replacement significantly improved the operation of the reactor. Additional improvement was obtained after installation of insulating baffles at the top and bottom of the furnace in the small gap between the reactor shell and furnace.

TEST CONDITIONS

One liter of sorbent was loaded into the bench-scale reactors for each multi-cycle test series. The gas flow rate for sulfidation was based on 2,000 bed volumes per hour at conditions of 60°F and 14.7 psia. Based on results of preliminary tests and discussions with the COTR, it was decided that the mass flow of gas should be maintained equivalent to that specified for the 60°F and 14.7 psia conditions. Therefore, the volumetric gas flow for the Golden, Colorado, conditions was approximately 2,500 bed volumes per hour for the sulfidation step. Gas flows and concentrations were calibrated using wet gas meters and gas analyses. The gas chromatograph was calibrated using standard gases, and its performance was verified periodically using Drager tube analyses.

The test series were carried out through 9 sulfidation cycles to a 200 ppm H₂S breakthrough value with a final 10th cycle carried out to near saturation (when the exit gas contained 1 percent H₂S). The sulfidation gas composition is shown in Table 10. Gas chromatograph analyses were performed during the multi-cycle test series so that the elapsed time (and sorbent sulfur sorption capacity) could be determined for a 200 ppm H₂S breakthrough as measured at the reactor outlet.

Table 10. Sulfidation Gas Composition

<u>Gas Component</u>	<u>Composition, Volume Percent</u>
CO	16.3
CO ₂	4.5
H ₂	10.6
H ₂ O	25.3
H ₂ S	1.0
N ₂	42.3

A standard sulfidation temperature of 1,022°F (550°C) was used. A preheater temperature of 1,022°F was found to provide the best control for the sulfidation step. Regeneration was conducted between 1,292 and 1,382°F (700 and 750°C). A preheater temperature of about 1,200°F (650°C) was found to provide the best control for the exothermic regeneration step. Regeneration was carried out until the dry exit gas SO₂ concentrations reached very low values (typically less than 0.1 percent).

During regeneration, a 92:8 steam:air mixture at a 1,500 bed volumes per hour flow was found to provide optimum control of reactor temperatures. This gas mixture was used throughout the program. Earlier tests performed using greater amounts of oxygen at lower flow rates resulted in temperatures which sometimes exceeded 1,470°F (800°C).

In general, one sulfidation or regeneration step could be performed in each reactor during a work day. Typically, both reactors were operated in the same mode (sulfidation or regeneration) in order to simplify gas analysis and data acquisition. The reactors were typically cooled to about 750°F (400°C) under a low flow of nitrogen overnight and during weekends. Several days were required to achieve sulfur saturation in the sorbent bed during the 10th cycle.

The sulfur sorption capacity at breakthrough and at saturation is generally reported in terms of the pounds of sulfur sorbed per 100 pounds of fresh sorbent. This value was calculated using the known gas flow rates and sulfur content, along with the starting sorbent bed weight. Sulfur sorption capacity at saturation was determined by chemical analysis of the sulfided sorbent.

BENCH-SCALE TEST RESULTS

Thirteen sorbents were selected for multi-cycle bench-scale testing during the base program. The physical characteristics of these sorbents are summarized in Tables 11 and 12 for the spherical pellet and cylindrical extrude shapes,

**Table 11. Physical Characteristics of Spherical Pellet
Sorbents Selected for Bench-Scale Testing**

<u>Sorbent Formulation</u>						
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 ₂ O ₃ Ratio	1.0	1.0	0.8	0.8	0.8	1.0
Bentonite, %	5	2	2	10	5	10
Kaolin, %	1.5	--	--	--	--	--
Starch, %	2	0	0	2	0	0
Na ₂ CO ₃ , %	0.2	--	--	--	--	--
MoS ₂ , %	0.2	--	--	--	--	--
<u>Induration Conditions</u>						
Temperature, °F	1825	1900	1900	1900	1900	1900
Time, hours	3	0.25	4	4	4	4
<u>Physical Properties</u>						
Bulk Density, kg/l	1.014	1.141	1.488	1.143	1.389	1.146
Crush Strength, lb	5.1	16.6	22.0	22.0	22.1	19.4
Attrition Resistance, %	45.4	80.5	89.0	80.9	90.7	82.4
Surface Area, m ² /g	1.01	2.63	1.68	1.21	1.76	1.95
Total Pore Volume, cm ³ /g	0.277	0.319	0.207	0.270	0.212	0.296
Average Pore Radius, Å	5490	2430	2460	4460	2410	3040
Porosity, %						
Pores >0.180 μm	48.5	59.7	49.1	52.7	48.8	56.8
Pores >0.012 μm	59.2	63.8	52.1	56.2	52.3	59.6
Calculated Porosity*	64	66	56	61	55	59
<u>Cyclic Test Number</u>	5	7	9	11	14	17

* From LSU calculations based on particle densities.

**Table 12. Physical Characteristics of Cylindrical Extrude
Sorbents Selected for Bench-Scale Testing**

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 ₂ O 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, %	0.5	0.5	0	0.5	0.5	0.5	0

Induration Conditions

Temperature, °F	1550	1700	1500	1900	1700	1500	1500
Time, hours	2	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	1.120
Crush Strength, lb/mm	3.5	4.4	2.5	5.3	3.3	3.1	3.7
Attrition Resistance, %	88.8	85.4	87.5	91.7	89.3	84.6	92.3
Surface Area, m ² /g	3.30	4.06	5.62	4.15	4.99	6.33	4.38
Total Pore Volume, cm ³ /g	0.256	0.239	0.265	0.249	0.250	0.279	0.263
Average Pore Radius, Å	1550	1180	940	1200	1000	880	1200
Porosity, %							
Pores >0.180 μm	50.1	39.8	20.3	36.4	23.9	31.9	44.7
Pores >0.012 μm	58.2	56.2	58.0	56.7	56.4	59.1	58.5
Calculated Porosity*	62	59	60	54	57	61	59

<u>Cyclic Test Number</u>	4	8	10	12	13	15	16
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* From LSU calculations based on particle densities.

respectively. These sorbents were selected on the basis of physical characteristics and single particle kinetics. The selections included the AMAX 1094-59 and UCI T-2465 base case sorbents. Selected breakthrough curves representing spherical pellet and cylindrical extrude shapes are shown in Figures 7 and 8, respectively. The curves represent the range of performance observed from the base case and new sorbents. The sulfur sorption capacity at breakthrough and at near saturation is shown in Figures 9 and 10 for the spherical pellet and cylindrical extrude shapes, respectively. Sorbent sulfur sorption performance is also summarized in Tables 13 and 14 for the spherical pellet and cylindrical extrude shapes, respectively. Included in these tables are the breakthrough and saturation sulfur sorption capacities, as well as the single particle kinetic results.

The sulfur sorption capacity at breakthrough was determined from the length of time required to reach a 200 ppm H_2S breakthrough. The sulfur sorption capacity at saturation was computed from a chemical analysis of a sulfur saturated sorbent sample removed from the bottom (inlet) portion of the fixed-bed reactor. The calculations were based on the change in weight associated with complete sulfidation of the zinc and iron oxides to ZnS and FeS . The weight percent sulfur was applied to this value to determine the weight of sulfur sorbed.

Pressure drop through the sorbent bed was monitored. No particular trends were observed which would indicate any sintering of the bed or plugging. This was consistent with observations of the sorbent upon removal from the reactors.

In general, the cylindrical extrude sorbents exhibited greater sulfur sorption capacity at saturation compared to spherical pellets. The cylindrical extrude sorbents selected for multi-cycle bench-scale testing were typically indurated under less severe conditions than the spherical pellets. This was a result of the effect of induration on physical characteristics and TGA reactivity.

Operating observations, problems, and comments pertinent to the interpretation of the experimental results are summarized in Appendix A.

Sulfur Sorption Capacity at Breakthrough

As shown in Figures 9 and 10, most sorbents exhibited a decrease in sulfur sorption capacity at breakthrough following the first sulfidation cycle. Only the UCI T-2465 base case cylindrical extrude sorbent exhibited a significant increase in sulfidation performance during the second sulfidation cycle. Most sorbents exhibited a steady or gradually decreasing sulfur sorption capacity at breakthrough during the 10 sulfidation cycles.

Figure 7. H₂S exit gas concentration during spherical pellet sorbent sulfidation.

Figure 8. H₂S exit gas concentration during cylindrical extrude sorbent sulfidation.

Figure 9. Sulfur sorption capacity at H₂S breakthrough for spherical pellet sorbents.

Figure 10. Sulfur sorption capacity at H₂S breakthrough for cylindrical extrude sorbents.

Table 13. Spherical Pellet Sorbent Sulfidation Performance

<u>Sorbent Sample Number</u>	1094-59	P11A	P6A	P27A	P37A	P22A
<u>Cyclic Test Series Number</u>	5	7	9	11	14	17
<u>Desulfurization Performance</u> <u>in Bench-Scale Reactor</u>						
Sulfur Sorption Capacity, g S sorbed/100 g fresh sorbent						
a) At 200 ppm H ₂ S Breakthrough:						
1st Cycle	1.3	25.2	16.1	13.3	1.7	16.2
2nd Cycle	1.5	20.2	14.3	16.0	2.6	13.9
3rd Cycle	3.4	11.0 ^a	13.0	12.7	2.4	14.5
4th Cycle	1.4	34.2	10.4	9.8	2.1	12.8
5th Cycle	1.4	33.0	8.5	10.4	2.2	12.5
6th Cycle	1.2	24.8	6.8	7.5	3.3	14.3
7th Cycle	1.4	24.0	7.7	7.2	2.0	12.0
8th Cycle	0.8	19.5	7.0	7.0	3.3	12.1
9th Cycle	0.8	20.3	7.6	7.9	1.9	11.5
10th Cycle	<u>1.3</u>	<u>21.0</u>	<u>8.0</u>	<u>7.7</u>	<u>2.8</u>	<u>14.2</u>
Average	1.2	24.7	9.9	10.0	2.4	13.4
b) At Saturation, Actual ^b	33.7	32.6	27.1	29.5	27.6	31.0
c) At Saturation, Theoretical	37.3	39.1	39.1	35.9	37.9	35.9
Percent of Theoretical Capacity Achieved	90.4	83.4	69.6	82.2	72.8	86.4
<u>Desulfurization Performance</u> <u>in TGA</u>						
Sulfur Sorption Capacity During First Cycle at t ¹ = 20 minutes, g S sorbed/100 g fresh sorbent						
	21.7	28.2	20.8	25.6	17.8	25.3
Reactivity Change, Increase or Decrease in Reactivity During 2nd Cycle, %						
	6	-16	-10	-12	-27	-11

^a Test cycle suspended early due to reactor system plugging.

^b Based on weight % S at bottom of reactor bed.

Table 14. Cylindrical Extrude Sorbent Sulfidation Performance

<u>Sorbent Sample Number</u>	T-2465	E13A	E7A	E24A	E28A	E32A	E2A
<u>Cyclic Test Series Number</u>	4	8	10	12	13	15	16
<u>Desulfurization Performance</u>							
Sulfur Sorption Capacity, g S sorbed/100 g fresh sorbent							
a) At 200 ppm H ₂ S Breakthrough:							
1st Cycle	13.7	17.6	25.6	16.2	9.3	8.8	13.5
2nd Cycle	28.6	15.3	14.9	14.7	5.5	12.6	11.0
3rd Cycle	26.3	17.7	11.5	14.0	5.6	9.6	14.0
4th Cycle	24.0	17.1	10.8	12.2	6.0	9.6	10.0
5th Cycle	22.2	15.3	12.4	11.3	6.2	8.9	10.8
6th Cycle	22.6	20.3	10.4	11.0	5.7	9.0	13.1
7th Cycle	22.2	16.1	8.8	10.1	5.9	9.5	12.4
8th Cycle	20.2	15.8	8.8	9.6	5.8	8.4	12.3
9th Cycle	20.4	16.6	9.5	9.5	5.9	9.5	13.1
10th Cycle	22.3	25.3	9.2	9.8	5.8	15.2	15.1
Average	22.3	17.7	12.2	11.8	6.2	10.1	12.5
b) At Saturation, Actual*	34.3	36.9	35.4	37.3	32.7	37.4	39.6
c) At Saturation, Theoretical	39.1	39.1	39.1	37.9	37.9	39.1	39.1
Percent of Theoretical Capacity Achieved	87.7	94.4	90.5	98.4	86.3	95.7	101.2
<u>Desulfurization Performance in TGA</u>							
Sulfur Sorption Capacity During First Cycle at t = 30 minutes, g S sorbed/100 g fresh sorbent							
	22.8	21.7	18.2	18.1	16.6	21.1	20.9
Reactivity Change, Increase or Decrease in Reactivity During 2nd Cycle, %							
	-11	-24	-19	-40	-20	-9	-16

* Based on weight % S at bottom of reactor bed.

The different sorbents exhibited a very wide range of sulfur sorption capacities measured at 200 ppm H₂S breakthrough (from about 1.5 to over 30 pounds sulfur sorbed per 100 pounds fresh sorbent). Only the P11A spherical pellet sorbent and the T-2465 cylindrical extrude sorbent provided consistent sulfur sorption capacities of greater than 20 pounds sulfur sorbed per 100 pounds fresh sorbent at breakthrough.

Sulfur Sorption Capacity at Saturation

Although the sulfur sorption capacities of the different sorbents measured at H₂S breakthrough exhibited a very wide range of responses, the sulfur sorption capacities at near saturation fell into a narrower range of values (from about 26 up to about 40 pounds sulfur sorbed per 100 pounds fresh sorbent). The spherical pellet sorbent which exhibited the lowest value of sulfur sorption capacity at breakthrough exhibited the greatest value of sulfur sorption capacity at near saturation (AMAX 1094-59 base case sorbent).

Tables 13 and 14 show the sulfur sorption capacities at near saturation for spherical pellet and cylindrical extrude sorbents, respectively, based on chemical analysis of the sorbents. Sulfur sorption capacities calculated from gas flows and compositions over the long duration of the final sulfidation step generally compared well with the directly measured values.

In general, the cylindrical extrude shapes resulted in greater values of sulfur sorption capacity at saturation than the spherical pellet shapes.

Sorbent Regeneration

Sorbent regeneration was characterized by the release of high levels of sulfur dioxide (up to about 10 volume percent in dry gas) with a gradual decrease in concentration until SO₂ concentrations dropped below about 0.1 percent. Figure 11 shows an SO₂ gas concentration profile from the regeneration of the UCI T-2465 base case sorbent following sulfidation to H₂S breakthrough. Sorbent bed temperatures were generally held to less than 1,380°F (750°C) during regeneration. Selection of the regeneration gas composition and flow rate and selection of furnace control temperatures provided control against rapid, localized overheating of the sorbent bed.

Figure 11. SO₂ concentration during regeneration (UCI T-2465 sorbent).

Chemical Analysis of Fresh and Sulfided Sorbents

Tables 15 and 16 contain the chemical analyses of fresh and sulfided sorbents. The sulfided sorbent analyses were obtained on samples taken from the top, middle, and bottom portions of the fixed bed at the completion of the test series. As shown in Tables 15 and 16, the sulfur analyses from the bottom to the top of the bed were generally uniform. Since the gas flow was upward for the sulfidation tests, it would be expected that the sulfur concentration at the top of the bed should be lowest if the entire bed were not entirely saturated.

Further analysis and discussion of sulfided sorbents are contained in the "Task 4. Bench-Scale Test Analysis" section.

SINGLE PARTICLE KINETIC STUDIES

Because sulfidation produces an increase in sorbent mass, a thermogravimetric analyzer (TGA) can be used to determine the progress of the reaction with time using a single sorbent pellet/extrude. Sorbents which exhibited suitable physical characteristics to be considered for multi-cycle bench-scale testing and those which could be utilized to determine the effects of sorbent preparation and induration conditions on sorbent reactivity were forwarded to LSU for TGA studies.

Table 15. Chemical Analysis of Fresh and Sulfided Spherical Pellet Sorbents

	<u>1094-59</u>	<u>P11A</u>	<u>P6A</u>	<u>P27A</u>	<u>P37A</u>	<u>P22A</u>
<u>Zinc, %</u>						
Fresh Sorbent	23.4	26.4	23.4	20.0	22.1	23.5
Sulfided Sorbent						
Top	21.7	22.5	21.5	20.0	20.3	21.1
Middle	21.8	22.6	22.2	20.0	20.8	21.3
Bottom	21.6	22.5	21.8	19.5	20.3	22.0
<u>Iron, %</u>						
Fresh Sorbent	34.2	44.9	42.8	41.2	39.2	41.0
Sulfided Sorbent						
Top	36.3	40.6	40.1	39.9	38.5	38.2
Middle	35.4	41.3	40.0	40.0	39.2	37.3
Bottom	35.7	40.9	39.9	41.1	40.5	37.6
<u>Sulfur, %</u>						
Fresh Sorbent	<0.01	0.06	0.02	<0.01	0.02	0.03
Sulfided Sorbent						
Top	24.0	31.5	23.5	26.8	19.9	31.8
Middle	28.1	27.1	23.9	25.8	22.4	29.4
Bottom	30.0	28.8	24.0	26.3	24.5	27.7

Table 16. Chemical Analysis of Fresh and Sulfided Cylindrical Extrude Sorbents

	<u>T-2465</u>	<u>E13A</u>	<u>E7A</u>	<u>E24A</u>	<u>E28A</u>	<u>E32A</u>	<u>E2A</u>
<u>Zinc, %</u>							
Fresh Sorbent	26.9	26.8	25.8	25.1	22.4	21.8	23.5
Sulfided Sorbent							
Top	23.5	23.4	23.8	22.7	20.7	21.2	21.4
Middle	23.5	23.6	23.5	22.8	20.4	20.7	20.4
Bottom	23.5	23.5	23.5	22.4	20.5	19.5	23.5
<u>Iron, %</u>							
Fresh Sorbent	44.4	45.0	41.5	42.7	38.3	41.4	46.1
Sulfided Sorbent							
Top	40.6	40.3	39.5	39.3	37.5	39.6	42.4
Middle	40.6	40.6	39.5	39.2	36.8	39.5	42.4
Bottom	40.6	40.0	39.0	37.1	36.3	37.4	42.0
<u>Sulfur, %</u>							
Fresh Sorbent	0.04	<0.02	<0.01	0.06	0.02	0.04	0.03
Sulfided Sorbent							
Top	30.2	32.5	31.7	32.8	27.2	22.5	38.2
Middle	29.8	32.9	30.9	33.3	29.1	32.1	37.3
Bottom	30.3	32.6	31.3	34.1	29.0	33.1	37.6

Complete results of the single particle kinetic studies are contained in Volume 2 of this report. Highlights of the results are summarized below.

Test Procedures and Conditions

The sulfidation gas composition used for the single particle studies was selected to be the same as that used at AMAX R&D for bench-scale testing. However, the H_2S gas concentration was increased to 2.7 percent (from 1.0 percent used during bench-scale testing) in order to speed the progress of the reaction. For regeneration, a gas containing 30 percent steam (versus 92 percent at AMAX R&D) was used as a result of the requirement to blanket the electrobalance mechanism in an inert, noncondensing gas. The actual oxygen concentration was 4 percent.

The single particle kinetic studies were conducted during 1-1/2 cycles consisting of sulfidation at $1,022^{\circ}F$ ($550^{\circ}C$), regeneration at $1,292^{\circ}F$ ($700^{\circ}C$), and a second sulfidation step at $1,022^{\circ}F$. Figure 12 shows a typical test profile. An initial reduction step (performed in the absence of hydrogen sulfide) was utilized in order to begin sulfidation following reduction of the zinc ferrite to ZnO and Fe_3O_4 . A subsequent sulfidation response could then be tracked more accurately since the weight loss reaction associated with reduction was performed separately. The sulfidation reaction in the TGA proceeds as follows:

Complete sulfidation according to Equation 3 would result in a final value of $W/W_0 = 1.133$, as shown in Figure 12.

Thirty-six new test sorbents and the two base case sorbents were analyzed by TGA. Additional test runs were performed to establish reproducibility and the effects of parameters such as regeneration temperature. To the extent possible, sorbent particles of comparable size were chosen. For extrudes, both the length and diameter were matched. For spherical pellets, the diameter was matched as closely as possible.

The single particle kinetic results were compared by using indices of reactivity and reactivity maintenance. These indices were determined from the weight gain observed at some fixed reaction time. For spherical pellets, a reference time of 20 minutes was selected. For the cylindrical extrudes, a reference time of 30 minutes was selected. Because of the differences in size and mass between spherical pellets and cylindrical extrudes, different reference times were selected for these two sorbent shapes.

Figure 12. Typical TGA response for 1-1/2 cycle test.

These times were selected to be at an intermediate point during sulfidation. Selection of a time too near the beginning of sulfidation would result in significant error from the very rapid initial reaction rate. Selection of a time too late during the sulfidation step would provide information only about the sulfur sorption capacity and not about the reactivity.

Based on complete sulfidation of zinc and iron oxides to ZnS and FeS, the final sorbent weight would be 1.133 times the initial sorbent weight (without accounting for inert material). This relationship was used in the determination of reactivity indices. The reactivity indices R20 (for spherical pellets) or R30 (for cylindrical extrudes) were calculated by dividing the mass of sulfur sorbed by the initial sorbent mass at the fixed elapsed times. These results, which are fractional values, correspond to the reporting of sulfur sorption capacity values obtained during bench-scale testing, in which results are reported as pounds of sulfur sorbed per 100 pounds of fresh sorbent. Tables 17 and 18 summarize the reactivity values for spherical pellet and cylindrical extrude sorbents, respectively.

Reactivity maintenance indices were calculated by dividing the R20 or R30 values obtained during the second sulfidation cycle by those obtained during the first sulfidation cycle.

Table 17. Comparison of Pellet Reactivity

<u>Sorbent</u>	<u>Reactivity*</u>	<u>Zn:Fe₂</u> <u>Ratio</u>	<u>Fe₂O₃</u> <u>Grade</u>	<u>%</u> <u>Bentonite</u>	<u>%</u> <u>Starch</u>	<u>Induration</u>	
						<u>Temperature,</u> <u>°F</u>	<u>Time,</u> <u>Hours</u>
P10	0.297	1.0	C	2	0	1,700	2.00
P5	0.290	0.8	P	2	0	1,900	0.25
P26	0.289	0.8	C	10	2	1,900	0.25
P11	0.285	1.0	C	2	0	1,900	0.25
P21	0.284	1.0	C	10	0	1,900	0.25
P52	0.278	0.8	C	5	2	1,900	4.00
P31	0.275	1.0	P	2	2	1,900	0.25
P12	0.257	1.0	C	2	0	1,900	4.00
P27	0.257	0.8	C	10	2	1,900	4.00
P22	0.253	1.0	C	10	0	1,900	4.00
P62	0.241	1.0	P	10	2	1,900	4.00
P47	0.222	1.0	C	5	0	1,900	4.00
1094-59	0.217	1.0	P	5	1.7	1,825	3.00
P6	0.208	0.8	P	2	0	1,900	4.00
P16	0.206	0.8	C	2	2	1,900	0.25
P32A	0.203	1.0	P	2	2	1,900	4.00
P17	0.197	0.8	C	2	2	1,900	4.00
P42A	0.194	1.0	P	5	2	1,900	4.00
P57	0.190	0.8	P	10	0	1,900	4.00
P37A	0.179	0.8	P	5	0	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 18. Comparison of Extrude Reactivity

<u>Sorbent</u>	<u>Reactivity*</u>	<u>Zn:Fe₂</u> <u>Ratio</u>	<u>Fe₂O₃</u> <u>Grade</u>	<u>%</u> <u>Bentonite</u>	<u>%</u> <u>Methocel</u>	<u>Induration</u>	
						<u>Temperature,</u> <u>°F</u>	<u>Time,</u> <u>Hours</u>
E7R	0.291	1.0	R	5	0	1,500	4.00
T-2465	0.228	1.0	C	2	0	1,550	2.00
E13	0.217	1.0	C	2	0.5	1,700	2.00
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
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	0.200	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	0.181	1.0	C	5	0.5	1,900	0.25
E28A	0.166	0.8	P	5	0.5	1,700	2.00
E9	0.156	1.0	P	2	0	1,900	0.25
E36	0.156	1.0	P	5	0	1,500	0.25
E16	0.154	0.8	C	5	0	1,500	0.25
E38	0.153	1.0	P	5	0	1,700	2.00
E15	0.085	1.0	C	2	0.5	1,900	4.00
E35	0.054	0.8	P	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.

This fractional difference in sorbent reactivity was expressed by the terms RM20 (for spherical pellets) and RM30 (for cylindrical extrudes). Tables 19 and 20 summarize reactivity maintenance values for spherical pellet and cylindrical extrudes, respectively.

The effects of sorbent preparation parameters on single particle kinetics are summarized in the following sections.

ZnO:Fe₂O₃ Ratio

Overall analysis of the TGA data obtained using spherical pellets and cylindrical extrudes showed no statistical correlation between reactivity or reactivity maintenance and the ratio of zinc and iron oxides.

Iron Oxide Grade

Analysis of the TGA data obtained using spherical pellets and cylindrical extrudes showed that catalyst-grade iron oxide generally resulted in greater sorbent reactivity than pigment-grade iron oxide. A cylindrical extrude sorbent formulated using Ruthner process iron oxide exhibited the greatest reactivity of any cylindrical extrude sorbent tested.

For reactivity maintenance, the test results suggested a slight advantage in using pigment-grade iron oxide for the spherical pellet shape and a slight advantage in using catalyst-grade iron oxide for the cylindrical extrude shape. The cylindrical extrude sorbent which exhibited the greatest value of reactivity maintenance was prepared using Ruthner process iron oxide.

Bentonite Content

Previous studies showed that bentonite binder additions retard reduction reactions.⁶ Retardation of reduction reactions may be desirable since the reduction reactions consume hydrogen and/or carbon monoxide and can also result in the formation of the less reactive iron oxide wustite (FeO) and in vaporization of zinc under some circumstances. Sorbents prepared using even the lowest bentonite addition level (2 percent) did not undergo reduction reactions at the conditions used during the program.

No clear correlations were observed between the spherical pellet or cylindrical extrude sorbent reactivity and the bentonite content.

Overall analysis of the TGA results suggests that reactivity maintenance improves with increasing bentonite content in spherical pellets. The reactivity maintenance of

Table 19. Comparison of Pellet Reactivity Maintenance

Sorbent	Reactivity Maintenance*	Zn:Fe ₂ Ratio	Fe ₂ O ₃ Grade	% Bentonite	% Starch	Induration	
						Temperature, °F	Time, Hours
1094-59	1.06	1.0	P	5	1.7	1,825	3.00
P62	0.99	1.0	P	10	2	1,900	4.00
P52	0.91	0.8	C	5	2	1,900	4.00
P6	0.90	0.8	P	2	0	1,900	4.00
P26	0.90	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	0.88	0.8	C	10	2	1,900	4.00
P42A	0.88	1.0	P	5	2	1,900	4.00
P21	0.88	1.0	C	10	0	1,900	0.25
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	0.83	0.8	C	2	2	1,900	0.25
P47	0.83	1.0	C	5	0	1,900	4.00
P12	0.82	1.0	C	2	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
P5	0.79	0.8	P	2	0	1,900	0.25
P17	0.78	0.8	C	2	2	1,900	4.00
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 20. Comparison of Extrude Reactivity Maintenance

<u>Sorbent</u>	<u>Reactivity Maintenance*</u>	<u>Zn:Fe₂</u> <u>Ratio</u>	<u>Fe₂O₃</u> <u>Grade</u>	<u>%</u> <u>Bentonite</u>	<u>%</u> <u>Methocel</u>	<u>Induration</u>	
						<u>Temperature,</u> <u>°F</u>	<u>Time,</u> <u>Hours</u>
E7R	1.02	1.0	R	5	0	1,500	4.00
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	1,550	2.00
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
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	0.75	0.8	C	5	0	1,500	0.25
E36	0.68	1.0	P	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
E35	0.63	0.8	P	2	0.5	1,900	4.00
E24	0.60	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.

cylindrical extrude sorbents is not significantly impacted by the bentonite addition level.

Organic Binder

The starch additions (2 percent) to spherical pellet sorbents produced no measurable effect on reactivity. Similarly, overall analysis of the cylindrical extrude data showed no clear correlation between Methocel addition (0.5 percent) and reactivity.

The addition of starch to the spherical pellet sorbents did result in improved reactivity maintenance based both on direct comparisons and overall analysis. The Methocel additions also improved cylindrical extrude reactivity maintenance.

Induration Conditions

The single particle kinetic studies identified induration conditions as one of the most important factors which influence sorbent reactivity. TGA results indicated that greater reactivity correlates with more mild induration conditions (lower temperatures and shorter times). Most of the spherical pellet sorbents were indurated at 1,900°F in order to achieve sufficient strength to be considered for further bench-scale testing. Direct comparisons made between identical spherical pellet sorbent compositions which were indurated for different times at 1,900°F showed that the sorbents indurated for the shorter time period almost always exhibited greater reactivity.

The cylindrical extrude sorbents generally achieved greater strength than the spherical pellet sorbents, which allowed for more candidate extrude sorbents to be utilized after induration at lower temperatures. For the cylindrical extrude sorbents, the overall TGA results suggested that at 1,500°F, induration time is not a significant variable. However, at 1,900°F, the induration time should be kept to a minimum to avoid poor reactivity.

Analysis of reactivity maintenance results showed that lower induration temperatures and longer times favor greater reactivity maintenance for the cylindrical extrude shape. The induration conditions did not have a strong effect on the spherical pellet reactivity maintenance. The results also suggest that perhaps lower temperatures (between 1,300 and 1,500°F) could be utilized with longer induration times to further enhance sorbent reactivity and reactivity maintenance.

Surface Area and Porosity

Sorbent porosity was calculated by LSU researchers on the basis of individual sorbent pellet and extrude densities and on

sorbent feed component concentrations and their densities. Surface area determinations were performed at AMAX R&D.

The TGA results suggest that greater surface area is generally important in achieving greater reactivity for spherical pellets. While the correlation between the surface area and reactivity was poor, the results indicate that a sorbent surface area greater than $2 \text{ m}^2/\text{g}$ is beneficial. Surface area was not found to be a significant indicator of cylindrical extrude sorbent reactivity.

Porosity was found to correlate with both spherical pellet and cylindrical extrude reactivity. Those sorbents which contained greater porosity also generally exhibited greater reactivity. Based on previous LSU work⁶ which suggested that the global sulfidation rate is controlled by transport resistances, particularly diffusion through the product layer, porosity would be expected to be a more important parameter than the surface area. The TGA results do indicate a more significant effect of porosity than surface area on reactivity.

Neither surface area nor porosity was found to correlate well with spherical pellet or cylindrical extrude sorbent reactivity maintenance. The results indicate that there is a general tendency for reactivity maintenance to increase with both surface area and porosity.

Effect of Regeneration Temperature

The effects of regeneration temperature on reactivity maintenance were determined for selected sorbents. Previous work at LSU⁶ had shown that lower regeneration temperatures improved reactivity maintenance when using a UCI cylindrical extrude sorbent. Temperatures ranging from 1,022 to 1,562°F (550 to 850°C) were investigated during the previous work. Table 21 summarizes the results from the present program which showed that second-cycle sulfidation performance (reactivity maintenance) was improved when using lower regeneration temperatures. Standard first cycle and second cycle sulfidation procedures were conducted on each sample tested. Only the regeneration temperature was varied. At 1,202 and 1,292°F (650 and 700°C), complete regeneration was achieved without sulfate formation. At 1,112°F (600°C), appreciable amounts of sulfate were formed. These results showed that on the basis of regeneration kinetics, a 1,292°F (700°C) temperature is preferred. However, on the basis of subsequent sulfidation performance, a temperature of 1,202°F (650°C) might be preferred.

Table 21. Effect of Regeneration Temperature

	<u>Reactivity Maintenance^a</u>		
	<u>1,292°F</u> <u>(700°C)</u>	<u>1,202°F</u> <u>(650°C)</u>	<u>1,112°F</u> <u>(600°C)</u>
Sorbent E2 (at time = 30 minutes)	0.84	0.93	1.00
Sorbent P21 (at (time = 20 minutes)	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.

ALTERNATE REGENERATION PROCEDURE TESTING

METC expressed interest in the potential of using a two-step process for regenerating zinc ferrite desulfurization sorbents. In the first regeneration step, a gas mixture consisting of 12 percent SO₂, 2 percent O₂, and 86 percent N₂ was used to convert zinc and iron sulfides to their sulfate forms using a sorbent bed inlet temperature of about 850°F (454°C). For the second step, the temperature was raised to about 1,400°F (760°C), and the sulfates were decomposed to oxides with the concurrent release of sulfur dioxide. The same gas composition used for the first step was also used for the second step. The proposed technique requires no steam and also has the advantage of producing a regeneration gas rich in sulfur dioxide. In a commercial operation, recirculating regeneration gas would be supplemented with air as required to supply the necessary oxygen. A bleed stream from regeneration (concentrated SO₂ gas in nitrogen) would constitute feed to sulfur recovery.

Tests were performed at the AMAX R&D bench-scale sorbent test facility using the UCI T-2465 sorbent. Fresh sorbent was sulfided to saturation prior to each of the regeneration test series. Gas compositions, temperature profiles, pressure drops, and solids properties were characterized during each sulfidation and regeneration test.

A separate report describing the two-stage regeneration procedure and test results was prepared and is included as Appendix B. The alternate regeneration procedure and test results are summarized below.

Two sets of tests were performed. Superficial gas velocities of 2 and 3 feet per second during sulfidation and

each regeneration step (calculated at the temperature of operation) were utilized. Gas flow was upward through a 12-inch-tall fixed bed during each process step.

The UCI T-2465 zinc ferrite sorbent was successfully regenerated using a simulated, recirculating regeneration gas composition. The tests verified that sulfate formation took place under the conditions of the first regeneration step. The tests also showed that the sulfates could be decomposed to oxides at higher temperatures with the concurrent release of sulfur dioxide gas. Although the individual sorbent particles became softer while in the sulfate phase, physical integrity of the sorbent was maintained throughout the regeneration procedure.

TASK 4. BENCH-SCALE TEST ANALYSIS

Task 4 centered on the interpretation of bench-scale test results and the effects of sorbent preparation parameters. Direct comparisons of sorbent desulfurization performance and durability factors to isolate the effects of a single sorbent preparation variable were not possible because of the large number of variables examined during the program. Many of the interpretations are based on observed trends in performance as a function of changes in a primary variable but with some changes in secondary variables as well. For instance, the effects of iron oxide grade on sorbent sulfidation and durability were determined by averaging the sulfur sorption capacity (or crush strength, attrition resistance, etc.) for all spherical pellet and cylindrical extrude sorbents by iron oxide grade. Included in the averaged performance results were sorbents which contained different levels of inorganic and organic binders and different $\text{ZnO}:\text{Fe}_2\text{O}_3$ ratios. In some cases, comparisons of the performance of two sorbents which contained very similar compositions were possible. Results are discussed in the following sections.

CORRELATION OF TGA WITH BENCH-SCALE TEST RESULTS

Results of the single particle kinetic studies performed by TGA were compared to the multi-cycle, bench-scale test results. The LSU R20 and R30 values trended with AMAX bench-scale sulfidation test data, as shown in Figure 13. Based on regression of the data, coefficients of determination (r^2) of 0.70 and 0.64 were obtained for the spherical pellets and cylindrical extrudes, respectively. These trends and the similarity of conclusions drawn from both TGA and bench-scale test data indicate that the TGA is a valuable tool for ranking sorbent performance and for screening potential sorbents prior to further evaluation.

CHEMICAL ANALYSES

The results shown in Tables 15 and 16 for spherical pellet and cylindrical extrude chemical analyses, respectively, show that sorbent composition was generally uniform through the depth of the reactor bed. In some cases, it can be seen that sulfidation to complete saturation was not achieved in the upper portion of the reactor bed (see sulfur analyses for sorbents 1094-59, P37A, and E32A). As a result, some slight differences in iron and zinc concentrations through the depth of the bed may have occurred in these samples. However, the results in Tables 15 and 16 do not indicate migration of zinc from the bottom of the reactor to the upper portion of the reactor as has been observed in the past.² Further, selected regenerated sorbent samples which were taken from the top of the reactor bed did not show the light colored coating of zinc

oxide which had been observed previously.² Selected regenerated sorbent samples taken from the top of the reactor bed following the 9th cycle contained less than 0.2 percent sulfur in each case.

Figure 13. Sulfur sorption capacity as a function of sorbent reactivity.

PHYSICAL PROPERTIES

Results from the activities conducted during Tasks 2 and 3 were analyzed to determine the effects of sorbent preparation conditions on desulfurization performance. Table 22 summarizes fresh and sulfided sample data for sorbents subjected to multi-cycle bench-scale tests.

The fresh AMAX 1094-59 base case sorbent exhibited the lowest crush strength, attrition resistance, surface area, and bulk density of any of the spherical pellet sorbents selected for bench-scale testing. Most of the UCI T-2465 base case sorbent properties were within the range of values determined for the new sorbents prepared during the program. However, the UCI sorbent exhibited the lowest fresh sorbent surface area of any of the cylindrical extrudes chosen for bench-scale testing.

The measurement of the amount of fines which were produced during the multi-cycle bench-scale tests generally trended with measured sorbent attrition resistance values. The greatest quantity of minus 20 mesh fines produced during multi-cycle testing (1.28 percent) resulted from testing of sorbent P11A. The smallest quantity of fines produced during multi-cycle testing (0.13 percent) occurred during the testing of another spherical pellet sorbent, P6A.

Measured dimensional changes which occurred as a result of sulfidation are also shown in Table 22. As shown in the table, only slight changes to the sorbent diameters were observed. Cylindrical extrude sorbent diameters in particular exhibited very little change in diameter following sulfidation. These sorbents were manufactured using a fixed-diameter die, while the spherical pellet sorbents were manufactured over a small range of sorbent diameters due to the nature of the disk pelletization technique. As a result, more variability occurred in the spherical pellet diameter measurements.

The effects of sorbent preparation conditions on the physical properties of spherical pellet and cylindrical extrude sorbents are discussed in the following sections.

EFFECT OF SORBENT SHAPE

The program results indicated that, in general, the cylindrical extrude shape resulted in greater overall strength and better sulfidation performance compared to the spherical pellet shape.

The greater cylindrical extrude sorbent strength may be due to the extrusion procedure, which employs high pressure during sorbent formation through a round die. Spherical pellets, on the other hand, are formed by agglomerating the dry powders to achieve the desired sorbent diameter. An "onion-skin" structure results from the disk pelletization technique. The greater compaction utilized during extrusion probably provides for greater interparticle contact and allows for greater strength and attrition resistance to be achieved using less severe induration conditions. Spherical pellets required more severe induration conditions to achieve the level of strength required for multi-cycle, bench-scale tests. The more severe induration conditions used for the spherical pellets to develop strength also probably resulted in closing internal pores which are important for sulfur sorption kinetics and sulfur sorption capacity.

Greater sulfur sorption capacity for the cylindrical extrudes could also be attributed in part to small fractures which were observed to form along an axial orientation. These fractures could have resulted from stresses induced during the sorbent formation procedure. The very small fractures could

Table 22. Physical Properties and Chemical Analyses of Fresh and Sulfided Sorbents

	Spherical Pellets						Cylindrical Extrudes						
	Base Case AMAX						Base Case UCI						
	1094-59	P11A	P6A	P27A	P37A	P22A	T-2465	E13A	E7A	E24A	E28A	E32A	E2A
<u>Iron Oxide Grade</u>	P	C	P	C	P	C	C	C	P	C	P	P	C
<u>Physical Properties</u>													
Crush Strength, lb (Pellets)													
lb/mm (Extrudes)													
Fresh Sorbent	5.1	16.6	22.0	22.0	22.1	19.4	3.5	4.4	2.5	5.3	3.3	3.0	3.7
Sulfided Sorbent	13.7	11.0	32.1	33.6	34.7	19.1	2.9	3.4	4.5	5.3	4.5	3.1	4.0
Attrition Resistance, %													
Fresh Sorbent	45.5	80.5	89.0	80.9	90.7	82.4	88.8	85.4	87.5	91.7	89.3	84.6	93.3
Sulfided Sorbent	69.1	68.8	97.4	83.0	96.8	79.4	78.2	82.7	90.8	89.9	93.9	93.2	88.0
Bulk Density, kg/l													
Fresh Sorbent	1.01	1.14	1.49	1.14	1.28	1.15	1.31	1.26	1.25	1.33	1.23	1.19	1.22
Sulfided Sorbent	1.12	1.28	1.59	1.25	1.51	1.27	1.46	1.42	1.40	1.49	1.36	1.33	1.37
Surface Area, m ² /g													
Fresh Sorbent	1.01	2.63	1.68	1.21	1.76	1.95	3.30	4.06	5.62	4.15	4.99	6.33	4.38
Sulfided Sorbent	3.53	1.27	2.05	1.45	2.25	1.42	1.53	2.22	5.85	2.70	6.79	4.86	2.42
Sorbent Diameter, mm													
Fresh Sorbent	4.6	4.9	4.7	4.9	4.4	4.9	5.0	4.9	4.8	4.8	4.7	4.8	4.9
Sulfided Sorbent	5.0	4.9	4.3	5.1	4.6	5.1	5.0	4.9	4.7	4.8	4.7	4.7	4.9
Fines Produced During Cyclic Testing, % +20 Mesh	0.97	1.23	0.13	0.46	0.08	0.53	0.61	0.48	0.27	0.31	0.20	0.26	0.24

P = Pigment-grade iron oxide.

C = Catalyst-grade iron oxide.

help in providing reaction pathways to the interior of the sorbent with a minimal loss in strength. The microstructure and mineralogy of the sorbents are discussed further under the "Sorbent Mineralogy" heading.

EFFECT OF IRON OXIDE GRADE

Table 23 shows the effect of sorbent shape and iron oxide grade on sulfur sorption capacity measured at sulfur saturation. The values in the table are derived from Tables 13 and 14. The catalyst-grade iron oxide formulations were found to provide greater sulfur sorption capacity. In addition, the cylindrical extrude shape resulted in greater sulfur sorption capacity at saturation. These results are consistent with the single particle kinetic study findings. The differences in the results obtained from sorbents prepared using pigment- and catalyst-grade iron oxide should be evaluated in terms of sorbent economics, since the pigment-grade iron oxide is less expensive than catalyst-grade iron oxide (about \$0.75 per pound versus up to \$2 per pound).

Table 23. Effect of Iron Oxide Grade on Sulfur Sorption Capacity

	Sulfur Sorption Capacity at Saturation, pound/ <u>100 pounds Sorbent</u>		Percent of Theoretical Capacity <u>Achieved</u>
	<u>Theoretical</u>	<u>Observed</u>	
<u>Pigment-Grade Fe₂O₃</u>			
Spheres	38.1	29.5	77.4
Extrudes	38.7	35.1	90.7
<u>Catalyst-Grade Fe₂O₃</u>			
Spheres	37.0	31.0	83.8
Extrudes	38.8	37.0	95.4

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.

The catalyst-grade iron oxide formulations were generally more durable than the pigment-grade iron oxide formulations. However, pigment-grade iron oxide led to improvements in crush strength and attrition resistance following sulfidation. The catalyst-grade iron oxide led to decreases in crush strength and attrition resistance following sulfidation when formulated

using a 1.0 ZnO:Fe₂O₃ ratio. The catalyst-grade iron oxide resulted in improved crush strength and attrition resistance following sulfidation when formulated using a 0.8 ZnO:Fe₂O₃ ratio.

EFFECT OF ZnO:Fe₂O₃ RATIO

Table 24 shows the effect of the ZnO:Fe₂O₃ mole ratio on sulfidation performance. Overall, the sorbents prepared using a 1.0 ZnO:Fe₂O₃ ratio performed better than those prepared using the 0.8 ZnO:Fe₂O₃ ratio. Only the sulfur sorption capacity for the extrude shape at saturation was improved using the 0.8 ratio; otherwise all comparisons favored the 1.0 ratio. As discussed above, the catalyst-grade iron oxide formulations generally provided better sulfidation performance than the pigment-grade iron oxide formulations.

Table 24. Effect of ZnO:Fe₂O₃ Ratio and Iron Oxide Grade on Sulfur Sorption Capacity

<u>Sorbent Shape</u>	<u>Iron Oxide Grade</u>	<u>Sulfur Sorption Capacity at Indicated ZnO:Fe₂O₃ Ratio, pounds S/100 pounds Sorbent</u>			
		<u>At Breakthrough</u>		<u>At Saturation</u>	
		<u>0.8</u>	<u>1.0</u>	<u>0.8</u>	<u>1.0</u>
Spherical Pellets	Pigment	6.2	1.2	27.4	33.7
	Catalyst	10.0	19.1	29.5	31.8
Cylindrical Extrudes	Pigment	8.2	12.2	35.1	35.4
	Catalyst	12.5	17.3	39.6	36.2

Table 25 shows the effect of the ZnO:Fe₂O₃ ratio on sorbent durability. The effect of the ZnO:Fe₂O₃ ratio was inconclusive for extrude crush strength. The 0.8 ratio was preferred for spherical pellet crush strength. The 0.8 ratio was also preferred for attrition resistance, especially for sulfided spherical pellets.

EFFECT OF BENTONITE CONTENT

Table 26 shows the effect of bentonite content on sorbent sulfidation performance. Sulfur sorption capacity at breakthrough was favored by lower bentonite additions for both sorbent shapes (even after correcting for the quantity of inert material). Sulfur sorption capacity at saturation was favored by higher bentonite content for spherical pellets. Results were inconclusive for cylindrical extrudes.

Table 25. Effect of ZnO:Fe₂O₃ Ratio and Iron Oxide Grade on Sorbent Durability

<u>Sorbent Shape</u>	<u>Iron Oxide Grade</u>	<u>Durability at Indicated ZnO:Fe₂O₃ Ratio</u>			
		<u>Crush Strength^a</u>		<u>Attrition Resistance, %</u>	
		<u>(Fresh/Sulfided)</u>		<u>(Fresh/Sulfided)</u>	
		<u>0.8</u>	<u>1.0</u>	<u>0.8</u>	<u>1.0</u>
Spherical Pellets	Pigment	22.1/33.4	5.1/13.7	89.9/97.1	45.5/69.1
	Catalyst	22.0/33.6	18.0/15.1	80.9/83.0	81.5/74.1
Cylindrical Extrudes	Pigment	3.2/3.8	2.5/4.5	87.0/93.6	87.5/90.8
	Catalyst	3.7/4.0	4.4/3.9	93.3/88.0	88.6/83.7

^a Units = Pounds for spherical pellets.
Units = Pounds/mm for cylindrical extrudes.

Table 26. Effect of Bentonite Content on Sulfur Sorption Capacity

<u>Sorbent Shape</u>	<u>Iron Oxide Grade</u>	<u>Sulfur Sorption Capacity at Indicated Bentonite Addition, %</u>					
		<u>At Breakthrough, Pounds S/100</u>			<u>At Saturation, Pounds S/100</u>		
		<u>Pounds Sorbent</u>			<u>Pounds Sorbent</u>		
		<u>2</u>	<u>5</u>	<u>10</u>	<u>2</u>	<u>5</u>	<u>10</u>
Spherical Pellets	Pigment	9.9	1.8	--	27.1	30.7	--
	Catalyst	24.7	--	11.7	32.6	--	30.3
Cylindrical Extrudes	Pigment	11.2	6.2	--	30.4	32.7	--
	Catalyst	17.5	11.8	--	36.9	37.3	--

Note: -- indicates conditions for which the sorbent was not prepared.

Table 27 shows the effect of bentonite content on sorbent durability. For cylindrical extrudes, greater bentonite additions would be preferred for greater crush strength and attrition resistance. For spherical pellets, greater bentonite additions might be slightly favored for sulfided sorbent strength. Results are inconclusive for fresh spherical pellet sorbents.

EFFECT OF ORGANIC BINDER

Table 28 shows the effect of the organic binder on sulfidation performance. Overall, sorbents prepared using the

Table 27. Effect of Bentonite Content on Sorbent Durability

<u>Sorbent Shape</u>	<u>Iron Oxide Grade</u>	<u>Durability at Indicated Bentonite Addition, %</u>					
		<u>Crush Strength^a (Fresh/Sulfided)</u>			<u>Attrition Resistance, % (Fresh/Sulfided)</u>		
		<u>2</u>	<u>5</u>	<u>10</u>	<u>2</u>	<u>5</u>	<u>10</u>
Spherical Pellets	Pigment	89.0/97.4	68.1/83.0	--	22.0/32.1	13.6/24.2	--
	Catalyst	80.5/68.8	--	81.7/81.2	16.6/11.0	--	20.7/26.4
Cylindrical Extrudes	Pigment	86.1/92.0	89.3/93.9	--	2.8/3.8	3.3/4.5	--
	Catalyst	89.2/83.0	91.7/89.9	--	3.9/3.4	5.3/5.3	--

^a Units = Pounds for spherical pellets.
Units = Pounds/mm for cylindrical extrudes.

Note: -- indicates conditions for which the sorbent was not prepared.

organic binder resulted in poorer sulfidation performance at breakthrough. The sulfur sorption capacity at saturation, however, was slightly better when the organic binder was used.

Table 28. Effect of Organic Binder Addition on Sulfur Sorption Capacity

<u>Sorbent Shape</u>	<u>Iron Oxide Grade</u>	Sulfur Sorption Capacity With and Without Organic Binder Addition, Pounds S/100 Pounds Sorbent			
		<u>At Breakthrough</u>		<u>At Saturation</u>	
		<u>Without</u>	<u>With</u>	<u>Without</u>	<u>With</u>
Spherical Pellets	Pigment	6.2	1.2	27.4	33.7
	Catalyst	19.1	10.0	31.8	29.5
Cylindrical Extrudes	Pigment	12.2	8.2	35.4	35.1
	Catalyst	17.4	14.8	37.0	37.1

Table 29 shows the effect of organic binder addition on sorbent durability. Organic binder additions resulted in improved fresh extrude sorbent crush strength. The effect on sulfided extrude sorbents was not clear. The organic binder also apparently reduced spherical pellet crush strength in sorbents prepared using pigment-grade iron oxide. The organic binder apparently improved spherical pellet crush strength in sorbents prepared using catalyst-grade iron oxide.

Table 29. Effect of Organic Binder Addition on Sorbent Durability

<u>Sorbent Shape</u>	<u>Iron Oxide Grade</u>	<u>Durability With and Without Organic Binder</u>			
		<u>Crush Strength^a</u>		<u>Attrition Resistance, %</u>	
		<u>(Fresh/Sulfided)</u>		<u>(Fresh/Sulfided)</u>	
		<u>Without</u>	<u>With</u>	<u>Without</u>	<u>With</u>
Spherical Pellets	Pigment	22.1/33.4	5.1/13.7	89.9/97.1	45.5/69.1
	Catalyst	18.0/15.1	22.0/33.6	81.5/74.1	80.9/83.0
Cylindrical Extrudes	Pigment	2.5/4.5	3.2/3.8	87.5/90.8	87.0/93.6
	Catalyst	3.6/3.5	4.9/4.4	91.1/83.1	88.6/86.4

^a Units = Pounds for spherical pellets.
Units = Pounds/mm for cylindrical extrudes.

The organic binder resulted in a slight decrease in fresh cylindrical extrude sorbent attrition resistance while resulting in a slight increase in sulfided sorbent cylindrical

extrude attrition resistance. The same observations generally hold for the spherical pellet shape (except for catalyst-grade formulations), but overall, results are inconclusive.

EFFECT OF INDURATION CONDITIONS

Observations related to the effect of induration conditions on spherical pellet performance show that less severe induration conditions lead to enhanced reactivity. Spherical pellet durability was improved with more severe induration conditions. The following points summarize the effect of induration conditions on spherical pellet performance.

- All new sorbents were indurated at 1,900°F.
- All were indurated for 4 hours, except P11A (0.25 hour).
- P11A exhibited the best sulfur sorption capacity at breakthrough of all of the new spherical pellet sorbents.
- P11A exhibited the lowest values of crush strength and attrition resistance of the new spherical pellets prepared during the program.

Table 30 summarizes the effect of induration conditions on cylindrical extrude sulfidation performance at breakthrough and at saturation, respectively. The lower temperatures were preferred for pigment-grade formulations in terms of sulfur sorption capacity at breakthrough. The same appeared to be generally true for the catalyst-grade formulations, although not as conclusively.

Table 30. Effect of Induration Conditions on Sulfur Sorption Capacity (Cylindrical Extrude Sorbents)

Iron Oxide Grade	Sulfur Sorption Capacity at Breakthrough at Indicated Induration Conditions, Pounds S/100 Pounds Sorbent			
	1,500°F	1,550°F	1,700°F	1,900°F
	<u>4 Hours</u>	<u>2 Hours</u>	<u>2 Hours</u>	<u>0.5 Hour</u>
Pigment	11.2		6.2	
Catalyst	12.5	22.3	17.7	11.8
Iron Oxide Grade	Sulfur Sorption Capacity at Saturation at Indicated Induration Conditions, Pounds S/100 Pounds Sorbent			
	1,500°F	1,550°F	1,700°F	1,900°F
	<u>4 Hours</u>	<u>2 Hours</u>	<u>2 Hours</u>	<u>0.5 Hour</u>
Pigment	36.4		32.7	
Catalyst	39.6	34.3	36.9	37.3

For pigment-grade iron oxide, the lower induration temperatures were preferred in terms of sulfur sorption capacity at saturation. Results for sulfur sorption capacity at saturation were not conclusive for the catalyst-grade formulations.

Table 31 summarizes the effect of induration conditions on cylindrical extrude sorbent durability. In general, higher induration temperatures and longer induration times resulted in greater sorbent crush strength and attrition resistance.

Table 31. Effect of Induration Conditions on Sorbent Durability (Cylindrical Extrude Sorbents)

Iron Oxide Grade	Crush Strength, lb/mm, at Indicated Induration Conditions (Fresh/Sulfided)			
	1,500°F	1,550°F	1,700°F	1,900°F
	4 Hours	4 Hours	2 Hours	0.5 Hour
Pigment	2.8/3.8	--	3.3/4.5	--
Catalyst	3.7/4.0	3.5/2.9	4.4/3.4	5.3/5.3

Iron Oxide Grade	Attrition Resistance, %, at Indicated Induration Conditions (Fresh/Sulfided)			
	1,500°F	1,550°F	1,700°F	1,900°F
	4 Hours	2 Hours	2 Hours	0.5 Hour
Pigment	86.1/92.0	--	89.3/93.9	--
Catalyst	93.3/88.0	88.8/78.2	85.4/82.9	91.7/89.9

Note: -- indicates conditions for which the sorbent was not prepared.

EFFECT OF POROSITY

The effect of porosity on sulfidation performance is shown in Figure 14. The bench-scale sulfidation performance was taken as the average sulfur sorption capacity at breakthrough (in units of pounds sulfur per 100 pounds fresh sorbent) obtained during 10 test cycles. Total porosity values (as determined by the mercury intrusion technique using pressures up to 15,000 psi) account for pores with diameters greater than 0.012 micron. These values did not correlate well with the single particle kinetic data or with the bench-scale test data. However, porosity values for pores greater than 0.18 micron did correlate with single particle kinetic data and bench-scale test data. Coefficients of determination of 0.84 and 0.55 were obtained for the spherical pellets and cylindrical extrudes, respectively. The larger pores apparently provide a pathway to the interior of the sorbent particles to allow for

the sulfur gases to continue reacting. * The smaller pores may become plugged fairly rapidly as the sulfidation reactions proceed (with a concurrent volume increase).

Figure 14. Sulfur sorption capacity as a function of sorbent porosity.

Similar relationships were observed when using the reactivity values from LSU single particle kinetic studies instead of the bench-scale sulfidation data. Figure 15 shows the R20 and R30 values as a function of porosity. (R20 and R30 represent the sulfur sorption capacity of spherical pellets at an elapsed time of 20 minutes and of cylindrical extrudes at an elapsed time of 30 minutes, respectively, obtained during TGA tests.) Coefficients of determination of 0.79 and 0.64 were found for the spherical pellets and cylindrical extrudes, respectively.

Porosity values based on LSU calculations using sorbent particle and sorbent component density values trend with the mercury intrusion porosity values, as shown in Figure 16. It would be expected that the calculated values would be generally somewhat greater than the measured values, since the measurements in this case do not detect closed pores and pores

Figure 15. Effect of porosity on sorbent reactivity.

Figure 16. Correlation of calculated porosity and measured porosity.

smaller than 0.012 micron in diameter. The calculated values would include closed pores and small pores.

Mercury intrusion porosimetry was performed on selected sulfided sorbents. Results are shown in Table 32, along with fresh sorbent porosity for comparison. Of the four sulfided sorbents which were analyzed, the three which exhibited the best reactivity also exhibited significantly decreased pore volume upon sulfidation. The sorbent which exhibited poor reactivity (1094-59) exhibited only a slight decrease in pore volume upon sulfidation to saturation. The average pore radius of the fresh 1094-59 sorbent was also much greater than most of the other fresh sorbents. In general, the spherical pellets exhibited larger average pore radius than the cylindrical extrudes. The more reactive sorbents exhibited greater differences in porosity between fresh and sulfided forms. The 1094-59 sorbent exhibited only a slight decrease in porosity upon sulfidation.

Table 32. Porosity of Fresh and Sulfided Sorbents

<u>Sorbent Identification</u>	<u>Total Pore Volume, cm³/g</u>	<u>Average Pore Radius, Angstroms</u>	<u>Porosity, %</u>	
			<u>Pores >0.180 μm</u>	<u>Pores >0.012 μm</u>
<u>T-2465</u>				
Fresh	0.256	1,550	50.1	58.2
Sulfided	0.121	1,580	28.6	32.4
<u>1094-59</u>				
Fresh	0.277	5,940	48.5	59.2
Sulfided	0.260	1,470	47.3	50.8
<u>P11A</u>				
Fresh	0.319	2,430	59.7	63.8
Sulfided	0.201	3,165	42.1	44.4
<u>P6A</u>				
Fresh	0.207	2,460	49.1	52.1
Sulfided	0.079	770	17.8	24.0

Note: Porosity was determined using the mercury intrusion technique. 0.180 μ m pores are measured at an applied pressure of 1,000 psi. 0.012 μ m pores are measured at an applied pressure of 15,000 psi.

EFFECT OF SURFACE AREA

Surface area data were analyzed to determine whether any trends with sulfidation performance could be found. Figure 17 shows the relationship between fresh sorbent surface area and the average sulfur sorption capacity at breakthrough exhibited by the sorbents. Although the coefficients of determination were low (0.68 and 0.49 for the spherical pellets and cylindrical extrudes, respectively), it appears that there is a trend of increasing reactivity with increasing surface area for the spherical pellets. On the other hand, the average sulfur sorption capacity drops with increasing cylindrical extrude surface area. Based on porosity and surface area determinations, it would appear that the surface area associated with very small pores does not contribute to coal gas desulfurization. No trends between the sulfur sorption capacity at saturation and the fresh sorbent surface area were observed.

Figure 17. Effect of fresh sorbent surface area on sulfur sorption capacity.

Sulfided sorbent surface areas were also examined. As shown in Figure 18, both sorbent shapes exhibited decreasing

sulfur sorption capacity at breakthrough as a function of increasing sulfided sorbent surface area. Apparently, surface area decreases as sulfidation proceeds. Those sorbents which exhibited very good sulfur sorption capacity at breakthrough exhibited the lowest sulfided sorbent surface area values. No trends of saturated sorbent surface area against sorbent sulfur sorption capacity at saturation were found.

Figure 18. Sulfur sorption capacity as a function of sulfided sorbent surface area.

Although sorbents prepared using the Ruthner process iron oxide demonstrated the greatest reactivity of any sorbent prepared and tested during the base program (as determined by TGA), this particular iron oxide powder feed exhibited the lowest surface area of the three potential feeds. The Mobay (Bayferrox pigment grade) iron oxide exhibited the highest surface area of the three iron oxide feed powders and generally produced sorbents exhibiting the lowest reactivity. Thus, the surface area of starting feed material is not necessarily a good indicator of sorbent product reactivity.

SORBENT MINERALOGY

Fresh and sulfided sorbents selected for multi-cycle bench-scale testing were analyzed by X-ray diffraction for the presence of mineral phases. Tables 33 and 34 summarize the results of these analyses for spherical pellets and cylindrical extrudes, respectively. Appendix C contains the individual mineralogy reports for the sorbents examined during the program.

Mineralogical analyses identified the phases indicated in Tables 33 and 34. It should be noted that the X-ray diffraction patterns for franklinite (ZnFe_2O_4) and magnetite (Fe_3O_4) are very similar. The mineralogy results shown in the tables report these values only as franklinite. Minor amounts of magnetite may be present in the sorbents. However, based on the sorbent formulations (many of which included a stoichiometric mixture of ZnO and Fe_2O_3 powders), it can be inferred that any magnetite concentration present in fresh sorbent is very low. ZnO was detected only in the fresh T-2465 sorbent. The total amount of unidentified phases was generally less than 2 percent. Unidentified phases might include minerals such as ZnO or FeO which exist in concentrations too low to adequately identify characteristic peaks.

It should be further noted that the estimated concentrations of phases shown in Tables 33 and 34 are intended to indicate relative differences in sorbent composition. For example, in some cases, the sorbent mineralogical analyses indicated the presence of more zinc sulfide than should exist based on the sorbent formulations. However, relative differences between sorbent sampled from the top and bottom portions of the reactors or between different sorbent types can still be examined.

The presence of hematite (up to 14 weight percent) in some of the fresh sorbent samples was noted. With the exception of the UCI T-2465 sorbent, each sorbent in which hematite was identified had been formulated using a stoichiometric deficiency of zinc oxide. The presence of hematite in the indurated sorbents could indicate a zinc deficiency, agglomerates of iron oxide which did not have sufficient zinc oxide with which to react, or inadequate induration severity for the conversion of the zinc and iron oxides to zinc ferrite.

Generally, sulfided sorbents sampled from the bottom of the reactor bed had the same or lower content of franklinite (zinc ferrite) as samples taken from the top of the bed. Since the sulfidation gas was introduced into the bottom portion of the reactor bed, it would be expected that a greater quantity of sulfides would be present near the bottom if the final

Table 33. X-ray Diffraction Analysis of Zinc Ferrite Spherical Pellet Sorbents

<u>Sample</u>	<u>Estimated Weight Percent of Indicated Phase</u>					
	<u>Franklinite</u> <u>(ZnFe₂O₄)</u>	<u>Sphalerite</u> <u>(B-ZnS)</u>	<u>Wurtzite</u> <u>(A-ZnS)</u>	<u>Pyrrhotite</u> <u>(Fe_{1-x}S)</u> <u>+ Troilite</u> <u>(FeS)</u>	<u>Hematite</u> <u>(Fe₂O₃)</u>	<u>Other Plus</u> <u>Unidentified</u>
<u>AMAX 1094-59</u>						
Fresh	100					
Sulfided (Top)	30	a		10		10
Sulfided (Bottom)	5	b		15		10
<u>P11A</u>						
Fresh	100					
Sulfided (Top)	13	30	12	45		<1
Sulfided (Bottom)	10	32	0	40		10
<u>P6A</u>						
Fresh	100					
Sulfided (Top)	35	25	15	25		
Sulfided (Bottom)	35	25	15	25		
<u>P27A</u>						
Fresh	92				7	<1
Sulfided (Top)	25	38	10	27		<1
Sulfided (Bottom)	25	38	10	27		<1
<u>P37A</u>						
Fresh	>98					<2
Sulfided (Top)	30	42	12	16		<1
Sulfided (Bottom)	20	40	13	27		<1
Regenerated	>98					<2
<u>P22A</u>						
Fresh	>98					<2
Sulfided (Top)	10	46	14	30		<1
Sulfided (Bottom)	16	46	12	26		<1
Regenerated	96				2	<2

a Total ZnS = 50.

b Total ZnS = 70.

Notes: "Top" and "bottom" refer to sulfided sorbent sampled from the top and bottom portions of the reactor bed. "Regenerated" refers to sorbent sampled from the top of the reactor bed following the 9th regeneration cycle.

Table 34. X-ray Diffraction Analysis of Zinc Ferrite Cylindrical Extrude Sorbents

Sample	Estimated Weight Percent of Indicated Phase					
	Franklinite ($ZnFe_2O_4$)	Sphalerite ($B-ZnS$)	Wurtzite ($A-ZnS$)	Pyrrhotite ($Fe_{1-x}S$) + Troilite (FeS)	Hematite (Fe_2O_3)	Other Plus Unidentified
UCI T-2465						
Fresh	>95				2	2% ZnO
Sulfided (Top)	10	a		20		10
Sulfided (Bottom)	10	b		20		10
E13A						
Fresh	100					
Sulfided (Top)	15	30	15	40		
Sulfided (Bottom)	18	40	12	30		
E7A						
Fresh	100					
Sulfided (Top)	20	40	20	20		
Sulfided (Bottom)	10	50	15	25		
E24A						
Fresh	>98					<2
Sulfided (Top)	8	40	22	30		<1
Sulfided (Bottom)	8	40	22	30		<1
E28A						
Fresh	95				5	<1
Sulfided (Top)	18	45	15	22		<1
Sulfided (Bottom)	12	42	15	30		<1
E32A						
Fresh	90				10	<1
Sulfided (Top)	28	38	16	18		<1
Sulfided (Bottom)	7	40	15	35		<3
Regenerated	>98					<2
E2A						
Fresh	85				14	<1
Sulfided (Top)	20	44	12	24		<1
Sulfided (Bottom)	8	40	18	34		<1
Regenerated	75				24	<1

a Total ZnS = 50.

b Total ZnS = 70.

Notes: "Top" and "bottom" refer to sulfided sorbent sampled from the top and bottom portions of the reactor bed. "Regenerated" refers to sorbent sampled from the top of the reactor bed following the 9th regeneration cycle.

sulfidation step were not carried out to complete saturation of the sorbent bed. In most cases, the amount of franklinite remaining in the sulfided sorbents was similar in the top and bottom portions of the reactor bed. The presence of up to 35 percent franklinite in sorbents which were exposed to sulfidation to near-saturation indicates that some of the potentially reactive oxides were not accessible to the sulfidation gas. For instance, sorbent P6A contained 35 percent franklinite in samples taken from both the top and bottom portions of the reactor bed. This sample was also shown to have achieved the lowest sulfur sorption capacity at saturation of any of the other sorbents tested.

During the later test series, a small sample of regenerated sorbent was taken from the very top of the reactor bed following the 9th regeneration step. In three of the four available samples (P37A, P22A, and E32A), at least 96 percent of the regenerated sorbent was accounted for by the mineral phase franklinite. In the other case (sorbent E2A), 75 percent of the regenerated sorbent was accounted for by franklinite. Nearly all of the remainder of the regenerated sorbent consisted of hematite. The fresh E2A sorbent also contained a significant quantity of hematite (14 percent).

X-ray diffraction analysis of the pigment- and catalyst-grade iron oxide feed powders showed hematite as the only detectable phase. The Ruthner process iron oxide was found to contain greater than 98 percent hematite.

Selected sorbent samples were also subjected to optical and scanning electron microscopy. Microscopic examination of the UCI T-2465 sorbent in polished section normal to the extrude axis showed small fractures which appeared following repeated cyclic testing. A sample of the T-2465 sorbent which was examined after only one sulfidation step did not exhibit fractures. The fractures could be the result of extrusion stresses which are introduced during sorbent production. The presence of these relief fractures could contribute to the permeability of the extrudes, apparently without great sacrifice of sorbent durability. These fractures were not detected in the spherical pellet shapes.

Additional samples were evaluated by electron microprobe to establish the association of sulfur, iron, and zinc in the sulfided sorbents. Analyses were performed near the edges and in the interior of the sulfided sorbents.

Microprobe analysis of the sulfided AMAX 1094-59 sorbent showed a fairly uniform distribution of zinc and iron near the edges and in the interior of the particles. Sulfur distribution was less uniform. Unreacted franklinite apparently accounts for the uneven distribution. (See Figure 2 of the October 12, 1987, mineralogy report in Appendix C.)

Silicate grains, which were not observed in the base case cylindrical extrude, were also identified. The edges of the sulfided sorbent sampled from the top and bottom of the reactor and the interior of the bottom sample exhibited more uniform zinc, iron, and sulfur distributions than the interior of the top sample. Concentric layers which were high in sulfur were noted during microprobe analysis of the 1094-59 sorbent sampled from both the top and bottom portions of the reactor.

The microprobe analysis of the UCI T-2465 sorbent showed that some segregation of zinc and iron existed. However, both the high-iron and high-zinc phases appeared to be well sulfided. (See Figure 1 of the October 12, 1987, mineralogy report in Appendix C.) Separation of the zinc and iron phases was more pronounced in the sulfided sorbent sampled from the bottom of the reactor and in the edges of sulfided sorbent sampled from the top of the reactor. This phase separation could be attributed to zinc migration during cyclic sulfidation and regeneration. However, the degree of zinc migration appeared very low compared to some previous zinc ferrite sorbents.²

SORBENT GRADING SYSTEM

A sorbent grading system was utilized to quantify the results. Table 35 shows the criteria used for the evaluations. The value ranges and grades were selected to cover the range of observed values from the test program. In cases where both sorbent shapes were subjected to the same measurements or test procedures, the value ranges for both shapes were kept the same. Some differences in the value ranges were required for the determination of crush strength due to the different units reported for spherical pellets and cylindrical extrudes. Note that due to the relatively poor correlations between porosity or surface area and sulfidation performance, these factors were given a low weighting factor (5 percent each). In addition, only two grades were assigned rather than the 5 possible grades assigned to the other categories. These assignments are based on the information shown in Figures 14 and 17, which illustrate different responses to porosity and surface area for the two sorbent shapes.

Tables 36 and 37 show the sorbent evaluations for the spherical pellets and cylindrical extrudes, respectively. Sulfur sorption capacity at breakthrough was evaluated in terms of the averages of the first 5 and last 5 cycles. Greater weighting was placed on the average sulfur sorption capacity achieved during the last 5 cycles (15 percent versus 5 percent for the first 5 cycles). Sulfur sorption capacity at saturation was given a weighting factor of 20 percent, since in a commercial unit much of the sorbent bed will be subjected to full sulfidation.

Table 35. Zinc Ferrite Sorbent Grading System Criteria

Evaluation Category	Value Range		Grade
	Spheres	Extrudes	
<u>Chemical Reactivity Factors</u>			
1. Sulfur Sorption Capacity (1b S/100 lb Fresh Sorbent) at 200 ppm H ₂ S Breakthrough	x < 5	x < 5	1
	5 ≤ x < 10	5 ≤ x < 10	2
	10 ≤ x < 15	10 ≤ x < 15	3
	15 ≤ x < 20	15 ≤ x < 20	4
	x ≥ 20	x ≥ 20	5
2. Sulfur Sorption Capacity (1b S/100 lb Fresh Sorbent) at Saturation	x < 25	x < 25	1
	25 ≤ x < 28	25 ≤ x < 28	2
	28 ≤ x < 31	28 ≤ x < 31	3
	31 ≤ x < 35	31 ≤ x < 35	4
	x ≥ 35	x ≥ 35	5
3. Fresh Sorbent Surface Area (m ² /g)	x < 1.2	x > 4.2	3
	x ≥ 1.2	x ≤ 4.2	5
4. Fresh Sorbent Porosity (%)	x < 55	x < 35	3
	x ≥ 55	x ≥ 35	5
<u>Physical Durability Factors</u>			
1. Crush Strength (lb) Fresh and Sulfided Sorbent	x < 10	x < 3.0	1
	10 ≤ x < 15	3.0 ≤ x < 3.5	2
	15 ≤ x < 20	3.5 ≤ x < 4.0	3
	20 ≤ x < 25	4.0 ≤ x < 5.0	4
	x ≥ 25	x ≥ 5.0	5
2. Attrition Resistance (%) Fresh and Sulfided Sorbent	x < 60	x < 60	1
	60 ≤ x < 70	60 ≤ x < 70	2
	70 ≤ x < 80	70 ≤ x < 80	3
	80 ≤ x < 90	80 ≤ x < 90	4
	x ≥ 90	x ≥ 90	5
3. Fines Produced During 10 Cycles (%)	x > 0.8	x > 0.8	1
	0.6 < x ≤ 0.8	0.6 < x ≤ 0.8	2
	0.4 < x ≤ 0.6	0.4 < x ≤ 0.6	3
	0.2 < x ≤ 0.4	0.2 < x ≤ 0.4	4
	x ≤ 0.2	x ≤ 0.2	5

Table 36. Zinc Ferrite Spherical Pellet Sorbent Performance

Sorbent Rating Category	Weighting Factor, %	1094-59		P11A		P6A		P27A		P37A		P22A	
		Grade	Points	Grade	Points	Grade	Points	Grade	Points	Grade	Points	Grade	Points
<u>Chemical Reactivity Factors</u>													
1. Sulfur Sorption Capacity at 200 ppm H ₂ S Breakthrough													
a. Average of First 5 Cycles	5	1	5	5	25	3	15	3	15	1	5	3	15
b. Average of Last 5 Cycles	<u>15</u>	1	<u>15</u>	5	<u>75</u>	2	<u>30</u>	2	<u>30</u>	1	<u>15</u>	3	<u>45</u>
Subtotal	20	--	20	--	100	--	45	--	45	--	20	--	60
2. Sulfur Sorption Capacity at Saturation	20	4	80	4	80	2	40	3	60	2	40	4	80
3. Fresh Sorbent Surface Area	5	3	15	5	25	3	15	3	15	3	15	5	25
4. Fresh Sorbent Porosity	<u>5</u>	3	<u>15</u>	5	<u>25</u>	3	<u>15</u>	3	<u>15</u>	3	<u>15</u>	5	<u>25</u>
Total	50	--	130	--	230	--	115	--	135	--	90	--	190
<u>Physical Durability Factors</u>													
1. Crush Strength													
a. Fresh Sorbent	10	1	10	3	30	4	40	4	40	4	40	3	30
b. Sulfided Sorbent	<u>10</u>	2	<u>20</u>	3	<u>30</u>	5	<u>50</u>	5	<u>50</u>	5	<u>50</u>	3	<u>30</u>
Subtotal	20	--	30	--	60	--	90	--	90	--	90	--	60
2. Attrition Resistance													
a. Fresh Sorbent	10	1	10	4	40	4	40	4	40	5	50	4	40
b. Sulfided Sorbent	<u>10</u>	2	<u>20</u>	2	<u>20</u>	5	<u>50</u>	4	<u>40</u>	5	<u>50</u>	3	<u>30</u>
Subtotal	20	--	30	--	60	--	90	--	80	--	100	--	70
3. Fines Produced During 10 Cycles	<u>10</u>	1	<u>10</u>	1	<u>10</u>	5	<u>50</u>	3	<u>30</u>	5	<u>50</u>	3	<u>30</u>
Total	50	--	70	--	130	--	230	--	200	--	240	--	160
Final Total	100		200		360		345		335		330		350
% of Maximum Possible Points			40		72		69		67		66		70

Note that maximum possible points = 500 (250 each for chemical reactivity and physical durability factors).

Table 37. Zinc Ferrite Cylindrical Extrude Sorbent Performance

<u>Sorbent Rating Category</u>	<u>Weighting Factor, %</u>	<u>UCI T-2465</u>		<u>E13A</u>		<u>E7A</u>		<u>E24A</u>		<u>E28A</u>		<u>E32A</u>		<u>E2A</u>	
		<u>Grade</u>	<u>Points</u>	<u>Grade</u>	<u>Points</u>	<u>Grade</u>	<u>Points</u>	<u>Grade</u>	<u>Points</u>	<u>Grade</u>	<u>Points</u>	<u>Grade</u>	<u>Points</u>	<u>Grade</u>	<u>Points</u>
<u>Chemical Reactivity Factors</u>															
1. Sulfur Sorption Capacity at 200 ppm H ₂ S Breakthrough															
a. Average of First 5 Cycles	5	5	25	4	20	4	20	3	15	2	10	2	10	3	15
b. Average of Last 5 Cycles	<u>15</u>	5	<u>75</u>	4	<u>60</u>	2	<u>30</u>	3	<u>45</u>	2	<u>30</u>	3	<u>45</u>	3	<u>45</u>
Subtotal	20	--	100	--	80	--	50	--	60	--	40	--	55	--	60
2. Sulfur Sorption Capacity at Saturation	20	4	80	5	100	5	100	5	100	4	80	5	100	5	100
3. Fresh Sorbent Surface Area	5	5	25	5	25	3	15	5	25	3	15	3	15	3	15
4. Fresh Sorbent Porosity	<u>5</u>	5	<u>25</u>	5	<u>25</u>	3	<u>15</u>	5	<u>25</u>	3	<u>15</u>	3	<u>15</u>	5	<u>25</u>
74 Total	50	--	230	--	230	--	180	--	210	--	150	--	185	--	200
<u>Physical Durability Factors</u>															
1. Crush Strength															
a. Fresh Sorbent	10	3	30	4	40	1	10	5	50	2	20	2	20	3	30
b. Sulfided Sorbent	<u>10</u>	1	<u>10</u>	2	<u>20</u>	4	<u>40</u>	5	<u>50</u>	4	<u>40</u>	2	<u>20</u>	4	<u>40</u>
Subtotal	20	--	40	--	60	--	50	--	100	--	60	--	40	--	70
2. Attrition Resistance															
a. Fresh Sorbent	10	4	40	4	40	4	40	5	50	4	40	4	40	5	50
b. Sulfided Sorbent	<u>10</u>	3	<u>30</u>	4	<u>40</u>	5	<u>50</u>	4	<u>40</u>	5	<u>50</u>	5	<u>50</u>	4	<u>40</u>
Subtotal	20	--	70	--	80	--	90	--	90	--	90	--	90	--	90
3. Fines Produced During 10 Cycles	<u>10</u>	2	<u>20</u>	3	<u>30</u>	4	<u>40</u>	4	<u>40</u>	5	<u>50</u>	4	<u>40</u>	4	<u>40</u>
Total	50	--	130	--	170	--	180	--	230	--	200	--	170	--	200
Final Total	100		360		400		360		440		350		355		400
% of Maximum Possible Points			72		80		72		88		70		71		80

Note that maximum possible points = 500 (250 each for chemical reactivity and physical durability factors).

The compromise between chemical reactivity and physical durability factors is evident from the values for these two different rating categories shown in the tables. In most cases, sorbents which exhibited good chemical reactivity exhibited poor physical durability and vice versa. Table 38 summarizes the sorbent evaluation results in terms of sorbent shape and iron oxide grade. Overall improvements in physical durability were achieved for both sorbent shapes relative to the base case sorbents. Significant improvement in reactivity was achieved for the spherical pellet sorbents relative to the base case. Reactivity of one cylindrical extrude (E13A) matched that of the base case cylindrical extrude sorbent. The E13A sorbent exhibited improvement in physical durability compared to the base case extrude. In general, the cylindrical extrude shape resulted in better overall performance. Chemical reactivity was consistently high for the cylindrical extrudes prepared using catalyst-grade iron oxide. Chemical reactivity was consistently poor for the spherical pellets prepared using pigment-grade iron oxide. Only spherical pellet sorbent P11A, which was formulated using catalyst-grade iron oxide, matched the level of reactivity observed in the catalyst-grade cylindrical extrudes. The greatest overall score was for cylindrical extrude sorbent E24A, which exhibited a good balance between reactivity and durability. The greatest overall score for spherical pellets was achieved using sorbent P11A. Several other spherical pellets approached the same value.

EFFECT OF SULFIDATION TEMPERATURE

The sulfur sorption capacity of the AMAX 1094-59 sorbent at 200 ppm H_2S breakthrough was unexpectedly low. Much of the previous testing at AMAX R&D had been performed at temperatures greater than the $1,022^{\circ}F$ ($550^{\circ}C$) currently used. In a separate test, the sorbent bed temperature was increased to $1,202^{\circ}F$ ($650^{\circ}C$) to determine the effect of sulfidation temperature. While maintaining the same gas flow, sulfur sorption capacity increased from the typical values of less than 2 pounds sulfur sorbed per 100 pounds fresh sorbent achieved at $1,022^{\circ}F$ ($550^{\circ}C$) up to a value of 13.9 pounds sulfur per 100 pounds fresh sorbent. This is comparable to the sulfur sorption capacity observed using similar sorbents during past AMAX R&D work.²

EFFECT OF SULFIDATION GAS FLOW RATE

Previous multi-cycle testing at AMAX R&D had been performed at flow rates about 20 percent lower than those used in the current program. In order to determine the effect of gas flow rate on the sulfidation performance of the AMAX 1094-59 sorbent, a sulfidation test was run using a gas flow of 2,000 bed volumes per hour. During this test, the sulfur sorption capacity at 200 ppm H_2S breakthrough increased from

about 1.5 to a value of 3.4 pounds sulfur per 100 pounds fresh sorbent.

Table 38. Summary of Sorbent Performance

	<u>Percentage of Maximum Possible Points</u>		
	<u>Chemical</u>	<u>Physical</u>	<u>Combined</u>
	<u>Reactivity</u>	<u>Durability</u>	<u>Physical and</u>
	<u>Factors</u>	<u>Factors</u>	<u>Chemical Factors</u>
<u>Spherical Pellets</u>			
Pigment-Grade Fe ₂ O ₃			
1094-59	52	28	40
P6A	46	92	69
P37A	36	96	66
Average	45	72	58
Catalyst-Grade Fe ₂ O ₃			
P11A	92	52	72
P27A	54	80	67
P22A	76	64	70
Average	74	65	70
Pellet Average	59	69	64
<u>Cylindrical Extrudes</u>			
Pigment-Grade Fe ₂ O ₃			
E7A	72	72	72
E28A	60	80	70
E32A	74	68	71
Average	69	73	71
Catalyst-Grade Fe ₂ O ₃			
T-2465	92	52	72
E13A	92	68	80
E24A	84	92	88
E2A	80	80	80
Average	87	73	80
Extrude Average	79	73	76

TASK 5. TOPICAL REPORT

A topical report describing the results of the base program was prepared and submitted to DOE/METC. This final report incorporates the topical report with the additional work described in the next section, which was performed under a contract option.

TASK 6. ADDITIONAL SORBENT TESTING

Based on preliminary results, a contract option was awarded to further investigate sorbents formulated using a low-cost Ruthner process iron oxide. This type of iron oxide is produced during the recovery of hydrochloric acid from steel plant pickling liquors.

On the basis of results obtained during the base program, some of the sorbent preparation variables were fixed for the additional testing. For example, the $\text{ZnO}:\text{Fe}_2\text{O}_3$ molar ratio was maintained at 1.0. Bentonite addition was fixed at 2 percent. Most of the sorbents were prepared as cylindrical extrudes, and the best extrude formulations were then applied to the spherical pellet shape. Whenever possible, the results obtained from the testing of Ruthner process iron oxide formulations have been compared to the results obtained using the base case T-2465 cylindrical extrude or 1094-59 spherical pellet sorbents. As described later, the sorbent grading system was also applied to the new sorbents.

A baseline cylindrical extrude formulation containing Ruthner process iron oxide was established and prepared. Modifications to the baseline extrude were then evaluated. Selected sorbents were forwarded to Louisiana State University (LSU) for single particle kinetic studies. Four sorbents were selected for multi-cycle bench-scale testing. The following sections describe the preparation and evaluation of sorbents formulated using Ruthner process iron oxide.

SORBENT PREPARATION AND CHARACTERIZATION

This section describes the preparation of additional sorbents using Ruthner process iron oxide. Techniques to remove the residual chlorine contained in Ruthner process iron oxide were also investigated.

The Ruthner process iron oxide contains about 99 percent Fe_2O_3 with chlorine present as the main impurity in amounts up to about 0.5 percent. Manganese is contained in concentrations of about 0.2 percent. Other impurities are generally present in amounts significantly less than 0.1 percent. The Ruthner process iron oxide is similar to the other iron oxide powders tested during the program in that it is nominally 98.8 percent passing 37 microns (400 mesh). Commercial costs for the material are about \$0.05 per pound.

Cylindrical Extrudes

Initial work centered on techniques to aid the extrusion of zinc oxide, Ruthner iron oxide, and bentonite mixtures. Preliminary work had shown that zinc ferrite feed formulations

containing Ruthner iron oxide were difficult to extrude. Difficulties included plugging of the extrusion chamber and very low sorbent production rates.

Wettability tests were conducted in order to determine whether a wetting agent should be included in the zinc ferrite formulation. Complete wetting of the dry powders used for extrusion would be expected to improve flow through the extrusion chamber and die. The tests were performed using a procedure which was adapted from the Draves test for wettability of textiles. Small amounts of a dry powder mixture containing a 1:1 molar ratio of zinc oxide to iron oxide with a 2 percent bentonite addition were dropped onto the surface of solutions containing water and different concentrations of surfactant. The surfactant used was Aerosol OT (sodium sulfosuccinate). The rate at which the dry powder wetted and fell through the solution surface was used to determine the effect of surfactant addition on wettability. The dry powder mixture was found to wet nearly instantly both with and without surfactant addition. As such, the addition of surfactant was not expected to improve the extrusion of the powdered oxide mixture.

Additional work centered on optimization of the extruder feed moisture content. During the base program, extrusions were produced using 24 to 27 percent moisture in the feed. This level of moisture was too great for the Ruthner process iron oxide formulations. Limited quantities of extrudes were successfully prepared from the Ruthner process iron oxide mixture when using 18 to 22 percent moisture. The level of moisture was further optimized to allow continuous extrusion. The moisture content is important to the flow characteristics of the extrudes and to the ability to prevent buildup and packing of the mixture in the extruder.

A baseline formulation containing Ruthner process iron oxide was established and successfully prepared. The baseline formulation consisted of Ruthner process iron oxide and ASARCO zinc oxide in a 1:1 molar ratio with a 2 weight percent bentonite addition. Continuous extrusion could be carried out when the moisture content of the extruder feed was maintained at 19 to 20 percent.

About 20 pounds of the baseline extrudes were prepared and dried. Five hundred-gram batches were then indurated using different times and temperatures. Table 39 summarizes the sorbent formulations, induration conditions, and physical properties for the baseline formulation (Run R1). Also shown in Table 39 are the formulations and properties of the cylindrical extrude base case sorbent prepared using catalyst-grade iron oxide (UCI T-2465), the initial E7R sorbent prepared using Ruthner process iron oxide (which was hand-pressed into a

Table 39. Zinc Ferrite Cylindrical Extrude Characteristics
(Ruthner Process Iron Oxide Formulations)

Sorbent Sample Number	Extrude Formulation				Induration Conditions		Physical Properties				BET	TGA Testing		
	Run No.	Fe ₂ O ₃ Grade	% Bentonite Other		Temperature, °F	Time, Hours	Bulk Density, kg/l	Crush Strength, lb/mm	Length, mm	Attrition Resistance, %	Surface Area, m ² /g	Pellet		
												R30	RM30	SG
T-2465	Base	Catalyst	2	0.5% Methocel	1,550	2.00	1.31	3.5	8.6	88.8	3.30	0.228	0.89	1.84
E7R	--	Ruthner	5	0	1,500	4.00	0.77	≈3.5	≈10	--	2.59	0.291	1.02	1.76
E51	R1	Ruthner	2	0	1,300	0.50	1.37	3.3	11.9	89.4	3.68	0.117	1.11	2.42
E41					1,400	0.25	1.39	3.1	11.2	89.2	--	--	--	--
E42					1,400	0.50	1.35	3.7	10.7	90.6	3.19	0.159	0.91	2.36
E43					1,500	0.25	1.33	3.7	11.3	91.0	--	--	--	--
E44					1,500	0.50	1.33	3.9	11.0	90.6	3.12	0.171	0.82	2.35
E44A					1,500	0.50	1.34	4.4	9.8	91.0	3.94	--	--	--
E45					1,500	2.00	1.30	4.3	12.1	90.2	--	--	--	--
E46					1,500	4.00	1.28	3.9	12.5	91.0	--	--	--	--
E47					1,700	0.50	1.30	4.3	11.5	91.9	3.15	0.134	0.72	2.50
E48					1,700	2.00	1.31	5.0	10.9	93.0	--	--	--	--
E49					1,900	0.25	1.32	5.3	10.5	94.3	2.49	--	--	--
E50					1,900	0.50	1.39	>7.1	9.2	95.9	--	--	--	--
E52	R2	Caustic- Washed Ruthner	2	0	1,300	0.50	1.35	3.0	11.1	87.4	6.00	0.099	1.03	2.35
E53					1,400	0.50	1.30	3.6	11.4	90.6	4.45	--	--	--
E54					1,500	0.50	1.30	4.0	11.6	91.2	3.65	0.142	0.84	2.45
E54A					1,500	0.50	1.26	4.0	11.1	92.3	3.95	--	--	--
E55					1,700	0.50	1.31	3.8	11.2	91.9	3.11	--	--	--
E56	R3	Ruthner	2	5% Coal	1,500	0.50	1.22	1.4	11.5	63.4	4.50	--	--	--
E57	R4	Ruthner	2	5% Starch	1,500	0.50	1.20	2.1	12.8	36.5	3.10	0.184	0.98	2.32
E58					1,500	1.00	1.19	2.6	12.6	74.6	1.67	0.184	0.91	--

**Table 39. Zinc Ferrite Cylindrical Extrude Characteristics
(Ruthner Process Iron Oxide Formulations) (Continued)**

Sorbent Sample Number	Extrude Formulation				Induration Conditions		Physical Properties				BET Surface Area, m ² /g	TGA Testing		
	Run No.	Fe ₂ O ₃ Grade	% Bentonite	Other	Temperature, °F	Time, Hours	Bulk Density, kg/l	Crush Strength, lb/mm	Length, mm	Attrition Resistance, %		R30	RM30	Pellet SG
E59	R5	Ruthner	2	5% Starch 5% EF113 Fiber	1,500	1.00	1.07	2.9	14.4	81.8	3.78	--	--	--
--	R6	Ruthner	2	5% Starch 0.5% Saffil Fiber	--	--	--	--	--	--	--	--	--	--
E60	R7	Ruthner	2	3% Starch 0.3% Saffil Fiber	1,500	1.00	1.24	3.2	12.5	88.8	2.02	--	--	--
E61	R8	Ruthner	2	3% Starch 3% EF113 Fiber	1,500	1.00	1.21	3.2	15.0	90.6	4.12	--	--	--
E62	R9	Ruthner	2	3% Starch 3% EF113 Fiber 3% Na Silicate	1,500	1.00	1.05	2.6	14.4	73.6	1.58	--	--	--
E63	R10	Ruthner	2	3% Starch	1,500	1.00	1.19	3.6	13.1	87.4	3.02	0.190	0.88	2.33
E63A					1,500	1.00	1.19	4.4	9.5	82.9	1.74	--	--	--
E64	R15	Catalyst	2	3% Starch	1,500	1.00	1.21	3.7	12.0	90.3	2.52	0.160	0.82	2.26

Note: All of the formulations shown contain a 1:1 ZnO:Fe₂O₃ molar ratio. R30 is the sulfur sorption capacity of the sorbent measured during the first sulfidation cycle after 30 minutes and is expressed as grams sulfur sorbed per gram initial sorbent weight. RM30 is the ratio of the sulfur sorption capacity during sulfidation Cycle 2 to Cycle 1. Pellet SG is based on the volume and weight of the single sorbent particles selected for TGA testing. An "A" designation in the sample number indicates preparation of a larger batch for cyclic testing.

cylindrical shape), and the other modified Ruthner iron oxide extrude formulations.

A wide range of induration conditions was utilized for the Ruthner process baseline extrude formulation R1 in order to establish the effects on strength and reactivity. Attrition resistance values of greater than 89 percent were obtained on all of the indurated sorbents. The sample which was indurated at 1,400°F for 0.25 hour was not completely converted to zinc ferrite based on the mixture of observed colors associated with both dry oxide powder mixtures and indurated sorbents.

The dried baseline sorbent exhibited crush strength values ranging from 0 to about 0.5 pound per millimeter versus the minimum of 3.1 pounds per millimeter exhibited by the indurated sorbents. Attrition resistance was not determined on the dried sorbent.

As shown in Table 39, indurated sorbent bulk density values fell within a narrow range for the baseline Ruthner process iron oxide formulation R1. Bulk density values ranging from 1.28 to 1.39 were observed. The dry sorbent bulk density was 1.41. Note that the low value of bulk density recorded for the E7R sample in Table 39 may be due to the limited amount of sample available, which necessitated the use of a smaller measurement container combined with the lower pressure utilized during hand-pressing of the E7R sorbent.

Another sorbent similar to the R1 baseline formulation was prepared using caustic-washed Ruthner process iron oxide. The caustic washing step was included for removal of residual chlorides prior to sorbent preparation. As shown in Table 39, the physical properties of the R2 formulation prepared using washed Ruthner iron oxide were similar to those of the baseline R1 formulation. Bulk density, crush strength, and attrition resistance values were within the range found for the R1 formulation. However, surface area values for the R2 sorbents which were indurated at temperatures below 1,700°F were somewhat greater than those for the corresponding R1 formulation conditions. Chlorine removal procedures and results are discussed in greater detail in a later section of the report.

Based on the results obtained during the base contract in which sorbent reactivity was found to increase with increasing sorbent porosity, efforts were made to reduce the density (or increase the porosity) of the cylindrical extrudes made using Ruthner process iron oxide. Up to 5 weight percent of burnable filler was incorporated in order to achieve increased sorbent porosity. Sorbent formulation R3 utilized 5 weight percent of a micronized, low-sulfur coal (Indiana VII seam) which had been physically cleaned to about 7 percent ash. Sorbent formulation

R4 utilized 5 weight percent of starch. After induration at 1,500°F for 0.5 hour, it was observed that very little coal had been burned from the sorbent structure. Most of the starch did, however, appear to be removed from the sorbent. Since oxygen is required to burn and remove most of the coal (except the volatile portion), very long induration times would be required to completely burn out the carbon residue. The starch is volatilized in the absence of oxygen and is, therefore, much easier to remove during induration.

The R4 formulation (containing 5 percent starch) exhibited significantly lower bulk density, crush strength, and attrition resistance compared to the baseline R1 formulation when indurated using the same conditions. An increased induration time of 1 hour at 1,500°F was selected for the R4 formulation (sorbent E58) in an attempt to volatilize all of the starch and improve sorbent durability. Significant improvement of attrition resistance (from about 37 to about 75 percent) and improvement of crush strength (from 2.1 to 2.6 pounds/mm) resulted from the longer induration time.

The R4 formulation was very difficult to extrude. Only limited quantities were successfully prepared using this formulation. Reinforcing agents were introduced to sorbent containing starch in order to further improve physical properties and to potentially improve extrusion characteristics. Sorbent formulations containing 5 percent starch, along with chopped aluminosilicate fiber (Carborundum Fiberfrax chopped fiber) or alumina fiber (ICI Saffil fiber), were used for sorbent formulations R5 and R6, respectively. In each case, only a very little sample was successfully extruded. The R5 formulation was produced in sufficient quantity to at least determine the effect of fiber addition on sorbent durability. As shown in Table 40, the reinforced extrude (E59) exhibited greater crush strength and attrition resistance than sorbent without fiber addition (E58) under the same induration conditions.

A reduction in the starch concentration was used for subsequent formulations to facilitate greater sorbent production. Formulations using a 3 weight percent starch addition were prepared. These formulations, R7 through R10 in Table 39, exhibited lower bulk density values than the baseline R1 formulation after induration. The addition of fiber reinforcement in formulations R7 and R8 (sorbents E60 and E61) improved attrition resistance while resulting in slightly lower crush strength compared to the R10 formulation (sorbent E63) which was prepared without fiber additions. A sorbent prepared using sodium silicate in addition to fibers (formulation R9/ sorbent E62) was difficult to extrude and exhibited lower crush strength and attrition resistance. Sodium silicate had been selected as a potential strengthening agent for the sorbents.

Table 40. Effect of Starch and Fiber Additions
on Cylindrical Extrude Sorbent Properties

<u>Sorbent Number</u>	<u>Component, Weight %</u>		<u>Bulk Density, kg/l</u>	<u>Crush Strength, lb/mm</u>	<u>Attrition Resistance, %</u>	<u>Induration</u>	
	<u>Starch</u>	<u>Fiber</u>				<u>Temperature, °F</u>	<u>Time, Hours</u>
E44	0	0	1.33	3.9	90.6	1,500	0.5
E45	0	0	1.30	4.3	90.2	1,500	2.0
E63	3	0	1.19	3.6	87.4	1,500	1.0
E61	3	3	1.21	3.2	90.6	1,500	1.0
E58	5	0	1.19	2.6	74.6	1,500	1.0
E59	5	5	1.07	2.9	81.8	1,500	1.0

Note: Each sorbent contained 2 percent bentonite and was prepared using as-received Ruthner process iron oxide.

The effects of starch and aluminosilicate fiber additions on the properties of sorbents prepared using Ruthner process iron oxide are summarized in Table 40. Formulations containing starch exhibited lower bulk density than the formulations prepared without starch. As shown in Table 40, the reinforcing fibers were slightly more effective in improving attrition resistance than crush strength. Because only limited quantities of sorbent containing 5 percent starch could be produced due to difficulty in extruding the feed mixture, 3 percent starch was set as the practical upper limit for larger scale production of sorbent using the available equipment. For these cylindrical extrude formulations, the reinforcing fiber appears to be of limited value.

In order to determine the effect of iron oxide grade, two sorbents were prepared in identical fashion except for the type of iron oxide used. E63 was prepared using Ruthner process iron oxide, while E64 was prepared using catalyst-grade iron oxide. Both formulations included a 3 percent starch addition with 2 percent bentonite. As shown in Table 39, the bulk density, crush strength, and attrition resistance values of the two sorbents were very similar. The surface area of the E63 sorbent ($3.02 \text{ m}^2/\text{g}$) was somewhat greater than that for the E64 sorbent ($2.52 \text{ m}^2/\text{g}$).

Spherical Pellets

Additional new sorbents were prepared using disk pelletization techniques to prepare a spherical shape. Table 41 summarizes the new spherical pellet sorbent formulations and properties. The formulations prepared using the spherical pellet shape were based on the formulations tested using the cylindrical extrude shape and were chosen in an attempt to provide a balance between sorbent durability and reactivity. Spherical pellet sorbents generally required more severe induration conditions than the cylindrical extrude sorbents to achieve a comparable level of physical durability. As a result, the spherical pellet sorbents were often less reactive than the cylindrical extrude sorbents. Burnable filler (starch) and/or reinforcement (aluminosilicate fibers) were utilized in some of the new spherical pellet formulations in an effort to enhance reactivity and durability.

Spherical pellet sorbents containing starch required modification of induration procedures in order to prevent localized reduction of iron and zinc compounds. A procedure in which the sorbent was indurated first at $1,500^\circ\text{F}$ allowed the starch to be removed without reaction with the iron or zinc oxide components. The sorbent could then be fired at higher temperatures to induce greater durability. Induration of sorbents containing starch using temperatures of $1,700^\circ\text{F}$ or greater resulted in formation of magnetite, zinc silicates, and

Table 41. Zinc Ferrite Spherical Pellet Characteristics
(Ruthner Process Iron Oxide Formulations)

Sorbent Sample Number	Pellet Formulation				Induration Conditions		Physical Properties				BET	IGA Testing	
	Run No.	Fe ₂ O ₃ Grade	% Bentonite	Other	Temperature, °F	Time, Hours	Bulk Density, kg/l	Crush Strength, lb	Diameter, mm	Attrition, Resistance, %	Surface Area, m ² /g	R20	RW20
P66	R11	Ruthner	2	5% Starch	1,500	1	0.97	5.0	5.3	29.2	1.92	--	--
P64				5% EF113	1,700	1	1.04	9.6	5.4	49.1	1.37	--	--
P65				Fiber	1,900	1	1.22	17.7	5.4	69.6	--	--	--
P67					1,900	1							
					*1,500	1	1.22	16.4	5.1	64.6	1.34	--	--
P68					1,900	1							
					*1,900	1	1.17	9.1	5.0	54.6	0.95	--	--
P69					1,700	1							
					*1,900	1	1.04	9.0	5.2	46.7	1.16	--	--
P70					1,500	1							
					*1,900	1	1.00	6.8	5.1	40.0	1.17	--	--
P76					1,500	1							
					*1,900	4	1.00	6.6	5.6	40.3	1.44	--	--
P71	R12	Ruthner	2	None	1,500	1	0.89	4.7	5.6	31.1	--	--	--
P73					1,500	1							
					*1,900	2	1.05	13.0	5.1	61.7	1.72	0.289	0.84
P73A					1,500	1							
					*1,900	2	1.05	9.7	5.3	54.0	1.70	--	--
P75					1,900	2	0.97	9.2	5.8	48.5	2.04	--	--
P77					1,500	1							
					*1,900	4	1.04	14.5	5.8	60.7	1.23	--	--

Table 41. Zinc Ferrite Spherical Pellet Characteristics
(Ruthner Process Iron Oxide Formulations) (Continued)

Sorbent Sample Number	Pellet Formulation				Induration Conditions		Physical Properties				BET Surface Area,	TGA Testing	
	Run No.	Fe ₂ O ₃ Grade	% Bentonite	Other	Temperature, °F	Time, Hours	Bulk Density, kg/l	Crush Strength, lb	Diameter, mm	Attrition, Resistance, %	m ² /g	R20	RM20
P79					1,900	1	0.96	8.4	5.6	49.2	1.71	--	--
P80					1,900	2							
					*1,900	1							
					**		0.99	10.8	5.6	50.5	1.52	--	--
P72	R13	Ruthner	2	5% Starch	1,500	1	0.95	2.2	5.5	21.8	--	--	--
P74					1,500	1							
					*1,900	2	1.00	5.1	5.3	33.3	1.36	--	--
P78					1,500	1							
					*1,900	4	0.98	6.1	6.1	35.5	1.48	--	--
P82	R16	Ruthner	2	5% EF113 Fiber	1,500	1	0.93	5.0	6.2	24.2	2.85	--	--
P81					1,500	1							
					*1,900	2	1.05	14.6	6.2	60.6	1.75	--	--

* Followed by

** With 0.5% Na silicate on surface.

Note: All of the formulations shown contain a 1:1 ZnO:Fe₂O₃ molar ratio. R20 is the sulfur sorption capacity of the sorbent measured during the first sulfidation cycle after 20 minutes and is expressed as grams sulfur sorbed per gram initial sorbent weight. RM20 is the ratio of the sulfur sorption capacity during sulfidation Cycle 2 to Cycle 1.

possibly some wustite. This type of sorbent exhibited a glazed surface appearance and was found to have very low surface area (about $0.5 \text{ m}^2/\text{g}$). Appendix C contains a memorandum which describes the mineralogy of sorbents taken from the same batch but which exhibited localized differences in characteristics, probably attributable to reduction by the starch.

The spherical pellets prepared using the Ruthner process iron oxide exhibited generally low crush strength and attrition resistance values. Table 42 summarizes the effects of starch and fiber additions on the properties of spherical pellet sorbents. The addition of starch weakened the spherical pellet sorbents (compare P71 with P72, P77 with P78, and P73 with P74). The addition of fiber along with starch helped to restore some of the strength lost by starch addition. However, as shown in Table 42, these sorbents were still generally less durable than those prepared using no starch or fiber. In addition, the bulk density (or the apparent porosity) was not improved noticeably by the addition of both starch and fiber.

The attrition resistance and crush strength values of the new spherical pellet sorbents prepared using Ruthner process iron oxide were lower than those for sorbents from the base program which were prepared and indurated under similar conditions. The greatest value of new spherical pellet attrition resistance (for sorbents which were not glazed as a result of the reduction of the metal oxides) was about 61 to 62 percent. Sorbents prepared without starch or fiber (P73 and P77) and the sorbent prepared using fiber without starch (P81) achieved attrition resistance values in this range. The maximum attrition resistance value for a spherical pellet sorbent prepared using a starch addition with fiber and indurated without reduction of the metal oxides was about 40 percent (P70 and P76). The maximum attrition resistance value for a spherical pellet sorbent prepared using starch without fiber and indurated without reduction of the metal oxides was about 36 percent (P78).

While the attrition resistance and crush strength values of the new spherical pellet sorbents prepared using the Ruthner process iron oxide were generally lower than those prepared during the base program, improvement over the AMAX 1094-59 base case sorbent was achieved.

Chlorine Removal

Residual chlorine in the Ruthner iron oxide (in amounts up to about 0.5 percent) needs to be removed prior to utilization as a desulfurization sorbent due to process equipment corrosion considerations and possible effects on the chemistry of the gas streams. Techniques, including caustic washing and heat

Table 42. Effect of Starch and Fiber Additions
on Spherical Pellet Sorbent Properties

<u>Sorbent Number</u>	<u>Component, Weight %</u>		<u>Bulk Density, kg/l</u>	<u>Crush Strength, lb/mm</u>	<u>Attrition Resistance, %</u>	<u>Induration</u>	
	<u>Starch</u>	<u>Fiber</u>				<u>Temperature, °F</u>	<u>Time, Hours</u>
P71	0	0	0.89	4.7	31.1	1,500	1.0
P72	5	0	0.95	2.2	21.8	1,500	1.0
P66	5	5	0.97	5.0	29.2	1,500	1.0
P82	0	5	0.93	5.0	24.2	1,500	1.0
P77	0	0	1.04	14.5	60.7	a	a
P78	5	0	0.98	6.1	35.5	a	a
P76	5	5	1.00	6.6	40.3	a	a
P73	0	0	1.05	13.0	61.7	b	b
P74	5	0	1.00	5.1	33.3	b	b
P81	0	5	1.05	14.6	60.6	b	b

Notes: Each sorbent contained 2 percent bentonite and was prepared using as-received Ruthner process iron oxide.

a Induration at 1,500°F/1 hour, followed by 1,900°F/4 hours.

b Induration at 1,500°F/1 hour, followed by 1,900°F/2 hours.

treatment, were investigated for the removal of residual chlorine.

As-received Ruthner iron oxide was washed in a pH 11 solution of sodium hydroxide in water. Following filtration and additional washing, the filter cake was dried and used for sorbent preparation (Run R2, Table 39). Analysis of chlorine in the as-received iron oxide and washed iron oxide was conducted. Table 43 summarizes the effects of washing the iron oxide, heat treating the iron oxide, and indurating formed sorbent particles on chlorine content. Most of the chlorine present in the Ruthner process iron oxide probably exists as chloride. Both the caustic washing and heat treatment techniques were successful in significantly reducing chlorine content. The as-received Ruthner iron oxide was used without caustic washing for all additional sorbent preparation except for preparation Run R2 described above.

Table 43. Chlorine Content of Ruthner Process
Iron Oxide Powder and Indurated Sorbents

<u>Sample Identification</u>	<u>Weight % Cl</u>
As-Received Ruthner Fe ₂ O ₃	0.50
Caustic-Washed Ruthner Fe ₂ O ₃	0.12
Heat-Treated, As-Received Ruthner Fe ₂ O ₃	
1,300°F/0.5 Hour	0.13
1,400°F/0.5 Hour	0.09
1,500°F/0.5 Hour	0.09
1,700°F/0.5 Hour	0.02
Indurated Batch R1 Sorbent	
E42 (1,400°F/0.5 Hour)	0.18
E47 (1,700°F/0.5 Hour)	0.02

BENCH-SCALE TESTING

Four new sorbents were selected for bench-scale testing. The test procedures were the same as those used during the base program described earlier in the report under "Task 3. Bench-Scale Testing". The sorbents selected for multi-cycle bench-scale testing are identified and characterized in Table 44. These sorbents were selected on the basis of physical properties and the single particle kinetic studies described in a later section of the report.

Bench-Scale Test Results

Sorbents E44A and E54A from preparation runs R1 and R2 were selected as the first two new sorbents for multi-cycle bench-scale testing. These two sorbents were prepared using

Ruthner process iron oxide in a 1:1 molar ratio with ASARCO zinc oxide and a 2 percent bentonite binder addition. Sorbent E44A was prepared using as-received iron oxide, while sorbent E54A was prepared using caustic-washed iron oxide. Both sorbents were indurated at 1,500°F for 0.5 hour.

Sorbents E63A and P73A were selected as the second two new sorbents for multi-cycle bench-scale testing. Sorbent E63A was formulated like E44A but with starch at a 3 percent addition level to the starting powder mixture. Induration time was increased to 1 hour in order to ensure complete removal of starch. Sorbent P73A contained the same formulation as E44A but was prepared as a spherical pellet instead of a cylindrical extrude. Induration was performed in two stages, as indicated in Table 44. This technique was found to increase durability during earlier testing of the Ruthner iron oxide formulations.

Table 44. Physical Characteristics of Sorbents
Formulated Using Ruthner Process Iron Oxide

<u>Sorbent Formulation</u>				
Sorbent Sample Number	E44A	E54A	E63A	P73A
Preparation Run Number	R1	R2	R9	R12
Iron Oxide Grade	Ruthner	Washed Ruthner	Ruthner	Ruthner
ZnO/Fe ₂ O ₃ Ratio	1.0	1.0	1.0	1.0
Bentonite, %	2	2	2	2
Starch, %	0	0	3	0
<u>Induration Conditions</u>				
Temperature, °F	1500	1500	1500	1500 + 1900
Time, Hours	0.5	0.5	1.0	1.0 + 2.0
<u>Physical Properties</u>				
Bulk Density, kg/l	1.34	1.26	1.19	1.05
Crush Strength, lb/mm (Extrudes) lb (Pellets)	4.4	4.0	4.4	9.7
Attrition Resistance, %	91.0	92.3	82.9	54.0
Surface Area, m ² /g	3.94	3.95	1.74	1.70
Total Pore Volume, cm ³ /g	0.219	0.236	0.236	0.316
Average Pore Radius, Å	1110	1190	2710	3720
Porosity, %				
Pores >0.180 µm	46.1	42.8	51.3	33.1
Pores >0.012 µm	52.3	54.3	54.1	33.3
<u>Cyclic Test Number</u>	20	21	23	22

Table 45 summarizes the multi-cycle bench-scale test results for the new sorbents. Also included for comparison is the performance of the base case T-2465 and 1094-59 sorbents. The new sorbents E44A and E54A exhibited desulfurization performance with an average of about 12 pounds sulfur sorbed per 100 pounds fresh sorbent. No significant decrease in performance was observed over the ten test cycles for these two cylindrical extrude sorbents.

Failure (shorting) of a furnace heating element resulted in rapid heating of sorbent E63A during regeneration after the third sulfidation cycle. A peak temperature of about 1,650°F (900°C) was present in the upper portion of the reactor bed during this upset. A subsequent attempt to sulfidize this sorbent resulted in immediate H₂S breakthrough. The reactor was then emptied in order to examine the sorbent and reactor. Although the reactor held pressure and was not determined to have been burned through by the furnace failure, some damage to the exterior of the reactor shell was observed at the point of the heating element failure. The sorbent removed from the upper half of the reactor was observed to be very hard and of a dark grey color. In addition, these sorbent particles had undergone noticeable shrinkage. About one-half of the total sorbent was replaced with fresh sorbent and the reactor assembly was replaced with a spare prior to starting again after replacement of the bad furnace heating elements.

In general, the breakthrough sulfur sorption capacity values exhibited by the new sorbents were greater than those obtained using pigment-grade iron oxide formulations and somewhat lower than those obtained using catalyst-grade iron oxide formulations. The new sorbents prepared using Ruthner process iron oxide achieved somewhat lower sulfur sorption capacity at saturation compared to most of the sorbents prepared using pigment- and catalyst-grade iron oxides. Overall, the Ruthner process iron oxide appears to be a good candidate sorbent raw material based on its performance and low cost.

Analyses for iron, zinc, sulfur, and chlorine were completed for the new fresh and sulfided sorbents. Table 46 summarizes the results. The low value of sulfur observed in sulfided E63A sorbent sampled from the bottom section of the reactor is probably due to some sorbent damage which occurred during an over-temperature condition resulting from the furnace heating element failure described earlier. Regenerated sorbents contained less than 0.2 percent sulfur in each case. Sorbents E44A and E54A were analyzed for chlorine content. As shown in Table 46, the E44A fresh sorbent contained only 0.02 percent chlorine. All sulfided and regenerated sorbents contained less than 0.01 percent chlorine.

Table 45. Performance of Sorbents Prepared Using Ruthner Process Iron Oxide

Sorbent Sample Number	<u>Cylindrical Extrudes</u>				<u>Spherical Pellets</u>	
	T-2465 (Base Case)	E44A	E54A	E63A	1094-59 (Base Case)	P73A
Cyclic Test Series Number	4	20	21	23	5	22
Desulfurization Performance in Bench-Scale Reactor						
Sulfur Sorption Capacity, g S Sorbed/100 g Fresh Sorbent						
a) At 200 ppm H ₂ S Breakthrough						
1st Cycle	13.7	12.7	11.8	10.0	1.3	9.6
2nd Cycle	28.6	11.9	13.4	10.9	1.5	11.5
3rd Cycle	26.3	12.5	12.8	13.0	1.4	10.7
4th Cycle	24.0	11.3	10.4	-- ^a	1.4	9.2
5th Cycle	22.2	11.6	13.1	7.1	1.4	9.4
6th Cycle	22.6	12.7	12.2	10.0	1.2	6.3
7th Cycle	22.2	14.4	13.4	8.9	1.4	6.5
8th Cycle	20.2	12.3	12.7	9.5	0.8	5.5
9th Cycle	20.4	12.4	12.2	10.5	0.8	4.6
10th Cycle	<u>22.3</u>	<u>12.5</u>	<u>11.6</u>	<u>9.2</u>	<u>1.3</u>	<u>4.9</u>
Average	22.3	12.4	12.4	9.9	1.2	7.8
b) At Saturation, Actual	34.3	30.0	31.8	27.0	33.7	26.9
c) At Saturation, Theoretical	39.1	39.1	39.1	39.1	37.3	39.1
Percent of Theoretical Capacity Achieved	87.7	76.7	81.3	69.1	90.4	68.8
Desulfurization Performance in TGA						
Sulfur Sorption Capacity During First Cycle, g S/100 g Fresh Sorbent						
	22.8	17.1	14.2	19.0	21.7	28.9
Reactivity Change, Increase, or Decrease in Reactivity During Second Cycle, %	-11	-18	-16	-12	6	-16

^a Immediate breakthrough due to sorbent damage caused by furnace heating element failure during 3rd oxidation cycle. Approximately one-half of the sorbent bed was replaced prior to starting the 5th sulfidation cycle.

Table 46. Chemical Analysis of Zinc Ferrite Sorbents Formulated Using Ruthner Iron Oxide

	<u>E44A</u>	<u>E54A</u>	<u>E63A</u>	<u>P73A</u>
<u>Zinc, %</u>				
Fresh Sorbent	26.6	26.8	25.9	25.5
Sulfided Sorbent				
Top	23.8	24.2	24.0	23.6
Middle	23.9	27.1	22.7	22.8
Bottom	23.8	24.3	24.0	23.8
Regenerated Sorbent	26.4	26.3	26.3	25.7
<u>Iron, %</u>				
Fresh Sorbent	43.9	43.4	42.6	43.4
Sulfided Sorbent				
Top	39.4	39.1	39.4	40.9
Middle	39.7	39.9	38.0	37.2
Bottom	39.0	38.8	40.6	39.6
Regenerated Sorbent	43.2	42.8	43.8	43.7
<u>Sulfur, %</u>				
Fresh Sorbent	0.018	0.013	0.018	<0.01
Sulfided Sorbent				
Top	25.8	28.3	23.4	28.8
Middle	28.9	27.8	28.4	27.5
Bottom	26.5	28.1	20.0	23.8
Regenerated Sorbent	0.155	0.097	0.063	0.087
<u>Chlorine, %</u>				
Fresh Sorbent	0.02	<0.01	--	--
Sulfided Sorbent	<0.01	<0.01	--	--
Regenerated Sorbent	<0.01	<0.01	--	--

Single Particle Kinetic Studies at LSU

Single particle kinetic studies of the new sorbents prepared using Ruthner process iron oxide were completed and are shown in Tables 39 and 41. While the reactivity indices for the new sorbents were lower than that observed for the hand-pressed sorbent E7R, many values were within the range observed for sorbents subjected to bench-scale testing using pigment- and catalyst-grade iron oxides during the base contract.

The cylindrical extrude reactivity indices (R30) for sorbent formulation R1, shown in Table 39, increased with increasing induration temperature up to 1,500°F and then dropped as the induration temperature was increased to 1,700°F. Reactivity maintenance indices (RM30) became lower as induration temperature was increased from 1,300 to 1,700°F.

Although only two data points are available for the R2 sorbent formulation, the same trend seems to apply.

The greatest value of new cylindrical extrude reactivity (0.190) was for the cylindrical extrude sorbent which was prepared using a 3 percent starch addition (E63). The greatest value of reactivity maintenance (1.11) was for the cylindrical extrude from the baseline R1 formulation, which was indurated at 1,300°F (E51).

Surface area analyses performed on the cylindrical extrude sorbent samples forwarded to LSU showed decreasing surface area as a function of increasing induration severity. Note that the greatest surface area value of 6.00 m²/g was obtained on the sample (E52) which exhibited the lowest R30 value. Apparently, the high surface area value results from the presence of very small pores which are not accessible to the hydrogen-sulfide-containing simulated coal gas. Similar trends of decreasing cylindrical extrude sorbent reactivity with increasing surface area were observed during work on the base contract.

Single particle kinetic studies indicated that a sorbent prepared using Ruthner process iron oxide (E63) exhibited improved reactivity and reactivity maintenance characteristics compared to a similar sorbent prepared using catalyst-grade iron oxide (E64). Sorbent E63 exhibited reactivity and reactivity maintenance indices of 0.190 and 0.88, respectively. Sorbent E64 exhibited reactivity and reactivity maintenance values of 0.160 and 0.82.

The E63 sorbent reactivity and reactivity maintenance values represent an improvement over the values measured for sorbent prepared without using the starch binder/filler. Sorbent E44, shown in Table 2, was prepared under conditions similar to those used to prepare E63, with the exception of starch content. The starch addition resulted in an improvement in reactivity from 0.171 to 0.190. The reactivity maintenance value increased from 0.82 to 0.88 with the starch addition.

The P73 spherical pellet sorbent prepared using Ruthner process iron oxide and submitted for single particle kinetic evaluation exhibited reactivity and reactivity maintenance values of 0.289 and 0.84, respectively. The reactivity value of 0.289 pound sulfur sorbed per pound of fresh sorbent (after 20 minutes reaction time in the TGA) was greater than any spherical pellet tested in the bench-scale reactors during the base program. The reactivity maintenance value is within the range of values noted for sorbents tested during the base program.

BENCH-SCALE TEST ANALYSIS

Analysis of the bench-scale test results was performed to determine the characteristics of the Ruthner process iron oxide formulations relative to characteristics of sorbents produced during the base program. Since the number of variables tested using the Ruthner process iron oxide additions was limited, effects of some variables such as bentonite binder and $\text{ZnO}:\text{Fe}_2\text{O}_3$ ratio could not be determined. However, some averaged performance comparisons and direct comparisons with sorbents prepared during the base program are possible, and those are made whenever possible in the following sections.

Correlation of TGA with Bench-Scale Test Results

The TGA test data generally trended with the results obtained during multi-cycle bench-scale testing. As shown in Table 45, the first-cycle sulfur sorption capacity values obtained from TGA tests showed that the T-2465 catalyst-grade base case sorbent exhibited greater reactivity than the new Ruthner iron oxide formulations. The same was found for the bench-scale test results. The TGA results indicated that the E63A sorbent should perform somewhat better than the E44A and E54A sorbents during bench-scale testing. However, the E63A sorbent did not perform quite as well as the E44A and E54A sorbents. This could be in part due to the process upset caused by a furnace failure during testing of the E63A sorbent. For the spherical pellet P73A, the TGA tests indicated a performance much better than the AMAX 1094-59 pigment-grade base case spherical pellet sorbent. This was verified during bench-scale testing.

Chemical Analyses

In general, the sulfided Ruthner process iron oxide formulations did not exhibit sulfur concentrations as great as those obtained using the catalyst-grade and pigment-grade formulations. The chemical analyses shown in Table 46 indicate that the sulfided sorbent compositions were generally uniform through the reactor bed. The variations observed in iron, zinc, and sulfur analyses for the E63A sorbent are probably due to the partial replacement of the sorbent bed after the furnace failure described earlier. It is possible that some partially damaged sorbent was present in the bed. The lower value of the sulfur analysis obtained for the P73A sulfided sorbent sampled from the bottom portion of the reactor is not consistent with the other metal analyses, which indicate more significant sulfidation.

Physical Properties

Table 47 summarizes the physical properties of the fresh and sulfided sorbents prepared using Ruthner process iron

Table 47. Physical Characteristics of Fresh and Sulfided Sorbents

	<u>Cylindrical Extrudes</u>				<u>Spherical Pellets</u>	
	<u>Base Case</u>				<u>Base Case</u>	
	<u>UCI T-2465</u>	<u>E44A</u>	<u>E54A</u>	<u>E63A^a</u>	<u>AMAX 1094-59</u>	<u>P73A</u>
<u>Iron Oxide Grade</u>	Catalyst	Ruthner	Washed Ruthner	Ruthner	Pigment	Ruthner
<u>Physical Properties</u>						
Crush Strength, lb (Pellets)						
lb/mm (Extrudes)						
Fresh Sorbent	3.5	4.4	4.0	4.4	5.1	9.7
Sulfided Sorbent	2.9	5.6	4.8	5.2	13.7	17.3
Attrition Resistance, %						
Fresh Sorbent	88.8	91.0	92.3	82.9	45.5	54.0
Sulfided Sorbent	78.2	86.8	77.7	92.5	69.1	58.7
Bulk Density, kg/l						
Fresh Sorbent	1.31	1.34	1.26	1.19	1.01	1.05
Sulfided Sorbent	1.46	1.52	1.43	1.49	1.12	1.17
Surface Area, m ² /g						
Fresh Sorbent	3.30	3.94	3.95	1.74	1.01	1.70
Sulfided Sorbent	1.53	1.75	1.45	1.53	3.53	1.02
Sorbent Diameter, mm						
Fresh Sorbent	5.0	4.9	4.9	4.7	4.6	5.3
Sulfided Sorbent	5.0	4.9	4.9	4.8	5.0	6.3
Fines Produced During Cycle Testing, %						
<20 Mesh	0.61	0.72	0.65	0.32	0.97	0.80

^a Sorbent bed partially replaced during 10-cycle test due to furnace heating element failure.

oxide. Also shown in the table are the results for the base case cylindrical extrude and spherical pellet sorbents. In general, the physical characteristics of the new cylindrical extrudes compared very favorably to the base case T-2465 sorbent. Consistently greater crush strength and attrition resistance were obtained for the new sorbents. The new spherical pellet sorbent P73A also exhibited improvement over the base case 1094-59 sorbent, but the physical properties were not as good as for other sorbents prepared during the base program. Surface areas for the new cylindrical extrude sorbents trended in a fashion similar to that observed for the T-2465 sorbent (i.e., sulfided sorbent surface area lower than fresh sorbent surface area).

Sorbent diameters for the sulfided cylindrical extrudes were essentially the same as those measured for the fresh sorbents. The spherical pellet sorbent exhibited an increase in diameter following sulfidation. However, due to variability in the sorbent diameter resulting from the production technique, the measurements are not as accurate as those obtained using the cylindrical extrudes. The amount of fines produced during bench-scale testing was similar to the amount observed from testing of the base case sorbents. The low amount of fines for the E63A sorbent is due to the upset caused by the furnace failure which necessitated removing the sorbent bed during the course of multi-cycle testing.

Effect of Sorbent Shape

For the Ruthner process iron oxide formulations, the cylindrical extrude shape was superior both in terms of physical properties and chemical reactivity. The breakthrough sulfur sorption capacity of the cylindrical extrude shapes remained steady through the multi-cycle testing, while that for the spherical pellet P73A exhibited gradually decreasing values. The sulfur sorption capacity at saturation was also lower for the spherical pellet shape.

Effect of Iron Oxide Grade

Table 48 summarizes the key findings of the effect of iron oxide grade. The comparisons were made by averaging the results obtained for all sorbents prepared using a particular iron oxide grade. The results are further broken down by sorbent shape. These averaged results do not take into consideration other variables such as induration conditions, organic and inorganic binder additions, and $\text{ZnO}:\text{Fe}_2\text{O}_3$ ratio. Note that new sorbent E63A was excluded from the averages due to the furnace failure and sorbent damage which occurred during multi-cycle testing.

The averaged performance results in Table 48 show that in each case, the cylindrical extrude shape is superior in terms

Table 48. Effect of Iron Oxide Grade on Sorbent Properties

	<u>Catalyst-Grade Fe₂O₃</u>		<u>Pigment-Grade Fe₂O₃</u>		<u>Ruthner Process Fe₂O₃</u>	
	<u>Spherical Pellets</u>	<u>Cylindrical Extrudes</u>	<u>Spherical Pellets</u>	<u>Cylindrical Extrudes</u>	<u>Spherical Pellets</u>	<u>Cylindrical Extrudes^a</u>
Sulfur Sorption Capacity, lb S/100 lb Fresh Sorbent						
At Breakthrough	16.0	16.1	4.5	9.5	17.8	12.4
At Saturation	31.0	37.0	29.5	35.2	26.9	30.9
Sorbent Crush Strength, lb (Pellets) or lb/mm (Extrudes)						
Fresh	19.3	4.2	16.4	2.9	9.7	4.2
Sorbent	21.2	3.9	26.8	4.0	17.3	5.2
Sorbent Attrition Resistance, %						
Fresh	81.3	89.8	75.1	87.1	54.0	91.7
Sulfided	77.1	84.8	87.8	92.6	58.7	82.3
Fines Produced During Multi- Cycle Testing, %	0.76	0.41	0.39	0.24	0.80	0.69

^a Sorbent E63A excluded due to furnace failure and sorbent damage.

of reactivity and durability factors. Within each category of sorbent shape, the averaged results show that sulfur sorption capacity at breakthrough decreases in the order of catalyst, Ruthner, and pigment grades. For sulfur sorption capacity at saturation, performance decreases in the order of catalyst, pigment, and Ruthner grades.

In terms of fresh spherical pellet crush strength, performance decreases in the order of catalyst, pigment, and Ruthner grades. For cylindrical extrudes, catalyst and Ruthner grades are comparable with performance decreasing for pigment-grade iron oxide. Sulfided spherical pellet crush strength decreases in the order of pigment, catalyst, and Ruthner grades. Sulfided cylindrical extrude crush strength decreases in the order of Ruthner, pigment, and catalyst grades. Attrition resistance values follow similar trends.

Sorbent Porosity

The porosity of the new fresh sorbents and of selected sulfided sorbents was determined by mercury intrusion techniques. Table 49 summarizes the results. The E44A and E54A sorbents exhibited fresh and sulfided sorbent porosity properties which were similar to those reported for the base case T-2465 sorbent shown in Table 32. For these sorbents, total pore volume and porosity decreased significantly upon sulfidation. The average pore radius, however, did not significantly change. The E63A sorbent which was prepared using a 3 percent starch addition exhibited nearly double the average pore radius of the similar E44A sorbent which was prepared without starch addition. The spherical pellet sorbent P73A was found to have much greater average pore radius compared to the new cylindrical extrudes, but total porosity was much less. This is probably attributable to the disk pelletization technique used for manufacture of the spherical pellets and to the more severe induration conditions required to achieve physical durability.

Sorbent Mineralogy

Mineralogical analyses of the new Ruthner iron oxide sorbents E44A, E54A, E63A, and P73A were completed. Appendix C describes the results. The fresh sorbents were estimated to contain greater than 97 percent franklinite (zinc ferrite). Except for sorbent P73A, from 10 to 15 percent franklinite was detected in the sulfided sorbents. P73A sulfided sorbent contained up to 26 percent franklinite. Greater than 90 percent franklinite was found in regenerated sorbent sampled from the top of the reactor following the 9th cycle. Most of the remainder of the regenerated sorbent was identified as hematite.

Table 49. Porosity of Fresh and Sulfided Sorbents Prepared Using Ruthner Process Iron Oxide

<u>Sorbent Identification</u>	<u>Total Pore Volume, cm³/g</u>	<u>Average Pore Radius, Angstroms</u>	<u>Porosity, %</u>	
			<u>Pores >0.18 μm</u>	<u>Pores >0.012 μm</u>
<u>E44A</u>				
Fresh	0.219	1,110	46.1	52.3
Sulfided	0.103	1,180	21.3	28.3
<u>E54A</u>				
Fresh	0.236	1,190	42.8	54.3
Sulfided	0.114	1,570	27.6	31.0
<u>E63A</u>				
Fresh	0.236	2,710	51.3	54.1
<u>P73A</u>				
Fresh	0.316	3,720	33.1	33.3

Sorbent Grading

The chemical reactivity and physical durability values obtained for the new sorbents were applied to the sorbent grading system established during the base program. Table 50 summarizes the results of the sorbent evaluations. The base case spherical pellet and cylindrical extrude evaluations are also included for comparison. The new cylindrical extrude sorbents exhibited overall performance roughly comparable to the UCI T-2465 base case sorbent. The new sorbents prepared using Ruthner process iron oxide exhibited generally improved physical durability and somewhat lower chemical reactivity compared to the base case sorbent. The new spherical pellet sorbent (P73A) exhibited performance roughly comparable to the AMAX 1094-59 base case sorbent.

PREPARATION OF A 1-CUBIC-FOOT SORBENT SAMPLE

A 1-cubic-foot sample of sorbent E44A was prepared for independent evaluation by METC. This sorbent was selected on the basis of overall performance and sorbent materials costs. Characteristics of the sorbent are summarized in Table 51.

These characteristics closely match those of the E44A sorbent which was utilized for multi-cycle bench-scale testing. As such, additional characterizations (such as porosity and single particle kinetics) which were performed on the smaller samples used during bench-scale testing can be applied to this larger sample.

Table 50. Ruthner Process Iron Oxide Formulation Sorbent Performance

Sorbent Rating Category	Weighting Factor, %	Spherical Pellets				Cylindrical Extrudes							
		1J94-59		P73A		T-2465		E44A		E54A		E63A	
		Grade	Points	Grade	Points	Grade	Points	Grade	Points	Grade	Points	Grade	Points
<u>Chemical Reactivity Factors</u>													
1. Sulfur Sorption Capacity													
at 200 ppm H ₂ S Breakthrough													
a. Average of First 5 Cycles	5	1	5	3	15	5	25	3	15	3	15	3	15
b. Average of Last 5 Cycles	<u>15</u>	1	<u>15</u>	2	<u>30</u>	5	<u>75</u>	3	<u>45</u>	3	<u>45</u>	2	<u>30</u>
Subtotal	20	--	20	--	45	--	100	--	60	--	60	--	45
2. Sulfur Sorption Capacity at Saturation													
	20	4	80	2	40	4	80	3	60	4	80	2	40
3. Fresh Sorbent Surface Area													
	5	3	15	5	25	5	25	5	25	5	25	5	25
4. Fresh Sorbent Porosity													
	<u>5</u>	3	<u>15</u>	3	<u>15</u>	5	<u>25</u>	5	<u>25</u>	5	<u>25</u>	5	<u>25</u>
Total	50	--	130	--	125	--	230	--	170	--	190	--	135
<u>Physical Durability Factors</u>													
1. Crush Strength													
a. Fresh Sorbent	10	1	10	2	20	3	30	4	40	4	40	4	40
b. Sulfided Sorbent	<u>10</u>	2	<u>20</u>	4	<u>40</u>	1	<u>10</u>	5	<u>50</u>	4	<u>40</u>	5	<u>50</u>
Subtotal	20	--	30	--	60	--	40	--	90	--	0	--	90
2. Attrition Resistance													
a. Fresh Sorbent	10	1	10	1	10	4	40	5	50	5	50	4	40
b. Sulfided Sorbent	<u>10</u>	2	<u>20</u>	1	<u>10</u>	3	<u>30</u>	4	<u>40</u>	3	<u>30</u>	5	<u>50</u>
Subtotal	20	--	30	--	20	--	70	--	90	--	80	--	90
3. Fines Produced During 10 Cycles													
	<u>10</u>	1	<u>10</u>	2	<u>20</u>	2	<u>20</u>	2	<u>20</u>	2	<u>20</u>	4	<u>40</u>
Total	50	--	70	--	100	--	130	--	200	--	180	--	220
Final total	100		200		225		360		370		370		355
% of Maximum Possible Points			40		45		72		74		74		71

Note that maximum possible points = 500 (250 each for chemical reactivity and physical durability factors).

Table 51. Characteristics of a
1-Cubic-Foot Sample of Sorbent E44A

Sorbent Formulation

Iron Oxide Grade	Ruthner
ZnO/Fe ₂ O ₃ Ratio	1.0
Bentonite Content, %	2.0
Organic Binder Content, %	0.0

Induration Conditions

Temperature, °F	1,500
Time, Hours	0.5

Physical Properties

Bulk Density, kg/l	1.33
Crush Strength, lb/mm	4.5
Attrition Resistance, %	98.7
Surface Area, m ² /g	2.92

SORBENT PREPARATION SPECIFICATIONS

Based on the program results, some guidelines can be established for preparation parameters during the large-scale production of zinc ferrite desulfurization sorbent. Factors important to the selection of feed materials, manufacture of sorbent, and quality control are discussed in this section. Information on suppliers of raw materials used during the program are included in Appendix D.

SELECTION OF SORBENT RAW MATERIALS

The largest single zinc ferrite sorbent component on a weight basis is the iron oxide. Therefore, selection of an economical feed material which will result in adequate reactivity and durability is important. The results from this program showed that in addition to the zinc oxide component, the Ruthner, pigment-, and catalyst-grade iron oxides all contributed to coal gas desulfurization. Although the program results indicated that the catalyst-grade iron oxide delivered overall better performance, many of the pigment-grade and Ruthner process iron oxide formulations delivered a good balance of chemical reactivity and physical durability. The Ruthner process iron oxide delivered good durability and reactivity at a very low sorbent materials cost. As stated in the "Recommendations" section, sorbent lifetime will need to be determined for sorbents manufactured using the different iron oxide types in order to establish utilization economics.

Only one zinc oxide feed was used during this program. The particular zinc oxide utilized for sorbent formulation was a French-process product. French-process zinc oxides are characterized by very high purity. The other main type of zinc oxide is produced by the American process. American-process zinc oxides are characterized by higher impurity levels. The American-process zinc oxides typically contain sulfur and some heavy metals such as lead and cadmium as the main impurities. In the United States, most zinc oxide production is via the French process. The French-process zinc oxide cost is apparently about the same or possibly less than the American-process material. Only one American-process zinc oxide source is still currently active in the United States.⁷ French-process zinc oxide is recommended for zinc ferrite sorbent formulations because of product quality, availability, and cost.

The bentonite binder selected for sorbent preparation should be typical of those routinely used for other size enlargement processes. Typically, bentonites from the western United States are used for pelletization of iron ores. Bentonite binders impart significant green strength to iron ore pellets. Montmorillonite clay is the predominant constituent

of bentonite. (The term "bentonite" is derived from the source of discovery, Fort Benton, Wyoming.⁸) Many bentonites are subject to significant swelling upon wetting. In general, sodium bentonites provide the greatest degree of swelling, green strength, and dry strength in agglomeration processes. However, calcium and other forms of bentonite are treated by ion exchange to produce desirable properties. Bentonite is used in ceramics to increase plasticity, improve homogeneity, and reduce crack formation upon drying.⁸

Two types of organic binders were utilized during this program. Corn starch is a commonly used, low-cost binder/filler. Methocel is a specialized polymer often used in the manufacture of ceramics and other extruded materials. Methocel has additional properties as a mold release agent and gelling agent to aid in uniform production and appearance. Based on the very large cost differential for the two products (about an order of magnitude) and the apparently small effect of the organic binder in this particular application, the use of starch or other low cost materials is recommended.

SORBENT MATERIALS COSTS

Sorbent raw materials costs were summarized earlier in Table 5. These materials costs were compiled into costs for preparation of sorbents containing the example cylindrical extrude formulations indicated in Table 52. The examples represent the UCI T-2465 base case sorbent and the new sorbents which provided the best sorbent performance on Tables 37 and 49 for the three types of iron oxide investigated. Included in Table 52 are the materials costs only. Other operating and capital costs for sorbent preparation are not included. However, the materials costs should provide a basis for comparison, since similar equipment would be utilized to produce the different formulations. Use of as-received Ruthner process iron oxide would require some additional expense for cleanup of chlorine from the iron oxide by aqueous washing, heat treatment prior to sorbent preparation, or induration of prepared sorbent.

The costs in Table 52 show that the Ruthner process iron oxide formulation is less expensive in terms of actual materials costs and in terms of cost per pound of sulfur sorbed. The values for sorbent materials costs per pound of sulfur sorbed at saturation are probably of more significance than those for sulfur sorbed at breakthrough, since most of the sorbent bed would see nearly saturated conditions.

Sorbent lifetime is of importance in determining the actual materials costs requirements. Assuming that sorbent lasts for 100 cycles, the materials costs per pound of sulfur sorbed would range from about 1.2 to 4.8 cents based on the

sulfur sorption at saturation reported for the four sorbents in Table 52.

Table 52. Sorbent Preparation Materials Performance and Costs

	Sorbent Sample Number			
	T-2465	E-24A	E7A	E44A
<u>Sorbent Formulation</u>				
Iron Oxide Grade	Catalyst	Catalyst	Pigment	Ruthner
ZnO:Fe ₂ O ₃ Ratio	1.0	1.0	1.0	1.0
Bentonite, %	2	5	2	2
Methocel, %	0.5	0.5	0	0
<u>Sulfur Sorption Capacity, lb S/100 lb Fresh Sorbent</u>				
At Breakthrough	22.3	11.8	12.2	12.4
At Saturation	34.3	37.3	35.4	30.0
<u>Sorbent Materials Costs, \$/100 lb Indurated Sorbent</u>				
Iron Oxide	129.80 ^a	125.80 ^a	49.32	3.25
Zinc Oxide	31.45	30.50	31.45	31.45
Bentonite	0.04	0.10	0.04	0.04
Methocel	1.75	1.75	--	--
Total	163.04	158.15	80.81	34.74
<u>Desulfurization Costs, \$ Sorbent Materials Costs per lb S Sorbed in 1 Cycle</u>				
At Breakthrough	7.34	13.40	6.62	2.80
At Saturation	4.75	4.24	2.28	1.16

^a Based on a cost of \$2 per pound for catalyst-grade Fe₂O₃.

SORBENT PREPARATION EQUIPMENT

The desired sorbent shape will in large part determine the requirements for sorbent preparation equipment. Fluidized and moving bed applications will probably require a nearly spherical sorbent shape. Fixed bed applications could use cylindrical, spherical, or other shapes. Disk and drum pelletization techniques are commonly used in the iron ore industry because of the desirability of a spherical shape, particle strength considerations, and production costs. Tableting processes to produce spheroidal or other product shapes are generally more expensive than disk pelletization.

Extrusion techniques are often used for ceramic processing such as for catalyst supports. Extrusion techniques can provide a very uniform product in terms of internal pore structure due to multi-stage processing to control particle size and other parameters during manufacture.

The results of this program suggest that the manufacturing stresses induced during extrusion may help in the development or maintenance of internal porosity as relief fractures form upon multi-cycle sulfidation and regeneration. At least one type of available equipment is capable of producing cylindrical extrusions which are then formed into nearly spherical shapes by centrifugal processing which rounds off the cylinder ends.⁹ This type of equipment may have merit in the production of zinc ferrite sorbents, since particles with sizes as small as about 0.5 millimeter can be prepared.

SORBENT QUALITY CONTROL

Observations and measurements taken during the course of sorbent manufacture can be used as quality control and operating guidelines. Some of these potential methods are summarized below.

The sorbent program results showed that for a given formulation, factors such as pellet density, bulk density, crush strength, and attrition resistance can often be used as a guideline to sorbent performance. For example, increasing bulk density observed during a production run would probably indicate that the sorbent will become more durable but less reactive.

Appearance of the sorbent can indicate the type of structure which is being formed. A rough spherical pellet surface appearance generally indicates less compaction than a smooth surface appearance when using the same feed formulation. Sorbent color changes during induration can be used as a qualitative indicator of the degree to which the sorbent raw materials have been converted to zinc ferrite. Cylindrical extrude appearance as the material exits the die plate can also provide some indication of sorbent physical properties. The degree of stress can be inferred by the amount of bending of the sorbent as it leaves the die. The appearance of many small cracks normal to the cylindrical axis could indicate a sorbent which will not be very durable after drying and indurating.

Process and quality control schemes based on observations and simple measurements can and should be used when a given formulation is to be produced on a routine basis. The above descriptions simply provide some suggestions.

CONCLUSIONS

The program results confirm that zinc ferrite sorbents are suitable for removing hydrogen sulfide from hot coal gas. The conclusions of the research program are summarized in this section. These conclusions are based on sorbent characterizations related to physical properties, single particle kinetics, and multi-cycle bench-scale testing.

- Each of the zinc ferrite sorbents tested was found to be capable of reducing hydrogen sulfide gas concentrations to low (few ppm) levels. In many cases, the zinc ferrite sorbents achieved nearly theoretical sulfur sorption capacity. Both the iron and zinc components of the sorbent were found to participate in coal gas desulfurization reactions.
- Single particle kinetic studies performed by TGA provided a good means of screening sorbents.
- Catalyst-grade iron oxide provided generally superior sulfidation performance. However, selected lower-cost pigment-grade iron oxide formulations also resulted in good chemical reactivity and physical durability.
- Lower sorbent density (either bulk density or sorbent particle density) appeared to have a major benefit for sorbent sulfur sorption capacity, apparently through the effects on internal reaction pathways. The internal structure of the sorbents may be as important as the iron oxide type in determining sorbent performance. This internal structure can be characterized by surface area and porosity properties.
- An alternate iron oxide powder, a very low-cost Ruthner process product, was found to provide very good reactivity and durability when formulated as zinc ferrite sorbent.
- Induration temperature and time were the primary factors which influenced the physical properties of the sorbents. Greater sorbent density (resulting from more severe induration conditions) led to greater sorbent durability and poorer sorbent reactivity.
- Zinc ferrite sorbents formulated using a $\text{ZnO}:\text{Fe}_2\text{O}_3$ mole ratio of 1.0 provided somewhat better desulfurization response than those sorbents formulated using a 0.8 ratio. The effects of the $\text{ZnO}:\text{Fe}_2\text{O}_3$ ratio on physical durability were not particularly significant.
- Zinc migration from the interior of the sorbent or from the lower portions of the sorbent bed to the top during multi-cycle bench-scale tests was not observed to any significant

extent as was the case during previous programs. The presence of bentonite may have helped to retard undesirable reduction reactions.

- Sulfur sorption capacity at a hydrogen sulfide gas breakthrough concentration of 200 ppm was somewhat greater for sorbents prepared using lower bentonite inorganic binder concentrations. Higher bentonite concentrations were somewhat favored for sulfur sorption capacity at sulfur saturation and for sorbent durability factors.
- The addition of an organic binder resulted in overall poorer sulfidation performance at breakthrough. However, sulfur sorption capacity at sulfur saturation was slightly improved for sorbent formulations which incorporated an organic binder.

RECOMMENDATIONS

The program results verified that zinc ferrite sorbents provide very effective hot gas desulfurization performance. In order to establish the commercial implementation of this technology, some additional areas for research efforts are recommended. These research areas address issues of economics, sulfur recovery from regenerated sorbent, and disposal of spent sorbent. The recommendations are summarized below.

- Perform longer-term multi-cycle testing to establish the useful lifetime of zinc ferrite desulfurization sorbent. This will help to establish the sorbent economics based on the performance of different grades of iron oxide. Longer-term multi-cycle testing using TGA could be utilized to some extent to reduce research costs.
- Study recovery of sulfur from the regeneration of zinc ferrite sorbents in order to determine the potential costs or revenues associated with sulfur compound disposal or sale. This information will greatly impact the overall feasibility of implementing zinc ferrite sorbent technology.
- Develop processes for the reprocessing and/or disposal of spent sorbent. Determine whether the spent sorbent can be reprocessed to improve desulfurization or regeneration performance. The cost of sorbent disposal or reprocessing will play a role in the overall economics of utilization.
- Investigate alternate sorbent manufacturing techniques such as the Luwa Marumerizer, which can produce spheroidal particles from cylindrical extrusions in order to produce stronger sorbent while maintaining reactivity.
- Further investigate lower-cost iron oxide feed material.

REFERENCES

1. Grindley, T. and Steinfeld, G., "Zinc Ferrite Hydrogen Sulfide Absorbent", Proceedings of the Third Annual Contractors Meeting on Contaminant Control in Hot Gas Streams, K. E. Markel (Editor), DOE/METC/84-6 (CONF-8305112), DE 84000216, Morgantown Energy Technology Center, Morgantown, West Virginia, 1983, pp. 145-171.
2. Jha, M. C., Hepworth, M. T., and Baltich, L. K., "Enhanced Sorbent Durability for Hot Coal Gas Desulfurization", Report DOE/MC/21168-2023, Final Report Prepared by AMAX Research & Development Center, Golden, Colorado, for the Morgantown Energy Technology Center under Contract No. DE-AC21-84MC21168, March 1986.
3. Westmoreland, P. R. and Harrison, D. P., "Evaluation of Candidate Solids for High Temperature Desulfurization of Low Btu Gases", Environmental Science & Technology, Volume 10, No. 7, July 1976, pp. 659-661.
4. Olsson, R. G. and Turkdogan, E. T., "Desulfurization of Hot Reducing Gas", U. S. Steel Patent 4,180,549, December 1979.
5. "The Making, Shaping, and Treating of Steel", Association of Iron and Steel Engineers, Herbeck and Held, 1985, p. 1086.
6. Focht, G. D., Sa, L. N., Ranade, P. V., and Harrison, D. P., "Structural Property Changes in Metal Oxide Hot Coal Gas Desulfurization Sorbents", DOE/MC/21116-2163, 1986.
7. "Annual Ceramic Mineral Resources Review", Ceramic Bulletin, Volume 67, No. 5, 1988, pp. 895-919.
8. "Bentonite", Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Volume 3, Interscience Publishers, New York, 1964, pp. 339-360.
9. Luwa Marumerizer Product Literature, Luwa Corporation Process Division, P. O. Box 16348, Charlotte, North Carolina.

APPENDIX A

MULTI-CYCLE TEST OPERATION NOTES AND OBSERVATIONS

Operating observations, problems, and comments pertinent to the interpretation of the experimental results are summarized below. Most routine maintenance and repairs which were conducted between test runs are not reported here. Maintenance and calibration of gas analysis equipment were conducted periodically during the course of the program. Drager tube analyses of the test gases were carried out routinely to verify analyses. Repairs of ancillary equipment are not reported here unless the repairs impacted the test series in some manner.

AMAX 1094-59

- Water injection pump repairs were conducted during the first sulfidation cycle after noting a loss of flow.
- Test Cycle 3 was performed using 2,000 bed volumes per hour flow rather than the standard 2,500 bed volumes per hour, resulting in a doubling of sulfur sorption capacity at breakthrough.
- Overall poor sulfidation performance was achieved at breakthrough.
- Sulfur sorption capacity at saturation was greater than the other spherical pellet test sorbents.
- Single particle kinetics showed improved performance during the second TGA test cycle. All other sorbents selected for bench-scale testing exhibited decreased performance during the second TGA sulfidation test cycle.
- Crush strength and attrition resistance values were lowest of all spherical pellet sorbents tested in the bench-scale reactor.

P11A

- Test Cycle 3 was suspended early due to plugging in the reactor piping. An apparent iron contamination in a carbon monoxide cylinder resulted in the formation of an iron sulfide plug in the tubing leading to the reactor inlet. The entire preheater assembly was replaced.
- This sorbent consistently achieved the greatest sulfur sorption capacity at breakthrough of all of the spherical pellet shapes tested.

P6A

- A defective thermocouple for recording the top bed temperature was replaced following the first test cycle.

- P6A contained the minimum quantity of inorganic and organic binders.

P27A

- P27A contained the maximum quantity of inorganic and organic binders.
- Both P6A and P27A were indurated at 1,900°F for 4 hours and both were formulated using a 0.8 ZnO:Fe₂O₃ ratio. Both sorbents exhibited comparable sulfidation performance at breakthrough.
- P27A exhibited crush strength comparable to P6A.

P37A

- The reactor was cooled to 392°F in order to sample regenerated sorbent from the top of the bed following the 9th cycle.
- Overall poor performance was obtained in both TGA and bench-scale units.
- A low level of sulfur sorption was achieved both at breakthrough and at saturation.
- This was the most durable sorbent tested in the bench-scale reactor on the basis of crush strength and attrition resistance.

P22A

- Sorbent was sampled from the top of the reactor bed following the 9th cycle.
- Sulfur sorption capacity at breakthrough was consistently greater than 11 percent during the 10 sulfidation cycles.
- Sulfur sorption capacity at saturation was greater than any other new spherical pellet sorbent tested.

UCI T-2465

- The water injection pump was repaired during the first sulfidation cycle after observing irregular flow rates.
- The data acquisition computer was placed on line during the 4th test cycle.
- This cylindrical extrude sorbent consistently achieved the greatest sulfur sorption capacity at breakthrough of all of the cylindrical extrudes tested in the bench-scale unit.

- TGA tests confirmed a high level of reactivity for this sorbent.
- This sorbent exhibited one of the lowest sulfur sorption capacity values at saturation for the cylindrical extrude shape.

E13A

- The water injection pump head was replaced and recalibrated after the first sulfidation cycle.
- The temperature in the bottom zone of the furnace exceeded 800°C during the 6th oxidation cycle due to an apparent controller malfunction. The furnace door was opened to cool the reactor to the set point conditions.
- The exit gas filter gasket was replaced during the 8th test cycle due to leaks.
- This sorbent exhibited sulfur sorption capacities at breakthrough consistently greater than 15 pounds sulfur per 100 pounds fresh sorbent.
- The sulfur sorption capacity at saturation was greater than the base case sorbent.

E7A

- A leaking exit sample valve was replaced after the third sulfidation cycle.
- The exit gas filter gasket was replaced during the 8th test cycle due to leaks.
- This cylindrical extrude sorbent exhibited the highest average sulfur sorption capacity at breakthrough for those prepared using pigment-grade iron oxide.

E24A

- The exit gas filter gasket was replaced during the 8th test cycle due to leaks.
- This sorbent was indurated twice at 1,900°F for 15 minutes due to lack of complete heat treatment during the first 15-minute induration.
- The sulfur sorption capacity at saturation approached the theoretical maximum value.

- This sorbent exhibited the greatest crush strength and one of the greatest attrition resistance values of the cylindrical extrudes selected for bench-scale testing.

E28A

- This sorbent exhibited a significant drop in reactivity following the first sulfidation cycle, after which sulfur sorption capacity remained near 6 pounds sulfur sorbed per 100 pounds fresh sorbent.
- The sulfur sorption capacity at saturation was the lowest of the cylindrical extrudes tested.

E32A

- Sorbent was sampled from the top of the reactor bed following the 9th cycle.
- This sorbent was formulated similar to E28A, except for lower bentonite content.
- E32A, which was indurated under less severe conditions, exhibited greater sulfur sorption capacity at breakthrough and at saturation than E28A.

E2A

- The middle furnace zone was accidentally raised to about 1,328°F during heat-up before the 7th sulfidation cycle. The reactor was cooled to below 1,112°F before starting the hydrogen sulfide gas flow.
- Sorbent was sampled from the top of the reactor bed following the 9th cycle.
- This sorbent exhibited the greatest sulfur sorption capacity at saturation of all the cylindrical extrude sorbents selected for bench-scale testing.

APPENDIX B
TWO-STAGE SORBENT REGENERATION

**TWO-STAGE REGENERATION OF ZINC
FERRITE DESULFURIZATION SORBENT**

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DOE Contract No. DE-AC21-86MC23172
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June 28, 1988

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TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
OBJECTIVES	2
SUMMARY AND CONCLUSIONS	3
EXPERIMENTAL PROCEDURES	4
SULFIDATION	4
FIRST-STAGE REGENERATION	4
SECOND-STAGE REGENERATION	6
RESULTS AND DISCUSSION	7
SULFIDATION	8
FIRST-STAGE REGENERATION	8
SECOND-STAGE REGENERATION	13
SORBENT CHARACTERIZATION	17
THERMODYNAMICS	18
REFERENCES	21
APPENDIX A	
MINERALOGICAL ANALYSIS OF ZINC FERRITE SORBENT	
A-2-L-OX	22
APPENDIX B	
MINERALOGICAL ANALYSIS OF ZINC FERRITE SORBENTS	
B-1-L-RD, B-1-L-OX, AND B-3-L-OX, TOP AND	
BOTTOM	27

LIST OF TABLES

		<u>Page</u>
Table 1.	Sulfidation Gas Composition	4
Table 2.	Summary of Two-Stage Regeneration Test Results (UCI T-2465 Sorbent)	7

LIST OF FIGURES

Figure 1.	Bench-scale test apparatus.	5
Figure 2.	Hydrogen sulfide gas concentration in exit gas during sulfidation to saturation (3 feet per second gas velocity).	9
Figure 3.	Temperature profiles during sulfidation to saturation (3 feet per second gas velocity).	9
Figure 4.	Hydrogen sulfide gas concentration in exit gas during sulfidation to saturation (2 feet per second gas velocity).	10
Figure 5.	Temperature profiles during sulfidation to saturation (2 feet per second gas velocity).	10
Figure 6.	Sulfur dioxide and oxygen gas concentrations during first-stage regeneration (3 feet per second gas velocity).	11
Figure 7.	Temperature profiles during first-stage regeneration (3 feet per second gas velocity).	11
Figure 8.	Sulfur dioxide and oxygen gas concentrations during first-stage regeneration (2 feet per second gas velocity).	12
Figure 9.	Temperature profiles during first-stage regeneration (2 feet per second gas velocity).	12
Figure 10.	Sulfur dioxide and oxygen gas concentrations during second-stage regeneration (3 feet per second gas velocity).	14

LIST OF FIGURES
(Continued)

	<u>Page</u>
Figure 11. Temperature profiles during second-stage regeneration (3 feet per second gas velocity).	14
Figure 12. Sulfur dioxide and oxygen gas concentrations during second-stage regeneration (2 feet per second gas velocity).	15
Figure 13. Temperature profiles during second-stage regeneration (2 feet per second gas velocity).	15
Figure 14. Equilibrium constant, K_p , as a function of temperature.	19

INTRODUCTION

The Morgantown Energy Technology Center (METC) of the U. S. Department of Energy (DOE) is interested in the potential of using a two-step process for regenerating the zinc ferrite desulfurization sorbent. In the first regeneration step, a gas mixture consisting of 12 percent SO_2 , 2 percent O_2 , and 86 percent N_2 is used to convert zinc and iron sulfides to their sulfate forms using a sorbent bed inlet temperature of about 850°F (454°C). For the second step, the temperature is raised to about $1,400^\circ\text{F}$ (760°C), and the sulfates are decomposed to oxides with the concurrent release of sulfur dioxide. The same gas composition used for the first step is also used for the second step. The proposed technique would require no steam and also has the advantage of producing a regeneration gas rich in sulfur dioxide. In a commercial operation, recirculating regeneration gas would be supplemented with air as required to supply the necessary oxygen. A bleed stream from regeneration (concentrated SO_2 gas in nitrogen) would constitute feed to sulfur recovery.

Tests were performed at the AMAX R&D bench-scale sorbent test facility using the UCI T-2465 sorbent. Fresh sorbent was sulfided to saturation prior to each of the regeneration test series. Gas compositions, temperature profiles, pressure drops, and solids properties were characterized during each sulfidation and regeneration test.

The test results demonstrated the technical feasibility of the proposed technique. Sorbents were successfully regenerated to the zinc ferrite form during the two-step process.

OBJECTIVES

The objectives of the study were to establish the feasibility of the two-step regeneration technique and to characterize the gas compositions and solids products when using superficial gas velocities of 2 and 3 feet per second in the AMAX bench-scale fixed-bed desulfurization test unit.

SUMMARY AND CONCLUSIONS

The UCI T-2465 zinc ferrite sorbent was successfully regenerated using a simulated, recirculating regeneration gas composition. The tests verified that sulfate formation took place under the conditions of the first regeneration step. The tests also showed that the sulfates could be decomposed to oxides at higher temperatures with the concurrent release of sulfur dioxide gas. Although the individual sorbent particles became softer while in the sulfate phase, physical integrity of the sorbent was maintained throughout the regeneration procedure.

The regenerated sorbent from the test which was conducted at a superficial gas velocity of 2 feet per second exhibited virtually no residual sulfate. The regenerated sorbent from the test conducted at a velocity of 3 feet per second did contain about 1.1 to 2.3 percent sulfur, mostly as sulfate, in the lower and upper portions of the fixed bed, respectively. While the results appear to favor the selection of the 2 feet per second gas velocity over the 3 feet per second flow on the basis of residual sulfate content, a somewhat longer allowance for the second-stage regeneration reaction time using the 3 feet per second velocity would probably result in lower residual sulfate content based on the profile of residual sulfur content which shows increasing residual sulfur as a function of distance from the inlet gas. In addition, as discussed in the report, there may have been some discrepancy in the oxygen analysis and oxygen concentrations during the regeneration of sorbent using the 2 feet per second gas velocity which might have favored more complete regeneration to oxide forms.

EXPERIMENTAL PROCEDURES

Two sets of tests were performed. Superficial gas velocities of 2 and 3 feet per second during sulfidation and each regeneration step (calculated at the temperature of operation) were utilized. Figure 1 shows the experimental apparatus used for the sulfidation and regeneration tests. Gas flow was upward through a 12-inch tall fixed bed for each process step. The test at 3 feet per second was run first. Some minor procedure changes (including withdrawal of sample from the top of the reactor bed following each sulfidation and regeneration step) were incorporated prior to running the next test series at 2 feet per second. The procedures used during each step of the sulfidation and regeneration process are summarized below.

SULFIDATION

A simulated coal gas containing 1 percent hydrogen sulfide was used for sulfidation of fresh UCI T-2465 sorbent. The sulfidation gas composition is shown in Table 1. Sulfidation was carried out to saturation (until the H_2S concentration in the exit gas reached 1 percent). The superficial gas flow rates were 2 and 3 feet per second based on a $1,100^\circ\text{F}$ (593°C) inlet temperature. Following sulfidation to saturation, a nitrogen purge of the reactor system was conducted at a temperature of about $1,000^\circ\text{F}$ (538°C). A sample was taken from the top of the reactor bed following sulfidation to saturation when using the 2 feet per second test velocity. This sample was analyzed for chemical content and mineralogical characteristics.

Table 1. Sulfidation Gas Composition

<u>Gas</u>	<u>Concentration, Volume %</u>
N_2	42.3
H_2	10.6
CO	16.3
CO_2	4.5
H_2S	1.0
H_2O	25.3

FIRST-STAGE REGENERATION

The gas composition used for both the first and second regeneration steps consisted of 12 percent SO_2 , 2 percent O_2 , and 86 percent N_2 . The flow rates for 2 and 3 feet per second gas velocities during the first stage of regeneration were

Figure 1. Bench-scale test apparatus.

based on a 1,200°F (649°C) temperature. As specified in the test plan, the reactor was operated to maintain the gas inlet temperature at about 850°F (454°C), with the average of the reactor top and bottom temperatures not to exceed 1,200°F (649°C). Reactor temperatures, pressure drop, and gas compositions were recorded during the regeneration procedure. A sample was taken from the top of the reactor bed following the first-stage regeneration test at 2 feet per second gas velocity.

SECOND-STAGE REGENERATION

Second-stage regeneration was carried out at a 1,400°F (760°C) bed temperature using the same gas composition as was used for the first stage. Reactor temperatures, pressure drop, and gas compositions were recorded during the second-stage regeneration step. The test at 3 feet per second was concluded following regeneration with the gas mixture. (The reactor was cooled under a low nitrogen flow and the sorbent was then discharged.) A sample was taken from the top of the reactor bed following the test at 2 feet per second. An additional nitrogen purge at 1,400°F followed the test at 2 feet per second in order to determine whether any additional sulfate decomposition would take place. The reactor was then cooled prior to disassembly and sampling of the sorbent.

RESULTS AND DISCUSSION

The feasibility of the two-stage regeneration procedure was demonstrated by the successful regeneration of sulfided sorbent to zinc ferrite. Physical properties and chemical analyses of the feed sorbent and the regenerated sorbent from each test are summarized in Table 2. Appendices A and B summarize the mineralogical characterizations of the sorbent following regeneration.

Table 2. Summary of Two-Stage Regeneration
Test Results (UCI T-2465 Sorbent)

		<u>After 2nd Stage Regeneration</u>	
	<u>Before Testing</u>	<u>3 Feet/ Second</u>	<u>2 Feet/ Second</u>
<u>Physical Properties</u>			
Crush Strength, lb	36.0	18.7	19.4
Bulk Strength, kg/l	1.32	1.38	1.37
Surface Area, m ² /g	3.55	3.08	3.07
Loss on Attrition, %	11.2	11.6	12.4
% <20 Mesh			
After Testing	--	0.22	0.44
<u>Chemical Analysis</u>			
Zinc, %			
Feed	26.3		
Bottom		25.1	28.5
Top		25.2	28.0
Top "Red Sorbent"		20.1	--
Iron, %			
Feed	44.9		
Bottom		42.3	44.0
Top		42.2	44.0
Top "Red Sorbent"		33.2	--
Total Sulfur, %			
Feed	0.04		
Bottom		1.07	0.093
Top		2.23	0.100
Top "Red Sorbent"		8.92	--
Sulfate Sulfur, %			
Feed	--		
Bottom		1.06	0.017
Top		2.26	0.018
Top "Red Sorbent"		9.11	--

More detailed results of the experimental program and of the characterization of the sorbent samples are summarized below for each of the two tests performed.

SULFIDATION

Figures 2 and 4 summarize the hydrogen sulfide gas content of the exit gas as a function of time for the tests at 3 and 2 feet per second, respectively. Figures 3 and 5 summarize the temperature profiles in the reactor for the same tests. The sulfidation curves are similar to those obtained during previous cyclic bench-scale sulfidation/regeneration testing performed at AMAX R&D with the UCI T-2465 sorbent using a 1,022°F (550°C) sulfidation temperature rather than the 1,100°F (593°C) temperature used in the current work. The temperature upsets illustrated in Figures 3 and 5 represent the daily start-up and shutdown of the reactor system and are not a reflection of temperature response to the steady-state sulfidation conditions. The pressure drop through the 12-inch tall fixed bed averaged about 2.8 and 8.1 inches of water for the tests at 2 and 3 feet per second, respectively. No clear trends of increasing or decreasing pressure drop as a function of time were observed.

X-ray diffraction analysis of the sulfided sorbent removed from the reactor during the 2 feet per second test series showed that the sorbent contained moderate to major amounts of sphalerite, troilite + pyrrhotite, and wurtzite, minor amounts of franklinite, and traces of unidentified material. Appendix B contains the mineralogy report which reviews the sulfided sorbent analysis from the 2 feet per second test series.

FIRST-STAGE REGENERATION

The first-stage regeneration step apparently produced sulfates from the sulfided sorbent based on the oxygen content of the reactor exit gas (which indicated oxygen take-up by the sorbent). Some remaining sulfates were also observed in the top portion of the reactor following the second-stage regeneration at 3 feet per second gas velocity. As discussed later, during the test at 2 feet per second, some excess oxygen may have been present in the reactor which resulted in a first-stage regeneration product which contained sulfates, sulfides, and oxides.

Figures 6 and 8 summarize the oxygen and sulfur dioxide exit gas concentrations for the tests at 3 and 2 feet per second, respectively. Figures 7 and 9 summarize the temperature profiles during the first-regeneration step for the same tests. A rapid temperature rise was noted immediately following start-up of first-stage regeneration in both cases. The temperature rise was most pronounced at the bottom of the reactor where the regeneration gas was introduced into the fully sulfided sorbent bed. Overall, the temperature profiles for the two tests followed the same trends. The temperature control became more steady during the later portions of the

Figure 2. Hydrogen sulfide gas concentration in exit gas during sulfidation to saturation (3 feet per second gas velocity).

Figure 3. Temperature profiles during sulfidation to saturation (3 feet per second gas velocity).

Figure 4. Hydrogen sulfide gas concentration in exit gas during sulfidation to saturation (2 feet per second gas velocity).

Figure 5. Temperature profiles during sulfidation to saturation (2 feet per second gas velocity).

Figure 6. Sulfur dioxide and oxygen gas concentrations during first-stage regeneration (3 feet per second gas velocity).

Figure 7. Temperature profiles during first-stage regeneration (3 feet per second gas velocity).

Figure 8. Sulfur dioxide and oxygen gas concentrations during first-stage regeneration (2 feet per second gas velocity).

Figure 9. Temperature profiles during first-stage regeneration (2 feet per second gas velocity).

first-stage regeneration when most of the sorbent had apparently been converted to sulfate form. Pressure drop through the bed averaged about 2.3 and 8.6 inches of water for the tests at 2 and 3 feet per second, respectively.

A gradual increase in oxygen breakthrough was observed during the test at 3 feet per second following initial detection after about 100 minutes of operation. The oxygen concentration gradually increased up to about 2 percent after about 700 minutes of first-stage regeneration. For the test at 2 feet per second, a rapid oxygen breakthrough occurred at about 110 minutes. The measured oxygen concentration remained at about 1 percent and then dropped to about 0.5 percent before gradually increasing during the remainder of the test. Subsequent analysis of the test run data indicated that the calibration of the oxygen analyzer was apparently in error during the final portion (about 1 hour) of the first regeneration step and the initial portion (about 4 hours) of the second regeneration step using the 2 feet per second gas velocity. As a result, the inlet gas may have contained about 4 to 6 percent oxygen rather than the desired 2 percent concentration. Exit gas oxygen concentrations are also suspect over the same time period. The sorbent sample withdrawn from the reactor after the first stage when using the 2 feet per second velocity contained moderate quantities of franklinite and hematite, minor-to-moderate quantities of sphalerite, minor quantities of troilite + pyrrhotite and zinkosite (zinc sulfate), and traces of wurtzite and an unidentified phase. The mineralogy of the first-stage regeneration sorbent for the 2 feet per second test is discussed in Appendix B. Although the sorbent sample was removed from the reactor while at a temperature of about 572°F (300°C), it is felt that due to the rapid temperature decrease, little further reaction of the sorbent occurred upon exposure to air. The mineralogical analysis (which shows the presence of oxides) supports the presence of higher oxygen concentrations during some portion of the first-stage regeneration at 2 feet per second.

SECOND-STAGE REGENERATION

Sorbents from the tests at 3 and 2 feet per second were largely regenerated to the zinc ferrite form during the second stage. Figures 10 and 12 summarize the oxygen and sulfur dioxide exit gas concentrations for the tests at 3 and 2 feet per second, respectively. Figures 11 and 13 summarize the corresponding temperature profiles for the same tests. As shown in Figure 10, very high concentrations of sulfur dioxide were observed during initial portions of the regeneration procedure at 3 feet per second gas velocity. The early portions of the test produced SO₂ gas concentrations in excess of the measurement capabilities of the infrared analyzer. Subsequent analyses were performed using gas chromatography.

Figure 10. Sulfur dioxide and oxygen gas concentrations during second-stage regeneration (3 feet per second gas velocity).

Figure 11. Temperature profiles during second-stage regeneration (3 feet per second gas velocity).

Figure 12. Sulfur dioxide and oxygen gas concentrations during second-stage regeneration (2 feet per second gas velocity).

Figure 13. Temperature profiles during second-stage regeneration (2 feet per second gas velocity).

Note in Figure 12 that during the tests at 2 feet per second, the exit gas SO_2 concentrations were generally lower than the inlet gas SO_2 concentrations. At some points, the measured SO_2 concentration was as low as about 3 percent. Due to discrepancies in the oxygen analyses of the feed and exit gases, the actual oxygen content of the inlet gas may have been different than the desired 2 percent. During this test, significant deposits of high-sulfur material were observed in the gas sampling lines. These deposits prevented the determination of the overall sulfur balance in the system. The presence of SO_3 , which would not be detected using the gas analysis system utilized for the study, could also occur under some circumstances, as discussed in the "Thermodynamics" section.

During the test at 2 feet per second superficial velocity, some additional gas samples were obtained from the reactor while operating with a nitrogen flow only. These samples were taken under conditions of very low nitrogen purge flows during the course of the second stage of regeneration as the reactor reached operating temperature just prior to valving in the process gases for the daily test run. Additional samples were also taken following the completion of second-stage regeneration using a 3 feet per second nitrogen flow. The analyses revealed that SO_2 was released from the reactor bed during the low-flow nitrogen purging. Although the amount was not quantified, it is expected that only a small amount of sulfur dioxide was released based on the low nitrogen flows used and the relatively short time that the sorbent was exposed to the operating temperature without the $\text{SO}_2/\text{O}_2/\text{N}_2$ gas mix. No sulfur dioxide was observed following the completion of the second-stage regeneration step while operating at 760°C with a 3 feet per second N_2 flow.

Pressure drop through the sorbent bed averaged 2.1 and 7.2 inches of water for the tests at 2 and 3 feet per second, respectively. No major trends of increasing or decreasing pressure drop were observed during the course of the second stage of regeneration.

As shown in Table 2, the sulfur content in the bottom portion of the sorbent bed was 0.09 and 1.07 percent for the tests at 2 and 3 feet per second, respectively. As discussed above, a part of the test at 2 feet per second apparently took place using a higher oxygen content than desired. For the test at 3 feet per second, the sulfur concentration profile in the sorbent bed from bottom to top showed a trend of increasing concentration. This probably indicates that lower total sulfur content in the bed would result from longer reaction times. Note that virtually all of the residual sulfur in the sorbent samples following the 3 feet per second test was in sulfate form based on the chemical analyses shown in Table 2. Only

about 20 percent of the total residual sulfur following the regeneration test at 2 feet per second occurred as sulfate sulfur. Complete mineralogical analyses of the sorbents are summarized in Appendices A and B.

SORBENT CHARACTERIZATION

Physical properties of the fresh and regenerated sorbents are summarized in Table 2. The average crush strength of the UCI T-2465 sorbent particles decreased from 36 pounds to about 19 pounds following each of the two regeneration tests. Some sorbent particles which were later identified as containing significant sulfated material ("red sorbent" in Table 2) were soft compared to the fully regenerated sorbent. Average attrition resistance remained about the same as that for fresh sorbent. Attrition loss was about 12 percent following regeneration versus about 11 percent exhibited by the fresh sorbent. The sorbent bulk density increased slightly from about 1.32 kg/l for fresh sorbent to about 1.38 in the regenerated sorbents. Surface area decreased from 3.55 m²/g in fresh sorbent to about 3.08 m²/g in the regenerated sorbents. The amount of minus 20 mesh fines produced in the sorbent bed was 0.22 percent for the 3 feet per second test and 0.44 percent for the 2 feet per second test. These values compare to a value of 0.61 percent minus 20 mesh fines generated after 10 cycles of conventional testing using the same UCI sorbent. (The amount of fines measured after conventional testing is determined when the sorbent is in the sulfide form.)

As shown in Table 2 and discussed in Appendix A, some of the sorbent particles remained (at least in part) in the sulfate form following the second stage of regeneration during the test at 3 feet per second. As the chemical analysis for the sulfate sulfur content shows, the concentration of sulfate sulfur in the top portion of the reactor bed was about twice that found in the lower portion of the bed. Some sorbent particles were noticeably different in color and were sampled separately for analysis. These are identified as "red sorbent" in Table 2. The analysis by X-ray diffraction and chemical analysis indicated that these particular particles consisted in large part of sulfated sorbent.

The secondary electron images and corresponding electron microprobe images for iron, zinc, and sulfur are presented in Appendix A for sorbents sampled from the top and bottom portions of the reactor bed after completion of the 3 feet per second regeneration test. The images were taken at the center portion of sorbent particles prepared in cross section. The sample from the bottom of the reactor bed was more typical of a regenerated zinc ferrite sorbent, while the sample from the top of the bed contained sulfated sorbent. Virtually no residual sulfur was observed in the sample from the bottom of the bed

(Figure 1 in Appendix A). However, in the sample taken from the top of the bed (Figure 2 in Appendix A), a different texture is noted in the secondary electron image. In addition, residual sulfur is observed, primarily in association with zinc. Note that regions high in iron content are low in sulfur content.

Additional samples were taken from the top of the reactor bed during the 2 feet per second test series. By reducing the reactor temperature under a low nitrogen flow, small samples of sulfided product, first-stage regeneration product, and second-stage regeneration product were obtained. As discussed in Appendix B, the sorbent following the first regeneration step contained minor amounts (3 to 10 percent) of zinkosite (ZnSO_4). Other phases present were identified as franklinite, hematite, sphalerite, wurtzite, and troilite + pyrrhotite.

The secondary electron images and corresponding electron microprobe images for iron, zinc, and sulfur are shown in Appendix B for sorbents sampled from the top and bottom portions of the reactor bed after completion of the 2 feet per second regeneration test. The images shown were taken near the center of individual sorbent particles which had been prepared in cross section. The appearance of the sorbent in the secondary electron image was similar for the samples taken from the top and bottom of the reactor bed. (Note that the microprobe images were taken at 1,000X magnification versus the 400X used for the previous test at 3 feet per second superficial gas velocity.) The X-ray maps for iron, zinc, and sulfur from both the top and bottom portions of the reactor bed showed the same result. Iron and zinc were evenly distributed, and only background noise was observed in the sulfur image (indicating no detectable sulfur phases).

THERMODYNAMICS

The equilibrium thermodynamics for the Zn-S-O system were calculated under the sorbent regeneration conditions of interest. The following chemical reactions were considered for the simplified system (which did not include the iron component).

Based on data from Ingraham and Kellogg,¹ the equilibrium constants as a function of temperature for the above reactions were calculated and are shown in Figure 14. Note that two phases of ZnSO_4 can exist. The α form is stable below 734°C , while the β form is stable above a temperature of 734°C .

Legend

$\text{SO}_2 + \frac{1}{2} \text{O}_2$	SO_3	_____
$\text{ZnSO}_4 (\alpha)$	$\text{ZnO} \cdot 2\text{ZnSO}_4 + \text{SO}_3$	
$\text{ZnSO}_4 (\beta)$	$\text{ZnO} \cdot 2\text{ZnSO}_4 + \text{SO}_3$	-----
$\text{ZnO} \cdot 2\text{ZnSO}_4$	$\text{ZnO} + \text{SO}_3$	-----

Figure 14. Equilibrium constant, K_p , as a function of temperature.

At the nominal second-stage regeneration temperature of 760°C, a significant presence of SO_3 is not indicated based on formation from the SO_2 and O_2 constituents in the inlet gas. However, SO_3 formation would be favored by lower temperatures and higher pressures. The formation of SO_3 at the first-stage regeneration temperature of 454°C would be inhibited by the lack of available oxygen which would result from sulfation of the sulfided sorbent. Furthermore, Fe_2O_3 is reported to catalyze the decomposition of SO_3 .²

In a static system in which zinc sulfate is decomposed at 760°C, an equilibrium gas composition of 56.2 percent SO_2 , 15.7 percent SO_3 , and 28.1 percent O_2 would exist. Virtually no sulfate decomposition would take place at the first-stage regeneration temperature of 454°C.

Decomposition of ZnSO_4 under flowing nitrogen based on a 2 feet per second superficial gas velocity would result in the following calculated equilibrium gas composition.

N_2	82.6
SO_3	2.7
SO_2	9.8
O_2	4.9

Decomposition of ZnSO_4 under flowing SO_2 , O_2 , and N_2 of the composition used for the bench-scale tests at a 2 feet per second gas velocity would result in the following calculated equilibrium gas composition.

N_2	79.6
SO_3	2.7
SO_2	15.9
O_2	1.8

Any SO_3 formed during the regeneration tests would not be detected by the gas chromatograph techniques utilized during this program.

Detailed thermodynamic studies of the Fe-Zn-O-S system have been performed by SRI International.² Stability diagrams for the zinc ferrite system were prepared by SRI for temperatures between 500 and 900°C. ZnSO_4 and $\text{Fe}_2(\text{SO}_4)_3$ are the stable phases indicated at a 500°C temperature for a 12 percent SO_2 /2 percent O_2 gas composition. Zinc and iron oxides would be expected to form at the higher 760°C second-stage regeneration test temperature.

REFERENCES

1. Ingraham, T. R. and Kellogg, H. H., "Thermodynamic Properties of Zinc Sulfate, Zinc Basic Sulfate, and the System Zn-S-O", Transactions of the Metallurgical Society of AIME, Volume 227, December 1963, pp. 1419-1426.
2. Krishnan, G. N., Lamoreaux, R. H., Brittain, R. D., and Wood, B. J., "Investigation of Sulfate Formation During Regeneration of Zinc Ferrite Sorbents", SRI International, Quarterly Technical Progress Report 1 (October - December 1983), DOE Contract No. DE-AC21-83MC20092.

APPENDIX A
MINERALOGICAL ANALYSIS OF ZINC
FERRITE SORBENT A-2-1-OX

AMAX RESEARCH & DEVELOPMENT CENTER
INTEROFFICE MEMORANDUM

Subject: Mineralogical Analysis of Zinc Ferrite
Sorbent A-2-L-OX (80270)

September 24, 1987

To: M. Jha

From: J.R. Odekirk

Introduction

A set of zinc ferrite extruded sorbent (UCI T-2465, cylindrical extrude) was investigated to determine the phases present and the distribution of iron, zinc and sulfur. The samples represent extrudes from the top and bottom portions of an oxidation-reduction reaction column where loading is accomplished from bottom to top. A specific sample of red colored extrudes from the top portion was analyzed in addition to the general top and bottom samples.

Results

X-ray diffraction analysis was used to identify the various phase constituents. The phases detected are as follows:

Sample	Phases		
	<u>ZnFe₂O₄</u>	<u>Fe₂O₃</u>	<u>ZnSO₄</u>
A-2-L-OX Bottom	Major	—	—
A-2-L-OX Top	Major	Minor	Minor
A-2-L-OX Top (red)	Moderate	Moderate	Moderate

The variation in the amount of phases present suggests that the top portion of the column still contains extrudes which were only partially oxidize during regeneration.

Microscopic and electron microprobe analyses of the extrudes showed that both the top and bottom samples had a layered structure. The layering consisted of a fine-grained, competent rim and a much softer, less competent core. Generally the rim is about one-fourth of the radius of the extrude. In the bottom sample, the rim and core consisted of ZnFe₂O₄, whereas, in the top sample only the rim consisted of ZnFe₂O₄, Figure 1. The core of the top sample contains what appears to be the ZnSO₄ phase, Figure 2.

X-ray mapping by electron microprobe shows that the granular texture of ZnFe_2O_4 (franklinite) that formed in the core of the bottom extrudes, Figure 1, has not developed in the core of the top extrudes, Figure 2. Comparison of the texture and the distribution of Zn, Fe and S in the core of the top and bottom samples suggests that the zinc sulfate phase (zinkosite) could be somewhat fluid and as sulfur is expelled the fine-grain texture of franklinite is formed. Also, during the oxidation stage zinc tends to be mobil and forms a more homogeneous zinc and iron distribution. Mobilization of zinc after repeated sulfidation could result in its migration to the sorbent surface.

J.R. Odekirk

/lc

copy to: M. Berggren
T.B. Cox

Min No.: 87-10 and 87-22

Figure 1. A-2-L-OX, Bottom-center.

- A. Secondary electron image showing the fine-grained texture of ZnFe_2O_4 (franklinite). 400X
- B. X-ray map showing iron distribution.
- C. X-ray map showing zinc distribution.
- D. X-ray map showing sulfur distribution. Spot density is largely attributed to background rather than sulfur.

Figure 2. A-2-L-OX, Top-center.

- A. Secondary electron image showing the texture of secondary zinc sulfate (zinkosite). 400X
- B. X-ray map showing iron distribution.
- C. X-ray map showing zinc distribution.
- D. X-ray map showing sulfur distribution. Sulfur is closely associated with zinc.

APPENDIX B

**MINERALOGICAL ANALYSIS OF ZINC FERRITE SORBENTS
B-1-L-RD, B-1-L-OX, AND B-3-L-OX, TOP AND BOTTOM**

AMAX Research & Development Center

5950 McIntyre Street • Golden, Colorado 80403-7499

(303) 279-7636

Subject: Mineralogical Analysis of Zinc Ferrite Sorbents B-1-L-RD, B-1-L-OX, and B-3-L-OX, TOP & BOTTOM (80270) April 15, 1988

To: Mark Berggren

From: Ron Corbett

INTRODUCTION

A set of four extruded cylindrical zinc ferrite sorbents was submitted for mineralogical examination. Sample designations are as follows:

<u>Number</u>	<u>Description</u>
B-1-L-RD	1st top sample, 11/24/87
B-1-L-OX	top sample, 2/3/88
B-3-L-OX TOP	regenerated sorbent
B-3-L-OX BOTTOM	regenerated sorbent

All four samples were to be scanned on the x-ray diffractometer for phase identification. In addition, the last two samples above were to be examined by SEM to determine the distribution of iron, zinc, and sulfur at the center of a typical extrude.

As listed above, the samples are black, dark brown to black, light brown, and brown, respectively.

RESULTS

Representative pellets from each sample were ground to a fine (-200 mesh) powder and scanned over the range $2\theta = 3-64^\circ$ for phase identification on the x-ray diffractometer. Semi-quantitative estimates, based on peak intensities, were made for the abundance of the phases detected. These results are presented in tabular form as follows:

PHASE & EST. AMOUNT*

Sample	Franklinite (ZnFe_2O_4)	Hematite (Fe_2O_3)	Sphalerite ($\beta\text{-ZnS}$)	Wurtzite ($\alpha\text{-ZnS}$)	Troilite(FeS) + Pyrrhotite(Fe_{1-x}S)	Zinkosite (ZnSO_4)	Total Unidentified
B-1-L-RD	m	--	MM	m-M	M	--	tr
B-1-L-OX	M	M	m-M	tr	m	m	m-tr
B-3-L-OX TOP	MM	--	--	--	--	--	tr
B-3-L-OX BOTTOM	MM	--	--	--	--	--	tr

*MAJOR = MM (>30%)
 MODERATE = M (10-30%)
 MINOR = m (3-10%)
 TRACE = tr (<3%)

The SEM was used to produce secondary electron images and x-ray "dot maps" for iron, zinc, and sulfur in the centers of polished cross-sections of typical extrudes for the top and bottom B-3-L-OX samples. Those images are attached to this memo as Figures 1 and 2. They are all at 1000X, which seemed to show the fine-grained texture of these extrudes better than the previous 400X.

The two samples imaged on the SEM are regenerated material, which is virtually all franklinite (ZnFe_2O_4), as indicated by XRD. The SEM images for iron and zinc tend to support this interpretation. They show that the distribution of these elements is pretty uniform. The sulfur images just indicate background, as there are no detectable sulfur phases in the XRD for these two samples.

 R. K. Corbett

/lc

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

MET. NO. 262

a

c

b

d

Figure 1. Sample B-3-L-OX (TOP), center, 1000X
a. Secondary electron image c. Zinc(Zn) x-ray map
b. Iron(Fe) x-ray map d. Sulfur(S) x-ray map

a

c

b

d

Figure 2. Sample B-3-L-OX(BOTTOM), center, 1000X
a. Secondary electron image c. Zinc(Zn) x-ray map
b. Iron(Fe) x-ray map d. Sulfur(S) x-ray map

APPENDIX C
MINERALOGY REPORTS

AMAX RESEARCH & DEVELOPMENT CENTER
INTEROFFICE MEMORANDUM

Subject: Phase Constituents in Zinc Ferrite
Extrudes (80270)

July 27, 1987

To: M. Berggren

From: J.R. Odekirk

Samples of roasted (indurated) zinc ferrite extrudes and iron oxide feedstock were analyzed by X-ray diffraction to determine the phases present. Phases detected are as follows:

Iron oxide feedstocks

Phases

Pigment - Grade
Catalyst - Grade

Hematite
Hematite

Zinc ferrite extrudes

Phases

E-2 (1500°F, 4 hrs)
E-4 (1900°F, 15 mins)

Franklinite (90%), Hematite (10%)
Franklinite (95%), Hematite (5%)

E-7 (1500°F, 4 hrs)
E-9 (1900°F, 15 mins)

Franklinite (100%)
Franklinite (100%)

The four zinc ferrite extrudes contained franklinite ($\text{Zn Fe}_2\text{O}_4$) except that samples E-2 and E-4 also contained unreacted hematite. Sample E-4 which was indurated at a higher temperature appears to contain less hematite.

J.R. Odekirk

/lc

cc: A. Blandon
R.M. Rowe

MIN No. 87-8

AMAX RESEARCH & DEVELOPMENT CENTER
INTEROFFICE MEMORANDUM

Subject: Mineralogical Analysis of Zinc
Ferrites 4-10-R-RD and 5-9-L-RD (80270)

October 12, 1987

To: M. Berggren

From: J.R. Odekirk

Samples of zinc ferrite sorbent which had been fully sulfidized were investigated by X-ray diffraction, microscopic and electron microprobe analyses to determine the phases present and the distribution of zinc, iron and sulfur. The samples were collected from the top and the bottom of the reactor beds and represent the 10th sulfidation cycle for sorbents 4-10-R-RD (UCI T-2465, cylindrical extrude) and 5-9-L-RD (AMAX 1094-59, spherical pellets).

The following characteristics were determined.

Sorbent 4-10-R-RD

X-ray diffraction analysis indicates that both the top and bottom samples contain similar and near equal amounts of the following phases:

<u>Sample</u>	<u>Phases (%)</u>			
	<u>ZnS</u>	<u>ZnFe₂O₄</u>	<u>FeS</u>	<u>Unknown</u>
Top	60	10	20	10
Bottom	60	10	20	10

The FeS phase includes pyrrhotite (Fe_{1-x}S , $x=0-0.17$) and troilite (FeS). The unknown phase is attributed to a significant diffraction peak occurring at $26.9^\circ 2\theta$. No ZnO , Fe_2O_3 , Zn_2SiO_4 or FeS_2 were detected.

Electron microprobe analysis of the edge and the center of the extrudes indicates that there is some segregation in the zinc and iron distribution. However, the high-zinc and high-iron phases appear to be well sulfidized, Figure 1. Separation of the zinc and iron phases is more pronounced in the bottom sample and in the edge of the top sample. Phase separation is attributed to zinc migration during loading and unloading.

Microscopic examination in polished section normal to the extrude axis shows that during extrusion stresses are introduced which result in relief fractures when the extrudes undergo repeated loading. It is suspected that the presence of the relief fractures contribute to the permeability of the extrudes. Development of these relief fractures was not evident after one cycle of loading, as in the case of sorbent A-2-L-OX.

X-ray diffraction analysis indicates that the sorbent at the top of the reactor contains significantly more franklinite (ZnFe_2O_4) than the sorbent at the bottom of the reactor. Approximate relative amounts of the constituent phases are as follows.

Sample	Phases			
	ZnS	ZnFe_2O_4	FeS	Unknown
Top	50	30	10	10
Bottom	70	5	15	10

The greater amount of franklinite in the top sample indicates that the sorbent is only partially sulfidized. The unknown phase is attributed to a diffraction peak at $26.8^\circ 2\theta$, which appears to be the same unknown phase detected in sorbent 4-10-R-RD. The FeS phase is attributed to pyrrhotite and troilite.

Electron microprobe analysis of the edge and the center of the spherical pellets indicates that zinc and iron have a fairly uniform distribution, whereas the sulfur distribution is less uniform. The less uniform distribution of sulfur is attributed to unreacted franklinite, Figure 2. This sorbent also contains silicate grains which were not observed in sorbent 4-10-R-RD. The edge and center of the bottom sample and the edge of the top sample have a more uniform zinc, iron and sulfur distribution than the center of the top sorbent. During probe analysis it was noted that both the top and bottom samples contain concentric layers which are high in sulfur.

Microscopic examination in polished section shows that the spherical pellets consist of concentric layers having variable porosity. It is unknown whether this porosity is a result of loading or is introduced during sample preparation. However, impregnation of void space with epoxy before sectioning of the pellets suggests that variable pore space is a feature of pellet formation or cyclic loading and unloading and not introduced during sample preparation.

The texture suggests that the pellets are agglomerates of smaller spheres and loose material which are formed into larger spheres. This would account for the layers of variable density and porosity. The extruded sorbent appears to have a more uniform texture than the spheres and also exhibits stress fractures related to extrusion. The starting material of the spherical sorbent appears to be coarser grained than the extruded sorbent.

J. R. Odekirk

/lc

copy to: M. Jha
T. B. Cox

Min No. 87-10 and 87-18

Figure 1. Sorbent 4-10-R-RD, Top-center.

- A. Secondary electron image showing some phase separation. 400X
- B. X-ray map showing iron distribution.
- C. X-ray map showing zinc distribution.
- D. X-ray map showing sulfur distribution.

Figure 2. Sorbent 5-9-L-RD, Top-center.

- A. Secondary electron image showing quartz grains (medium gray) dispersed in partially reacted sorbent. 400X
- B. X-ray map showing iron distribution.
- C. X-ray map showing zinc distribution.
- D. X-ray map showing sulfur distribution.

AMAX RESEARCH & DEVELOPMENT CENTER
INTEROFFICE MEMO

Subject: Mineralogical Analysis of Zinc Ferrite
Samples 8-10-R-RD, Top & Bottom (80270)

To: M. Berggren

From: R. K. Corbett

Date: January 6, 1988

Samples of zinc ferrite sorbent 8-10-R-RD from top and bottom of the column were submitted for x-ray diffraction analysis and for element distribution imaging for zinc, iron, and sulfur by electron microprobe.

The work was done and the data were collected by J. R. Odekirk. This report is my interpretation and summarization of his findings.

SORBENT 8-10-R-RD (TOP)

An x-ray diffractometer scan on sorbent extrude material from the top of the column gives the following estimates (semi-quantitative) of the phases present:

<u>PHASE</u>	<u>COMPOSITION</u>	<u>EST. %</u>
Sphalerite	ZnS	30
Pyrrhotite + Troilite	Fe_{1-X}S ($X=0-0.17$) FeS	40
Franklinite	ZnFe_2O_4	15
Wurtzite (?)	ZnS	15

These are my estimates, based on patterns run by J. Odekirk. My estimates are based on peak areas and my own experience with diffraction characteristics of these phases. Their correspondence with percentage estimates he would make from these or similar samples is not well known, and the estimates should not be interpreted quantitatively, in too strict a sense.

Polished sections of sorbent pellets from the top of the column were examined in the electron microprobe for distribution of zinc, iron, and sulfur, both in the center of a typical pellet and along the edge of a pellet. Zinc is rather strongly segregated from iron and sulfur, both in the center

and along the edge of a representative extrude pellet. The zinc is concentrated in irregular areas averaging 30-50 micrometers (μm) in size near the center of a pellet, and in more evenly distributed areas averaging 15-35 μm along the pellet edge. In both areas, zones of high Zn concentration are zones relatively depleted in Fe and S. In other words, sulfur is preferentially associated with iron, rather than zinc. Agreement with the diffraction interpretation is only fair in this respect, but then the pellet selected for microprobe imaging may not have been totally representative of the bulk "top" sample, either.

Photographs from the microprobe of secondary electron image, iron distribution, zinc distribution, and sulfur distribution, all at 400X magnification, for both center and edge of a pellet from the column top, have been printed (four of each) and accompany this report. We have retained the negatives and originals.

SORBENT 8-10-R-RD (BOTTOM)

A diffraction pattern on material from the bottom of the column shows the same suite of compounds identified from the top, but with slightly different estimated amounts. These are as follows:

<u>PHASE</u>	<u>EST. %</u>
Sphalerite	40
(Pyrrhotite + Troilite)	30
Franklinite	18
Wurtzite (?)	12

Identification of wurtzite (the hexagonal dimorph of ZnS, distinct from sphalerite) is tentative, based on only one weak diffraction peak at about 26.9° of 2θ . This may be the "unknown phase" J. Odekirk referred to in earlier memos.

Element distribution images from the microprobe for center and edge of a representative pellet from the bottom of the sorbent column show much more uniform distribution of zinc, iron, and sulfur than at the top. Distribution of all three elements is very uniform at the center of the extrude pellet selected for examination. At the edge of the pellet, the sulfur is somewhat more strongly associated with zinc in some areas, and with iron in others, but it shows little preference for either element overall.

A similar suite of photographs (four copies of each), for center and edge of a bottom pellet, also accompany this memorandum.

R. K. Corbett

RKC/rmp

Encl

cc: T.B. Cox
Project File

Met. No. 169

AMAX Research & Development Center

5950 McIntyre Street • Golden, Colorado 80403-7499

(303) 279-7636

Subject: X-Ray Diffraction Analysis of January 13, 1988
Zinc Ferrite Samples 9-10-L-RD,
Very Top and Very Bottom (80270)

To: M. Berggren

From: R. K. Corbett

X-ray diffractometer scans on representative powdered material from the very top and very bottom of the column gave the following semi-quantitative estimates for the phases identified:

<u>Phase</u>	<u>Comp.</u>	<u>Est. Amount</u>	
		<u>V. Top</u>	<u>V. Bottom</u>
Franklinite	ZnFe_2O_4	35	35
Sphalerite	$\beta\text{-ZnS}$	25	25
Pyrrhotite + Troilite	Fe_{1-x}S } FeS	25	25
Wurtzite (?)	$\alpha\text{-ZnS}$	15	15

As indicated, the two samples gave essentially identical XRD patterns. The identification of wurtzite is tentative, being based on only one relatively weak peak.

For the present time, we will only run x-ray diffraction for compound identification on this type of sample, unless requested to do SEM or other additional analysis.

R. K. Corbett

/lc

cc: T. B. Cox
Project File

MET. No. 207

AMAX Research & Development Center

5950 McIntyre Street • Golden, Colorado 80403-7499

(303) 279-7636

Subject: XRD Analysis of Six Zinc
Ferrite Sorbent Samples (80270)

January 28, 1988

To: M. Berggren

From: R. K. Corbett

The six samples submitted have the following designations:

T-2465
E7A
E13A
1094-59
P6A
P11A

The first three listed are cylindrical extrudes, and the last three are pellets which are roughly spherical in shape.

A portion of each sample was crushed to a fine (-200m) powder and scanned on the x-ray diffractometer for phase identification.

All samples except T-2465 appear to be essentially pure franklinite (ZnFe_2O_4 , JCPDS No. 10-467), with no other identifiable compounds. Sample T-2465 also shows very major (>95%?) franklinite, plus a percent or two each of free zinc oxide (ZnO = zincite, JCPDS No. 5-664) and iron III oxide (Fe_2O_3 = hematite, JCPDS No. 13-534).

R. K. Corbett

/lc

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

Met No. 223

AMAX Research & Development Center

5950 McIntyre Street • Golden, Colorado 80403-7499

(303) 279-7636

Subject: X-Ray Diffraction Analysis of February 3, 1988
Zinc Ferrite Samples 10-10-R-RD,
Very Top & Very Bottom (80270)

To: M. Berggren

From: R. K. Corbett

X-ray diffractometer scans on representative powdered material from the very top and very bottom of the column gave the following semi-quantitative estimates for the phases identified:

<u>PHASE</u>	<u>COMP.</u>	<u>EST AMOUNT %</u>	
		<u>V. TOP</u>	<u>V. BOTTOM</u>
SPHALERITE	β -ZnS	40	50
FRANKLINITE	ZnFe ₂ O ₄	20	10
PYRRHOTITE +	Fe _{1-x} S	20	25
TROILITE	FeS		
WURTZITE	α -ZnS	20	15

R. K. Corbett

/lc

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

MET NO. 238

AMAX Research & Development Center

5950 McIntyre Street • Golden, Colorado 80403-7499

(303) 273-7200

Subject: X-Ray Diffraction Analysis of May 12, 1988
Six Zinc Ferrite Sorbents (80270)

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:

<u>E24A</u>	<u>P27A</u>
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.

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

<u>SAMPLE</u>		<u>FRANKLINITE</u> <u>(ZnFe₂O₄)</u>	<u>SPHALERITE</u> <u>(β-ZnS)</u>	<u>WURTZITE</u> <u>(α-ZnS)</u>	<u>PYRRHOTITE(Fe_{1-x}S)</u> + <u>TROILITE(FeS)</u>	<u>HEMATITE</u> <u>(Fe₂O₃)</u>	<u>TOTAL</u> <u>UNIDENTIFIED</u>
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 (≤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: Summarization of Old XRD
Results of Two P11A Sorbents,
7-10-R-RD TOP & BOTTOM (80270)

May 16, 1988

To: Mark Berggren

From: Ron Corbett

Diffraction patterns were run on the two subject samples in August, 1987 by J. R. Odekirk but the results were apparently not summarized. The patterns were located, and this memo is to document the results.

The two diffractograms are very similar, except for the presence of one moderately strong, unidentified peak at about 27.7° of 2θ ($\text{CuK}\alpha$) on the 7-10-R-RD VERY BOTTOM pattern that is not present on the pattern from the VERY TOP sample.

If the samples are still available, we might be able to go back and rerun the VERY BOTTOM scan and try to make some sense out of that "stray" peak.

Percentage estimates for the two samples, based on comparison of peak intensities with other, similar patterns are given below as follows:

<u>PHASE</u>	<u>COMP.</u>	<u>% IN SAMPLE</u> (7-10-R-RD)	
		<u>V. TOP</u>	<u>V. BOTTOM</u>
SPHALERITE	$\beta\text{-ZnS}$	30	32
PYRRHOTITE + TROILITE	Fe_{1-x}S } FeS	45	40
WURTZITE	$\alpha\text{-ZnS}$	12	8
FRANKLINITE	ZnFe_2O_4	13	10
TOTAL UNIDENTIFIED		<1	10

R. K. Corbett

/lc

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

MIN NO. 87-18

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:

<u>Sample</u>	<u>Color</u>
<u>E28A</u>	
13-10-R-RD Feed	Brown
13-10-R-RD Top	Black
13-10-R-RD Bottom	Black
<u>P37A</u>	
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

Diffraction 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

RKC:jb

Enclosure

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

X-Ray Diffraction Analysis
of
Zinc Ferrite Sorbents

PHASE AND ESTIMATED WEIGHT PERCENT

<u>Sample</u>	Frank- linite (ZnFe_2O_4)	Spha- lerite ($\beta\text{-ZnS}$)	Wurtzite ($\alpha\text{-ZnS}$)	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)

AMAX Research & Development Center

5950 McIntyre Street • Golden, Colorado 80403-7499

(303) 279-7636

Subject: Re-Examination of 7-10-R-RD June 1, 1988
Sorbent Samples by XRD (80270)

To: Mark Berggren

From: Ron Corbett

Samples 7-10-R-RD "bottom" and "very bottom" were scanned on XRD to try and identify the stray peak at 27.7° that I mentioned in my memo of May 16, 1988. This peak had appeared, with moderate strength, on the scan of the "very bottom" sample when run by J. Odekirk in August, 1987.

The subject peak was not detectable at all on either scan (bottom or very bottom) this time. I would have to conclude that 1) samples then and now are somewhat different, or 2) the peak was from contamination, or 3) the peak was an electronic "glitch" or noise spike. I would tend to disregard it at this point.

Ron K. Corbett

/lc

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

MET. NO. 351
MIN. NO. 87-18

AMAX Research & Development Center

5950 McIntyre Street • Golden, Colorado 80403-7499

(303) 273-7200

Subject: X-Ray Diffraction Analysis of E32A
Zinc Ferrite Sorbents & Iron Oxide
Feedstock (80270)

July 25, 1988

To: Mark Berggren

From: Ron Corbett

Four sorbent samples from group E32A (cylindrical) and one iron oxide feedstock sample (Ruthner Fe_2O_3 , red powder) were submitted for semi-quantitative phase analysis by x-ray powder diffraction. The number, description, and color for the four sorbents are as follows:

<u>Sample No.</u>	<u>Description</u>	<u>Color</u>
15-10-R-RD	Feed	Brown
15-9-R-OX	Top, regen. sorbent	Ochre (yel. brown)
15-10-R-RD	Top, sulfided sorbent	Black
15-10-R-RD	Bottom, sulfided sorbent	Black

Representative portions of each sorbent sample were ground to fine (minus 200 mesh) powders and scanned on the diffractometer over the two theta range 3-64° ($\text{CuK}\alpha$ radiation). The iron oxide feedstock was already a fine powder as received, and no further grinding was necessary on it.

Abundance estimates were made for the phases present, based on peak intensities and comparison with previous patterns of similar material. Those estimates are given in tabular form on a following page.

A standard mixture, using known weight percentages of franklinite (15-9-R-OX, Top) and hematite (Ruthner Fe_2O_3), was used to help in making the estimate for 15-10-R-RD Feed.

R.K. Corbett

RKC:jb

cc: T.B. Cox
M.C. Jha
Proj. File
Met. No. 416

X-Ray Diffraction Analysis
of
Sorbents and Feedstock

<u>Sample</u>	<u>Phase and Estimated Weight Percent</u>					<u>Total</u>
	<u>Franklinite</u> <u>(ZnFe₂O₄)</u>	<u>Sphalerite</u> <u>(β-ZnS)</u>	<u>Wurtzite</u> <u>(α-ZnS)</u>	<u>Pyrrhotite</u> <u>(Fe_{1-x}S) +</u> <u>Trillite (FeS)</u>	<u>Hematite</u> <u>(Fe₂O₃)</u>	
1. 15-10-R-RD, Feed	90	-	-	-	10	tr (<1)
2. 15-9-R-OX, Top, Regen	98+	-	-	-	-	<2
3. 15-10-R-RD, Top, Sulfided	28	38	16	18	-	tr (<1)
4. 15-10-R-RD Bottom, Sulfided	7	40	15	35	-	<3
5. Ruthner Fe ₂ O ₃ Alt. Feedstock	-	-	-	-	98+	<2

AMAX Research & Development Center

5950 McIntyre Street • Golden, Colorado 80403-7499

(303) 273-7200

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

October 6, 1988

To: Mark Berggren

cc: T.B. Cox

From: Ron Corbett

M.C. Jha

Proj. File

Met No. 464

The sample designations covered by this report are:

GROUP OR TYPE E2A

16-10-L-RD FEED
16-10-L-RD TOP, SULFIDED
16-10-L-RD BOTTOM, SULFIDED
16-9-L-OX REGEN. SORBENT

GROUP OR TYPE P22A

17-10-R-RD FEED
17-10-R-RD TOP, SULFIDED
17-10-R-RD BOTTOM, SULFIDED
17-9-R-OX REGEN. SORBENT

The same procedures were employed as with previous runs (e.g., see my memo of 6/28/88, Met. No. 384). Semi-quantitative estimates for the compounds identified are given in tabular form on an attached page.

R.K. Corbett

RKC:jb

Attachments

X-RAY DIFFRACTION ANALYSIS
of
ZINC FERRITE SORBENTS

PHASE AND ESTIMATED WEIGHT PERCENT

Sample	Frank- linite (ZnFe_2O_4)	Sphalerite ($\beta\text{-ZnS}$)	Wurtzite ($\alpha\text{-ZnS}$)	Pyrrhotite (Fe_{1-x}S) + Troilite (FeS)	Hematite (Fe_2O_3)	Total Unidentified
1. 16-10-L-RD, Feed	85	-	-	-	14	tr (≤ 1)
2. 16-10-L-RD, Top, Sulfided	20	44	12	24	-	tr (≤ 1)
3. 16-10-L-RD Bot., Sulfided	8	40	18	34	-	tr (≤ 1)
4. 16-9-L-OX, Regen. Sorb.	75	-	-	-	24	tr (≤ 1)
5. 17-10-R-RD, Feed	98+	-	-	-	-	tr (< 2)
6. 17-10-R-RD Top, Sulfided	10	46	14	30	-	tr (≤ 1)
7. 17-10-R-RD Bot., Sulfided	16	46	12	26	-	tr (≤ 1)
8. 17-9-R-OX, Regen. Sorb.	96	-	-	-	2	tr (< 2)

AMAX Research & Development Center

5950 McIntyre Street • Golden, Colorado 80403-7499

(303) 273-7200

Subject: XRD Analysis of Three Zinc
Ferrite Sorbents (80270)

February 16, 1989

To: Mark Berggren

cc: T.B. Cox
Proj. File
Met. No. 615

From: Ron Corbett

The following three fine powders were submitted for
analysis:

<u>Sample No.</u>	<u>Color</u>	<u>Ferro- Magnetic (?)</u>	<u>Surface Area</u>
P67, Mag	Black	Yes	0.56 m ² /g
P67, Non-Mag	Dark Red-Brown	No	1.12 m ² /g
P67, Rust Color	Rust	No	2.33 m ² /g

Each powder was scanned over the range of $2\theta = 3-64^\circ$ (CuK α radiation) on the x-ray diffractometer for semi-quantitative phase identification, with abundance estimates based on relative peak intensities.

Results of the scan interpretations are presented in
tabular form as follows:

X-Ray Diffraction Analysis

<u>Mineral</u>	<u>Composition</u>	<u>Est. Amount* in</u>		
		<u>P67, Mag</u>	<u>P67, Non-Mag</u>	<u>P67, Rust</u>
Franklinite	ZnFe ₂ O ₄	-	Major	Major
Magnetite	Fe ₃ O ₄	Major	-	-
Hematite	Fe ₂ O ₃	Minor-Trace	Minor-Moderate	-
Zincite	ZnO	Minor	Minor-Trace	-
Willemite	Zn ₂ SiO ₄	Minor	-	-
Hemimorphite(?)	Zn ₄ (OH) ₂ Si ₂ O ₇ ·H ₂ O	Trace(?)	-	-
Wüstite(?)	FeO	Minor(?)	-	-
Total Unident.	?	Minor-Trace	Trace	Minor-Trace

* Major >30%
Moderate 10-30%
Minor 3-10%
Trace <3%

R.K. Corbett

RKC:jb

AMAX Research & Development Center

5950 McIntyre Street • Golden, Colorado 80403-7499

(303) 273-7200

Subject: X-Ray Diffraction Analysis of
Eight Zinc Ferrite Sorbent Samples

June 27, 1989

To: M. O'Sullivan

cc: M. Berggren
M. Jha

From: R. Corbett

K. Young
Proj. File
Met. No. 777

Eight samples of brown and black cylindrical extrudes were submitted for semi-quantitative phase analysis by x-ray powder diffraction. The lot numbers, sample numbers, descriptions, and colors of the samples are as follows:

<u>Lot No.</u>	<u>Sample No.</u>	<u>Description</u>	<u>Color</u>
E44A	20-10-L-RD	Feed	Brown
E44A	20-10-L-RD	Top, sulfided sorbent	Black
E44A	20-10-L-RD	Bottom, sulfided sorbent	Black
E44A	20-9-L-OX	Top, regen. sorbent	Brown
E54A	21-10-R-RD	Feed	Brown
E54A	21-10-R-RD	Top, sulfided sorbent	Black
E54A	21-10-R-RD	Bottom, sulfided sorbent	Black
E54A	21-9-R-OX	Top, regen. sorbent	Brown

A representative portion of each sample was ground to a fine powder and scanned on the x-ray diffractometer over the range $2\theta = 3-64^\circ$ (CuK α radiation) for phase identification.

The amount of each phase identified was estimated from peak intensities and comparison with previous scans on similar material.

The resulting estimates are given in tabular form on a separate page. Although numerical estimates are given, they are subject to at least 10% relative error.

R.K. Corbett

RKC:jb

X-Ray Diffraction Analysis Zinc Ferrite Sorbents
Phase and Estimated Weight Percent

Sample	Franklinite (ZnFe_2O_4)	Sphalerite ($\beta\text{-ZnS}$)	Wurtzite ($\alpha\text{-ZnS}$)	Pyrrhotite (Fe_{1-x}S) + Troilite (FeS)	Hematite (Fe_2O_3)	Total Unidentified
1. 20-10-L-RD, Feed	97+	-	-	-	-	< 3
2. 20-10-L-RD, Top, Sulfided	15	45	12	28	-	tr (< 1)
3. 20-10-L-RD, Bottom, Sulfided	11	48	10	30	-	≤ 1
4. 20-9-L-OX, Top, Regen.	90	-	-	-	10	tr (< 1)
5. 21-10-R-RD, Feed	97+	-	-	-	-	< 3
6. 21-10-R-RD, Top, Sulfided	10	45	13	32	-	tr (< 1)
7. 21-10-R-RD, Bottom, Sulfided	12	50	10	28	-	tr (< 1)
8. 21-9-R-OX, Top, Regen.	90+	-	-	-	8	< 2

AMAX Research & Development Center5950 McIntyre Street • Golden, Colorado 80403-7499
(303) 273-7200 FAX (303) 273-7204**Subject:** X-Ray Diffraction Analysis of
Eight Zinc Ferrite Sorbent
Samples (80270)**August 16, 1989****To:** M. O'Sullivan**cc:** M. Berggren
M. Jha**From:** R. CorbettK. Young
Proj. File
Met. No. 855

Four samples of brown and black spherical pellets from Lot #P73A and four samples of brown and black cylindrical pellets from Lot #E63A were submitted for semi-quantitative phase analysis by x-ray powder diffraction. The lot numbers, sample numbers, descriptions, and colors of the 8 samples follow:

<u>Lot No.</u>	<u>Sample No.</u>	<u>Description</u>	<u>Color</u>
P73A	22-10-L-RD	Feed	Brown
P73A	22-10-L-RD	Top, sulfided sorbent	Black
P73A	22-10-L-RD	Bottom, sulfided sorbent	Black
P73A	22-9-L-OX	Top, regen. sorbent	Brown
E63A	23-10-R-RD	Feed	Brown
E63A	23-10-R-RD	Top, sulfided sorbent	Black
E63A	23-10-R-RD	Bottom, sulfided sorbent	Black
E63A	23-9-R-OX	Top, regen. sorbent	Brown

Experimental procedures are the same as those described in my memo of June 27, 1989. Resulting mineral estimates follow on an attached page. They are subject to at least $\pm 10\%$ relative error.

R.K. Corbett

RKC:jb

X-Ray Diffraction Analysis of Zinc Ferrite Sorbents
Phase and Estimated Weight Percent

Sample	Franklinite (ZnFe_2O_4)	Sphalerite ($\beta\text{-ZnS}$)	Wurtzite ($\alpha\text{-ZnS}$)	Pyrrhotite (Fe_{1-x}S) + Troilite (FeS)	Hematite (Fe_2O_3)	Zincite (ZnO)	Total Unidentified
1. 22-10-L-RD, Feed	97+	-	-	-	-	-	<3
2. 22-10-L-RD, Top, Sulfided	10	50	12	28	-	-	tr (<1)
3. 22-10-L-RD, Bottom, Sulfided	26	38	10	26	-	-	tr (<1)
4. 22-9-L-OX, Top, Regen.	95	-	-	-	3-5	1-2	tr (<1)
5. 23-10-R-RD, Feed	97+	-	-	-	-	1 (?)	<2
6. 23-10-R-RD, Top, Sulfided	15	46	12	27	-	-	tr (<1)
7. 23-10-R-RD Bottom, Sulfided	13	46	12	29	-	-	tr (<1)
8. 23-9-R-OX, Top, Regen.	95	-	-	-	2-4	1-2(?)	tr (<1)

APPENDIX D
SORBENT MATERIALS SUPPLIERS

Catalyst-Grade Iron Oxide (L-2796 Catalytic Grade):

United Catalysts Inc.
P. O. Box 32370
Louisville, KY 40232
(502) 634-7200

Pigment-Grade Iron Oxide (Bayferrox 645T):

Mobay Chemical Corporation
Inorganic Chemicals Division
Mobay Road
Pittsburgh, PA 15205
(412) 777-2000

Ruthner Process Iron Oxide:

Arus-Andritz-Ruthner, Inc.
Robinson Plaza Three
Pittsburgh, PA 15205
(412) 787-5380

French Process Zinc Oxide (AZO-77):

ASARCO
P. O. Box 538
Hillsboro, IL 62049
(217) 532-3931

Methocel Organic Binder (K15MS):

Dow Chemical USA
Midland, MI 48674
(800) 258-2436