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TWO-STAGE REGENERATION OF ZINC FERRITE DESULFURIZATION SORBENT

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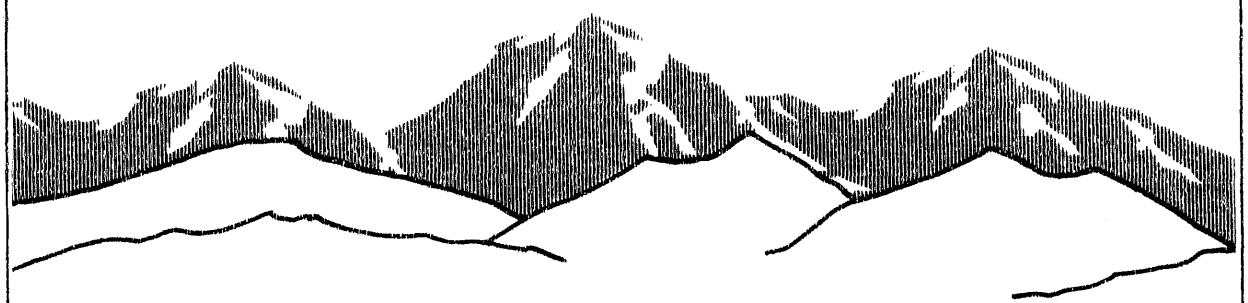

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DISCLAIMER

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES
(Continued)

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°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°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°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

Gas	Concentration, Volume %
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

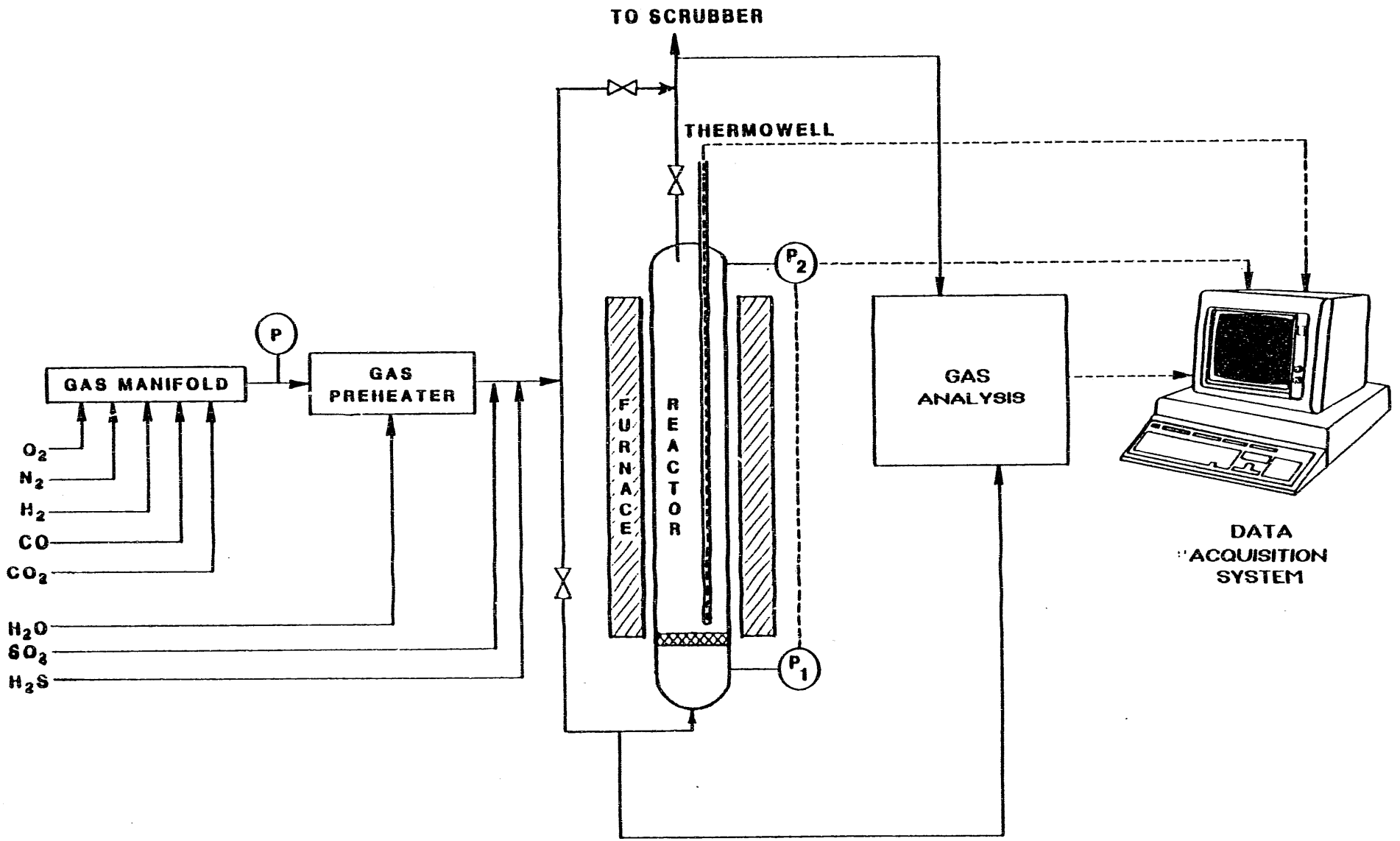


Figure 1. Bench-scale test apparatus.

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)

	Before Testing	After 2nd Stage Regeneration 3 Feet/ Second	After 2nd Stage Regeneration 2 Feet/ Second
Physical Properties			
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
Chemical Analysis			
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

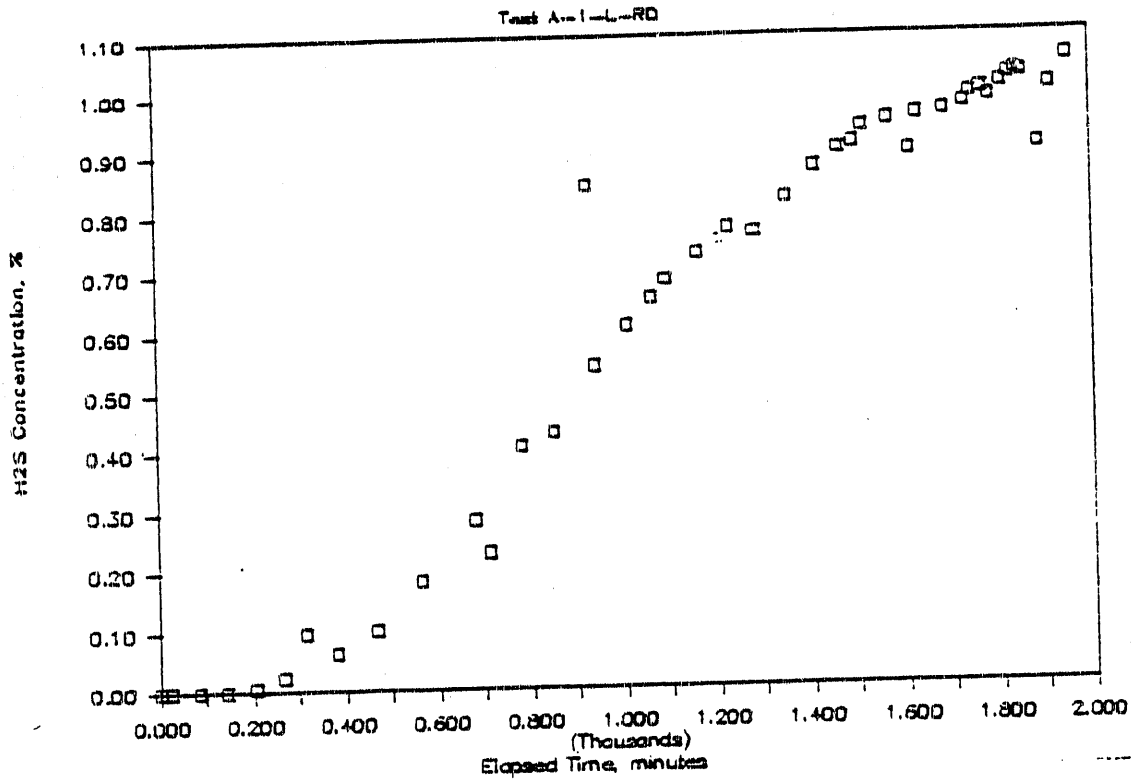


Figure 2. Hydrogen sulfide gas concentration is exit gas during sulfidation to saturation (3 feet per second gas velocity).

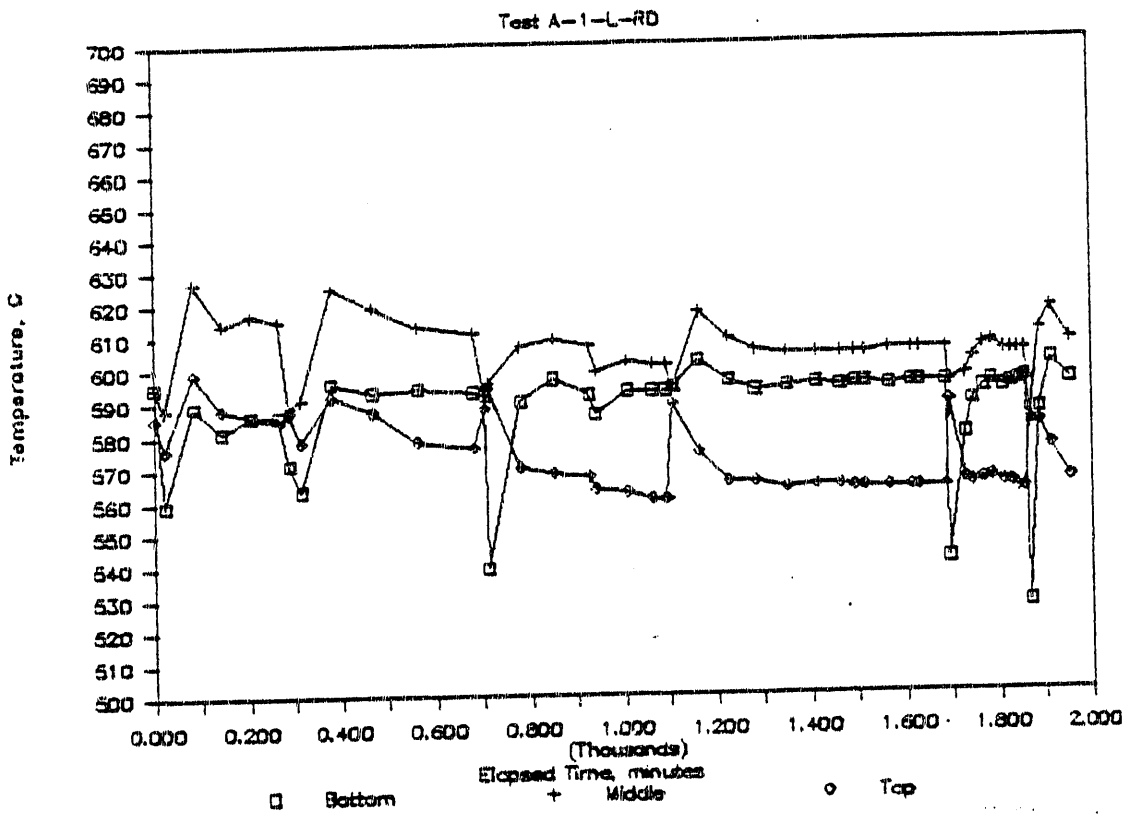


Figure 3. Temperature profiles during sulfidation to saturation (3 feet per second gas velocity).

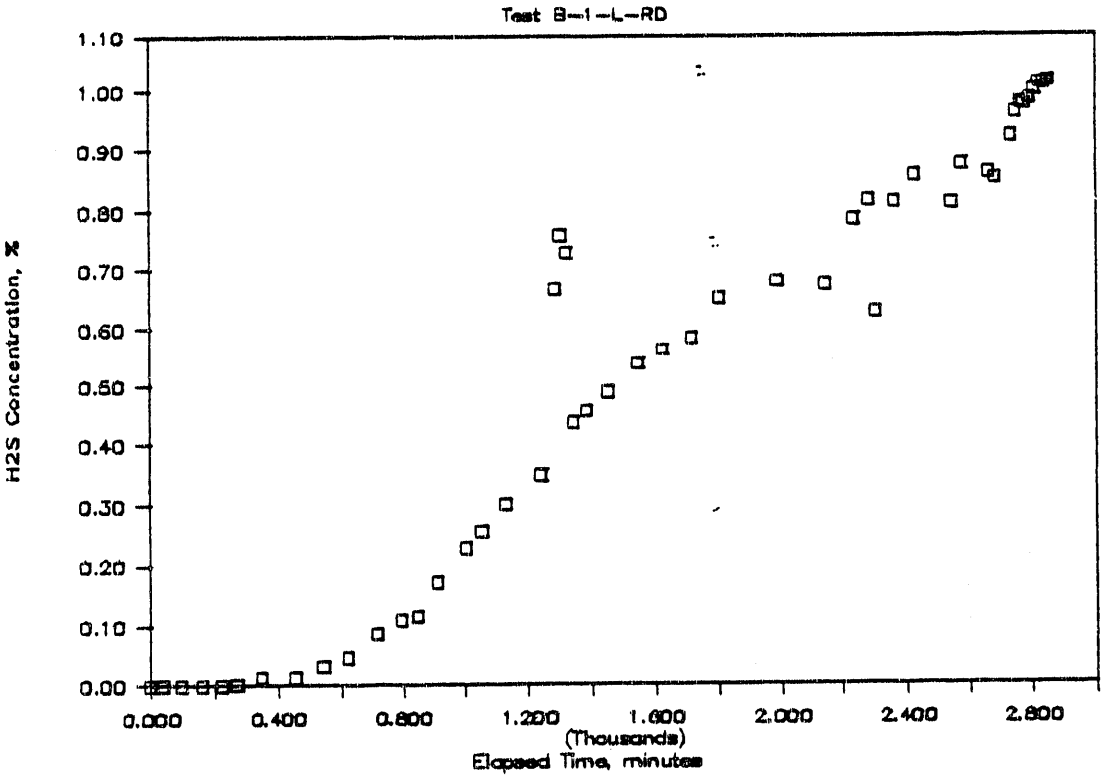


Figure 4. Hydrogen sulfide gas concentration in exit gas during sulfidation to saturation (2 feet per second gas velocity).

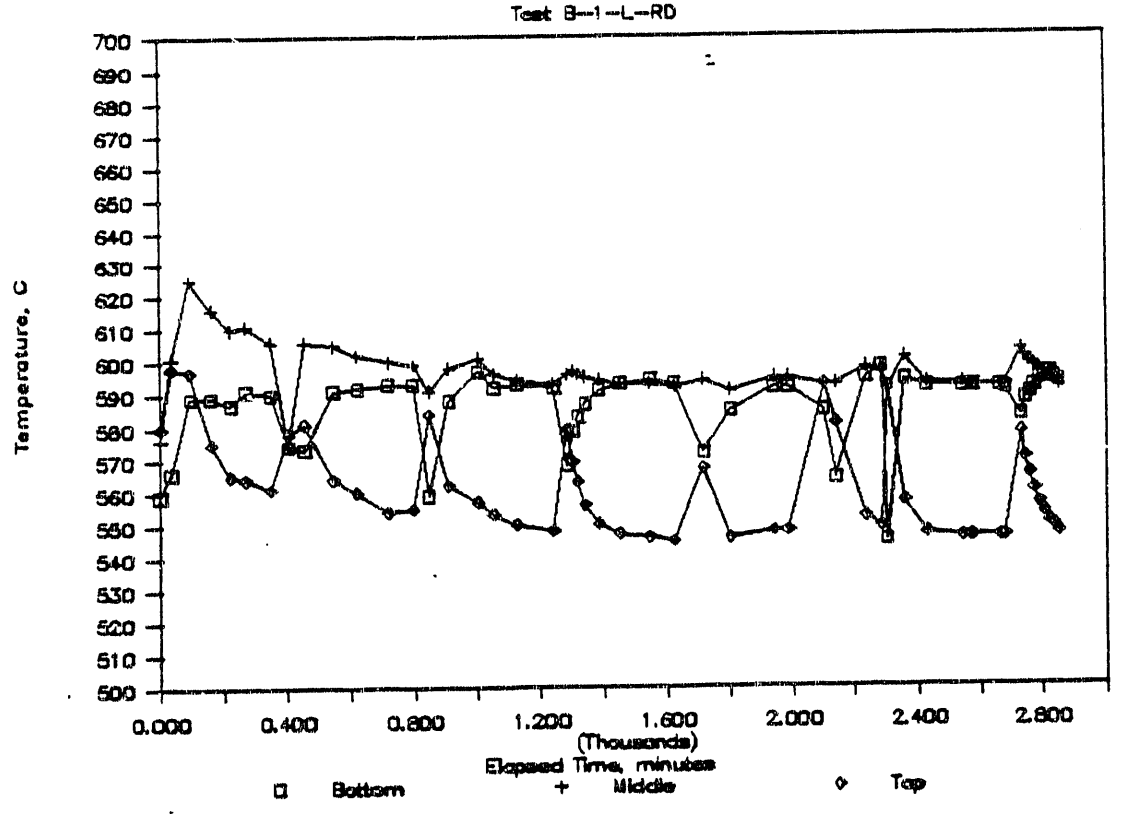


Figure 5. Temperature profiles during sulfidation to saturation (2 feet per second gas velocity).

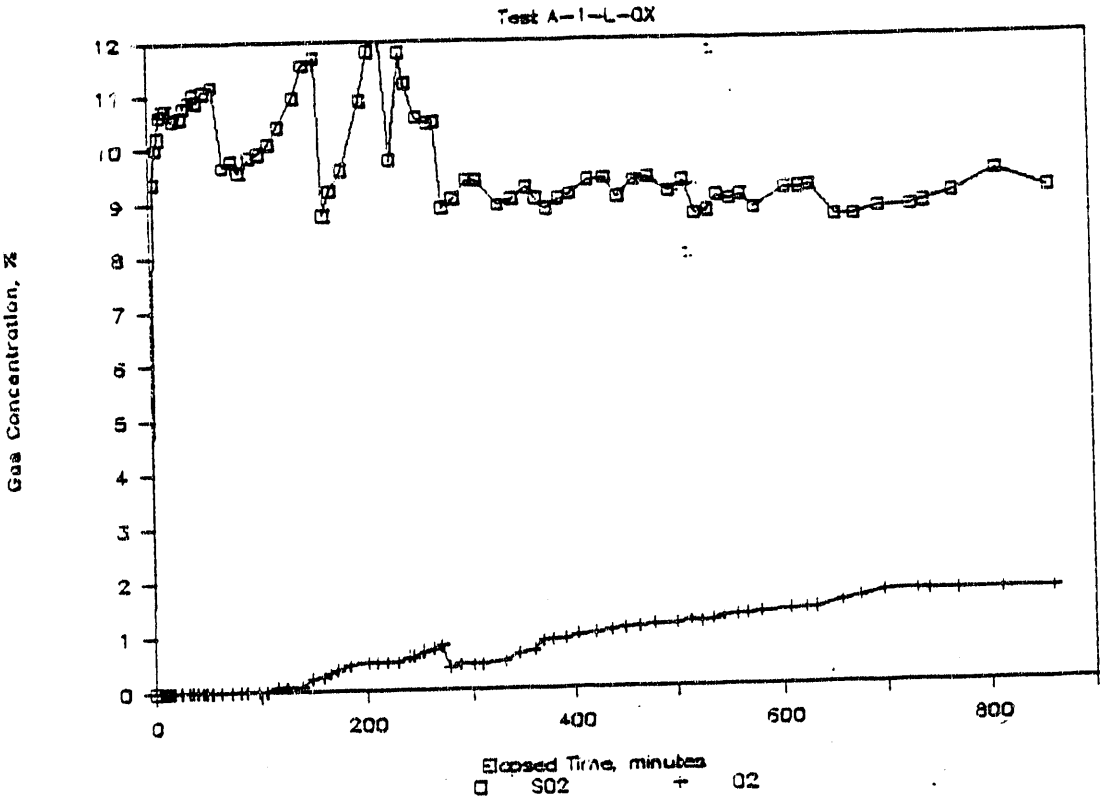


Figure 6. Sulfur dioxide and oxygen gas concentrations during first-stage regeneration (3 feet per second gas velocity).

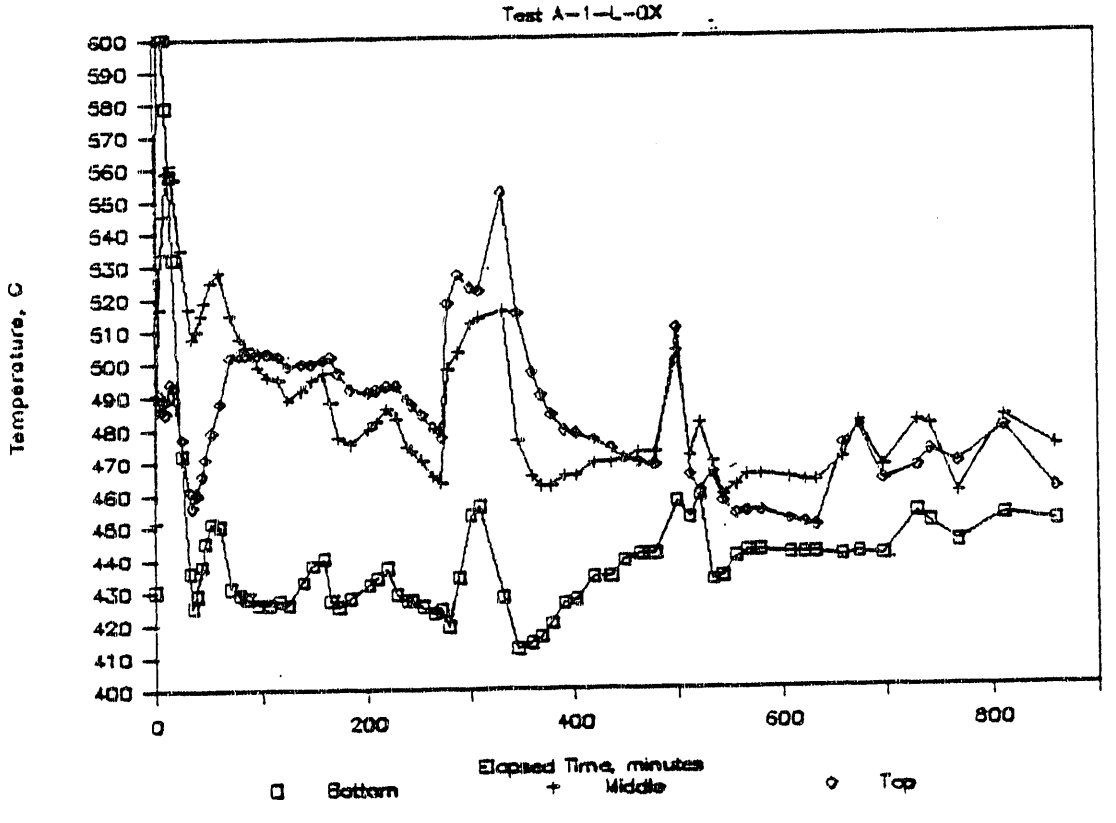


Figure 7. Temperature profiles during first-stage regeneration (3 feet per second gas velocity).

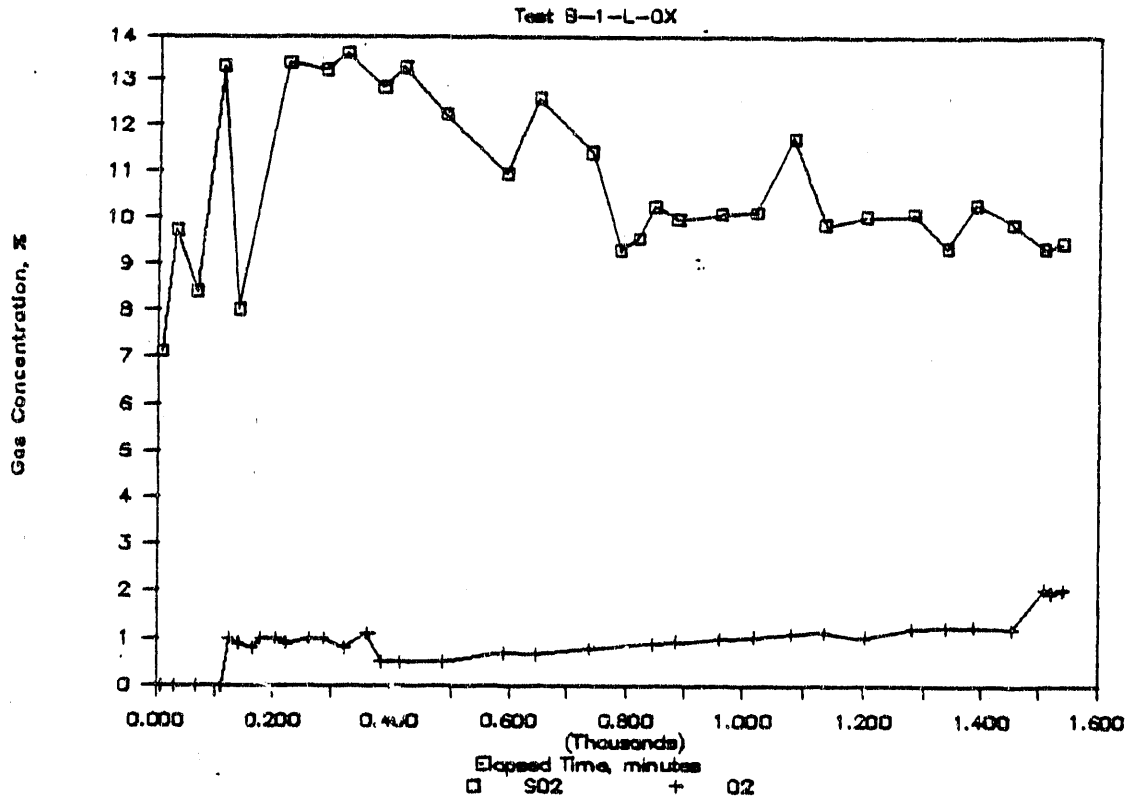


Figure 8. Sulfur dioxide and oxygen gas concentrations during first-stage regeneration (2 feet per second gas velocity).

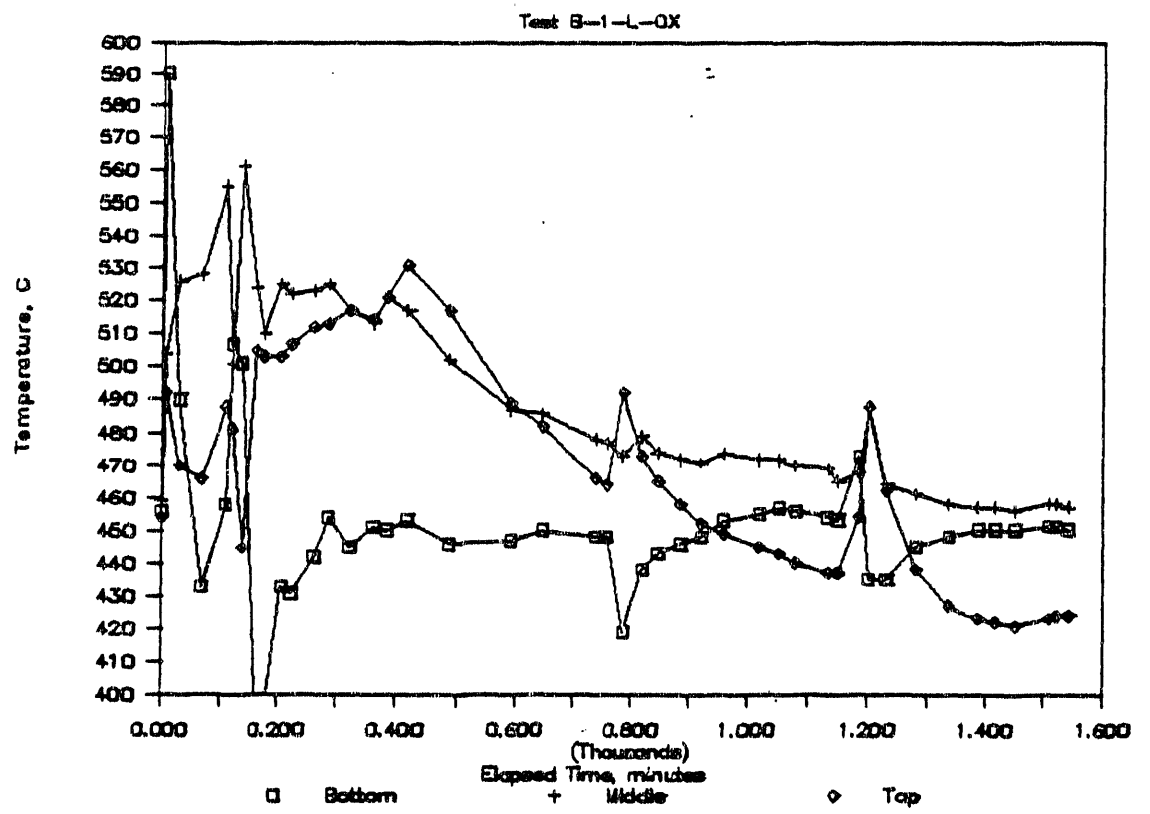


Figure 9. Temperature profiles during first-stage regeneration (2 feet per second gas velocity).

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 SO_2 gas concentrations in excess of the measurement capabilities of the infrared analyzer. Subsequent analyses were performed using gas chromatography.

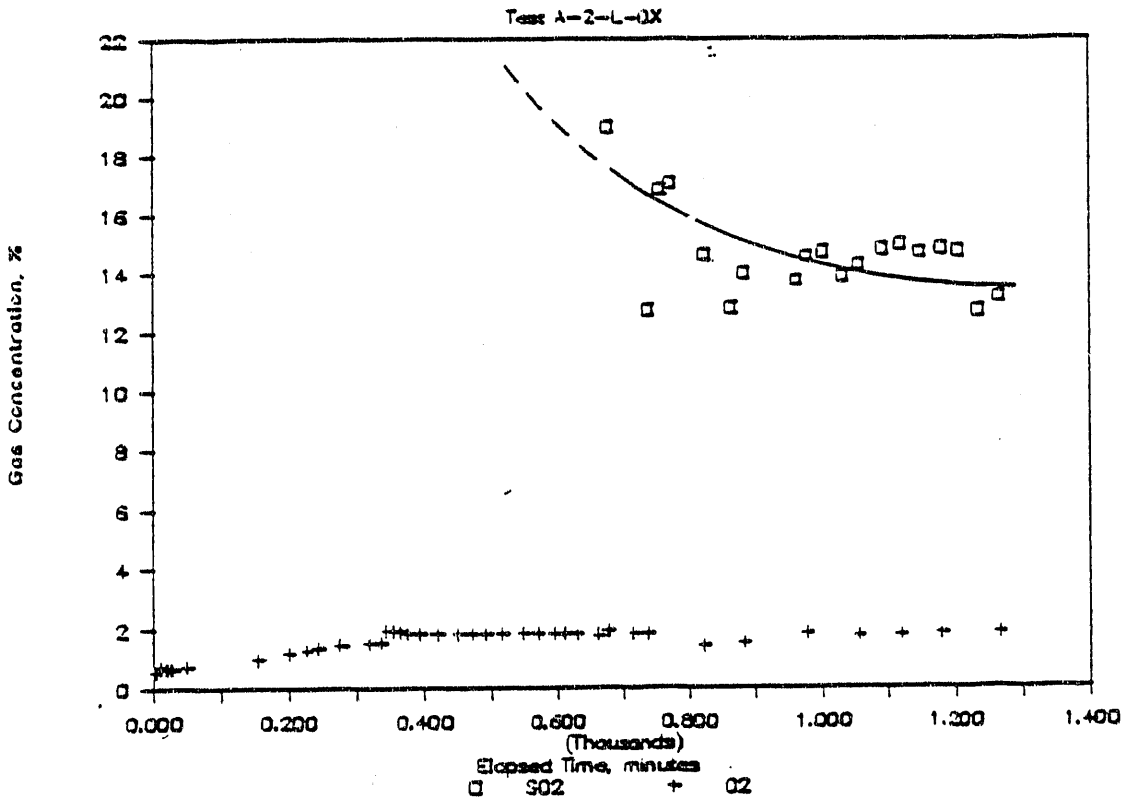


Figure 10. Sulfur dioxide and oxygen gas concentrations during second-stage regeneration (3 feet per second gas velocity).

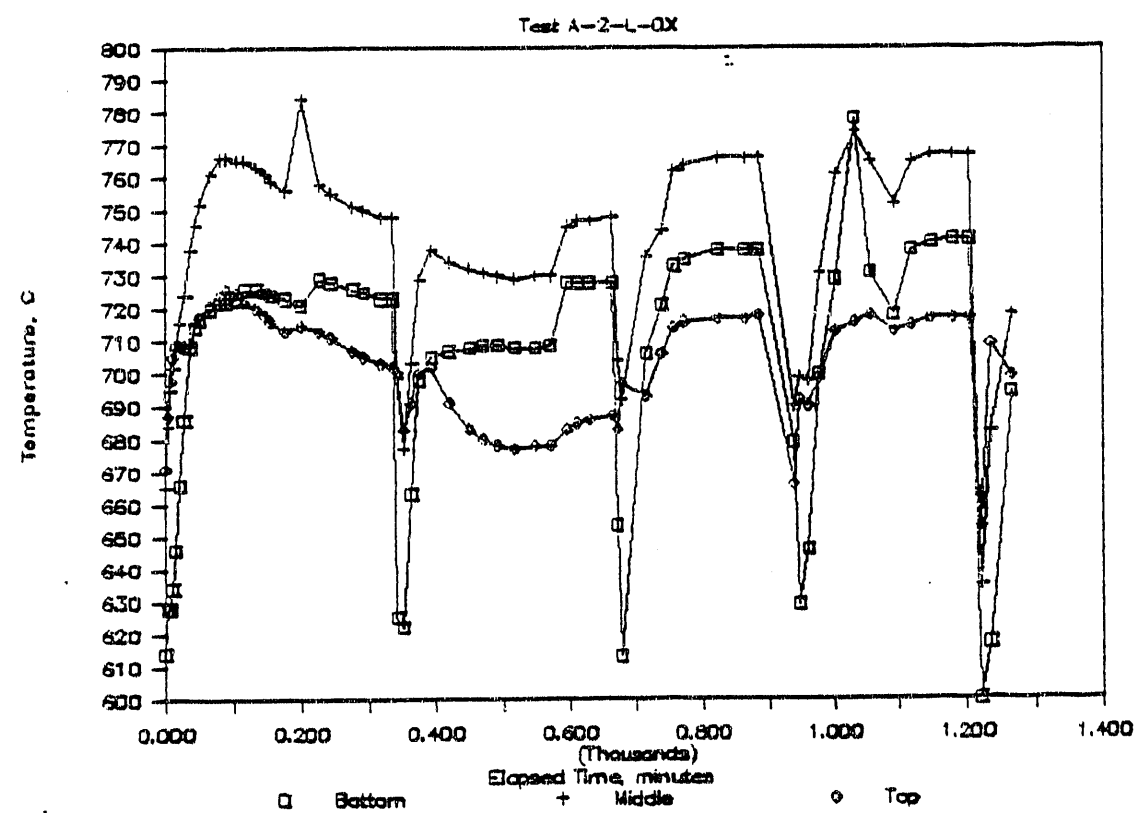


Figure 11. Temperature profiles during second-stage regeneration (3 feet per second gas velocity).

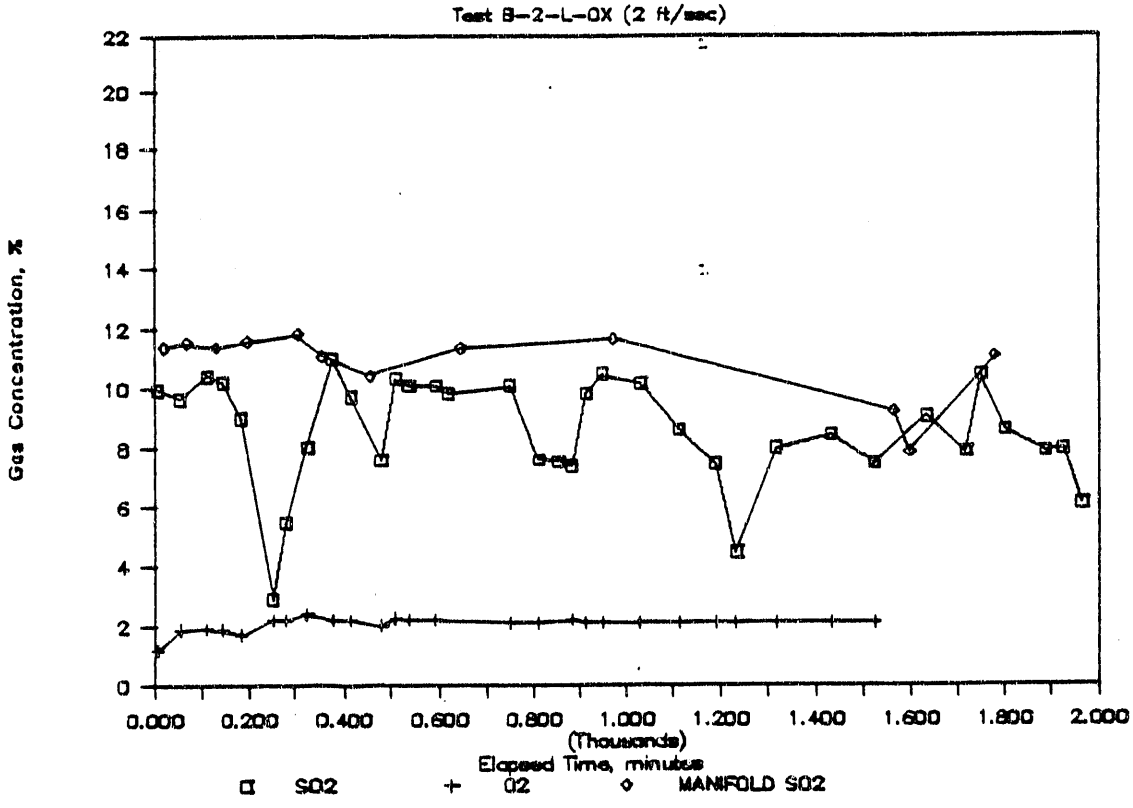


Figure 12. Sulfur dioxide and oxygen gas concentrations during second-stage regeneration (2 feet per second gas velocity).

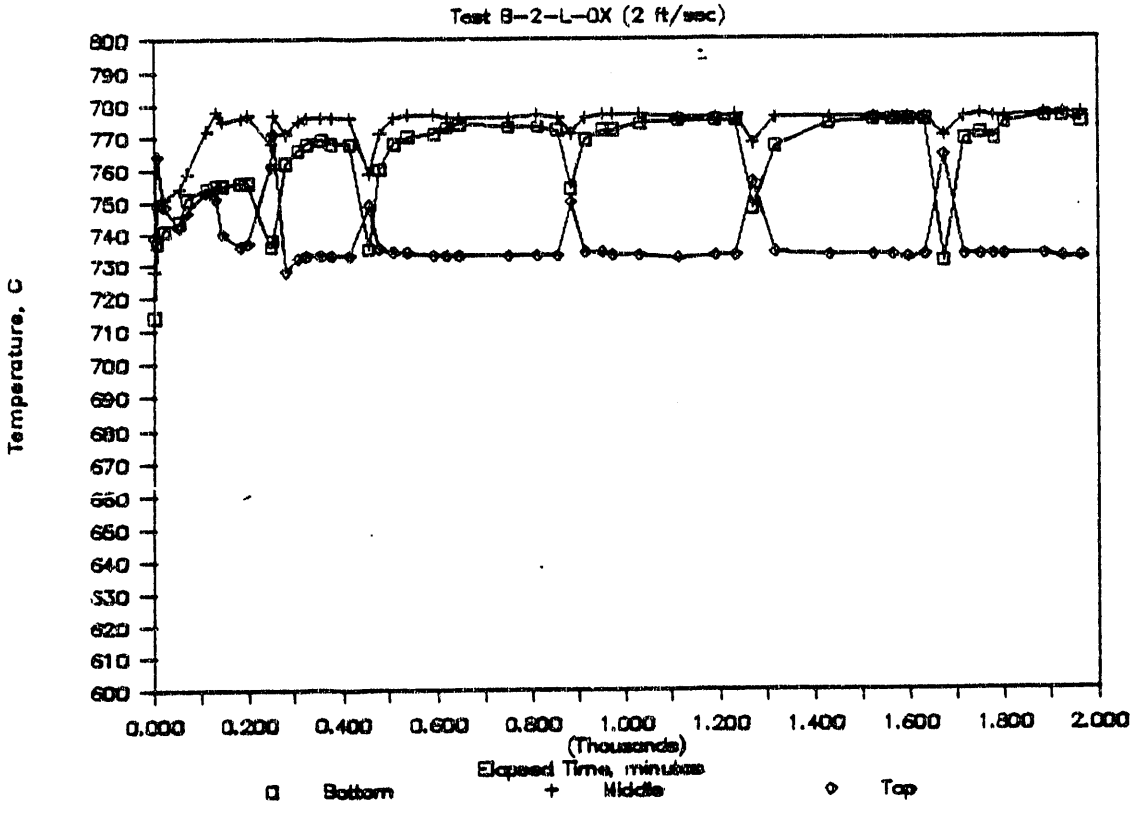


Figure 13. Temperature profiles during second-stage regeneration (2 feet per second gas velocity).

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 $SO_2/O_2/N_2$ 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 m^2/g in fresh sorbent to about 3.08 m^2/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

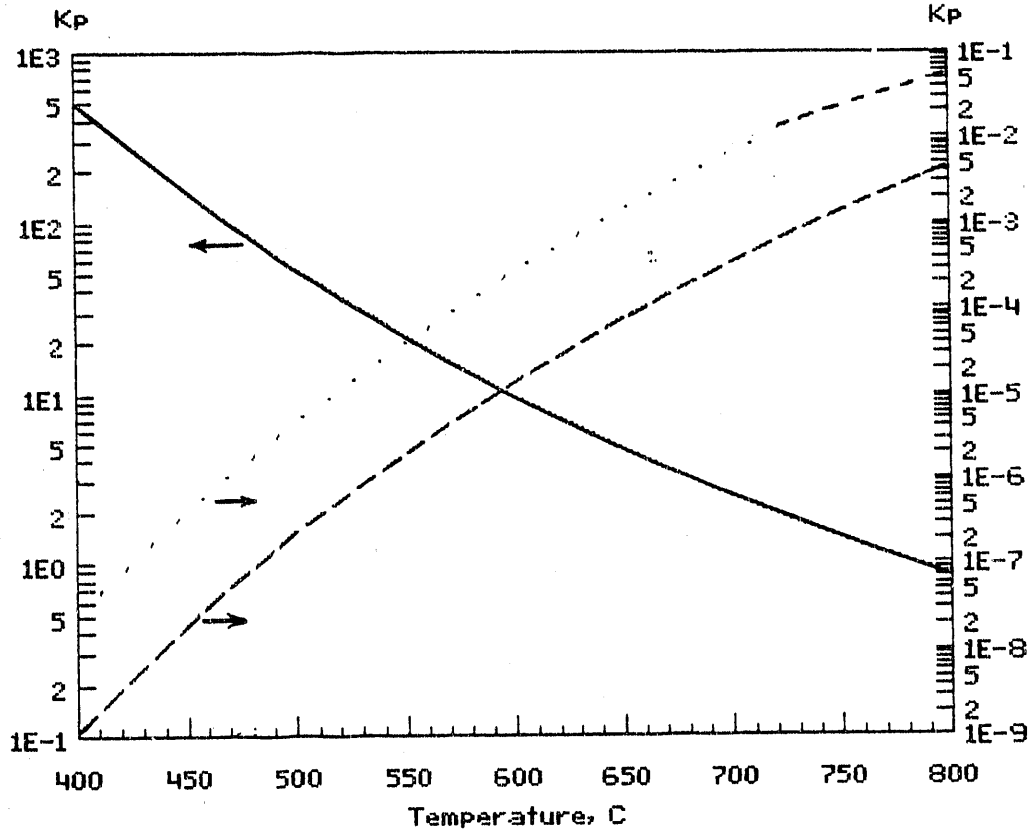
The equilibrium thermodynamics for the Zn-S-O system were calculated under the sorbent regeneration conditions of interest. The following chemical reactions were considered for the simplified system (which did not include the iron component).

$$3\ ZnSO_4 = ZnO \cdot 2ZnSO_4 + SO_3 \qquad (1)$$

$$1/2\ ZnO \cdot 2ZnSO_4 = 3/2\ ZnO + SO_3 \qquad (2)$$

$$SO_2 + 1/2\ O_2 = SO_3 \qquad (3)$$

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

$SO_2 + 1/2\ O_2 \rightleftharpoons SO_3$ ——————

$ZnSO_4\ (\alpha) \rightleftharpoons ZnO \cdot 2ZnSO_4 + SO_3$ . . . . .

$ZnSO_4\ (\beta) \rightleftharpoons ZnO \cdot 2ZnSO_4 + SO_3$ ----------

$ZnO \cdot 2ZnSO_4 \rightleftharpoons ZnO + SO_3$ — — — — —

Figure 14. Equilibrium constant, Kp, 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 $Fe_2(SO_4)_3$ 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		
	$ZnFe_2O_4$	Fe_2O_3	$ZnSO_4$
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 $ZnFe_2O_4$, whereas, in the top sample only the rim consisted of $ZnFe_2O_4$, Figure 1. The core of the top sample contains what appears to be the $ZnSO_4$ 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

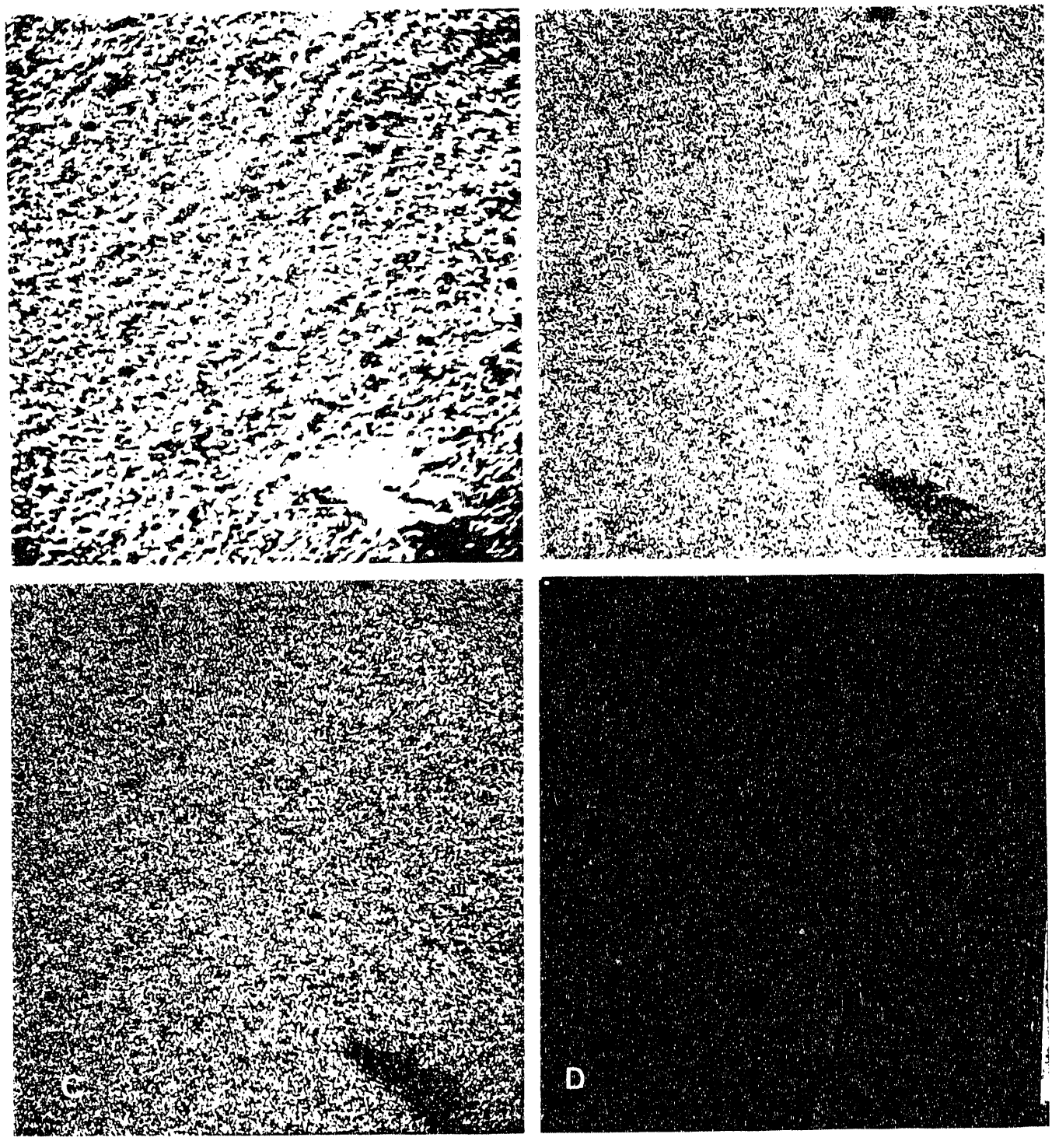


Figure 1. A-2-L-OX, Bottom-center.

A. Secondary electron image showing the fine-grained tecture 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 densite is largely attributed to background rather than sulfur.

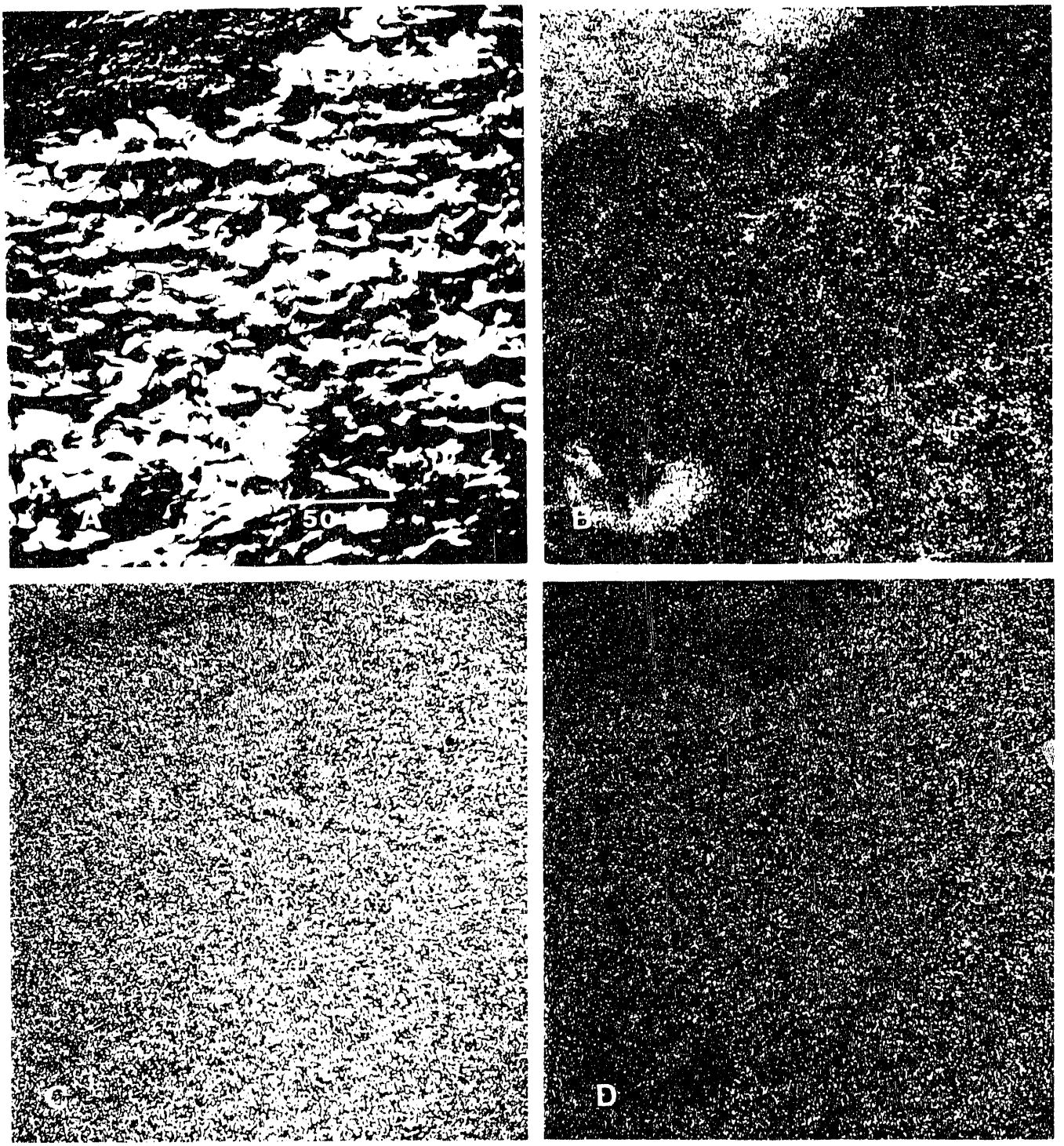


Figure 2. A-2-L-OX, Top-center.

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:

Number	Description
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 $2\theta = 3\text{-}64°$ 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:

AMAX MINERALS + ENERGY

PHASE & EST. AMOUNT*

Sample	Franklinite ($ZnFe_2O_4$)	Hematite (Fe_2O_3)	Sphalerite (β-ZnS)	Wurtzite (α-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

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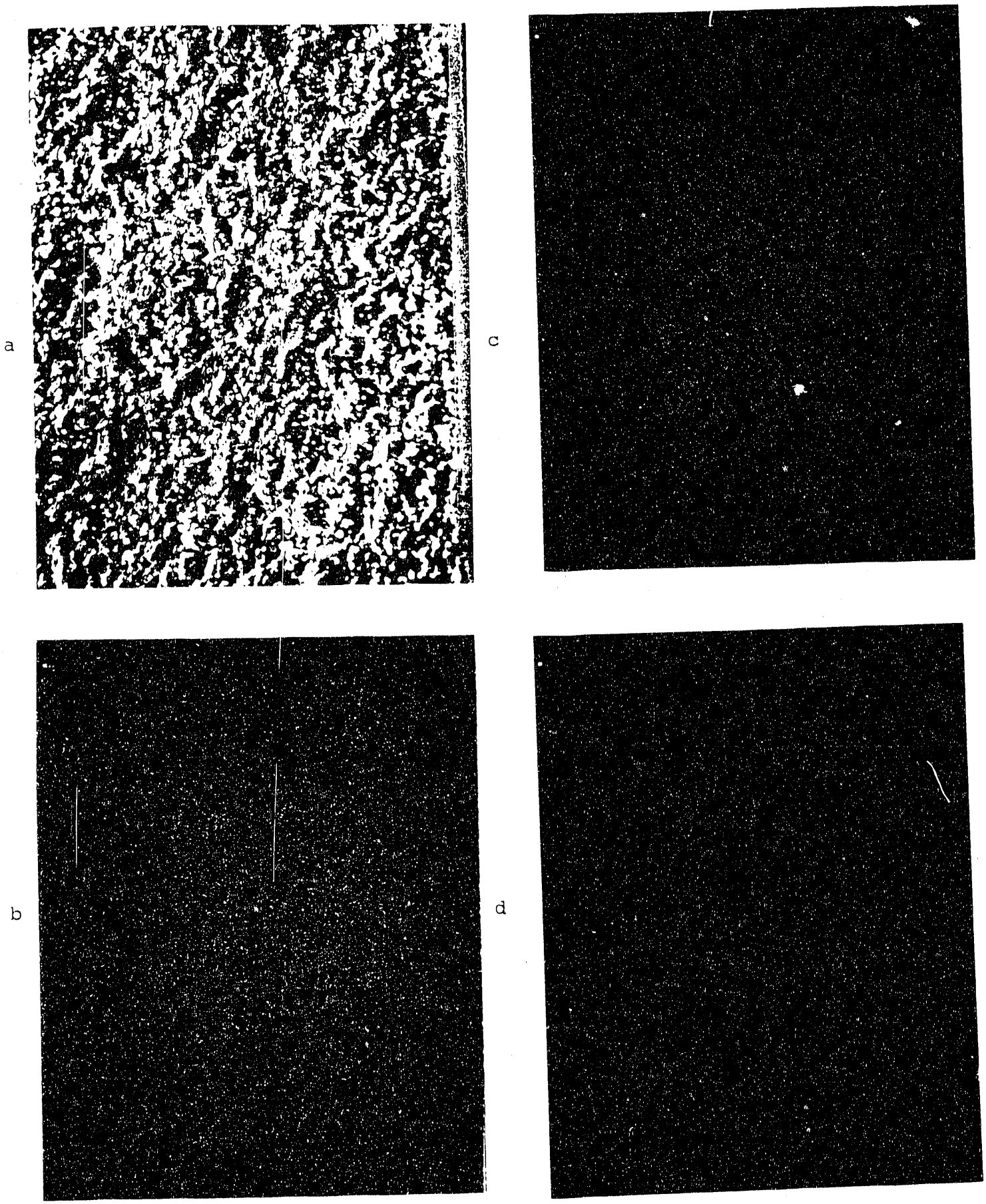

Figure 1. Sample B-3-L-OX (TOP), center, 1000X
a. Secondary electron image
b. Iron(Fe) x-ray map
c. Zinc(Zn) x-ray map
d. Sulfur(S) x-ray map

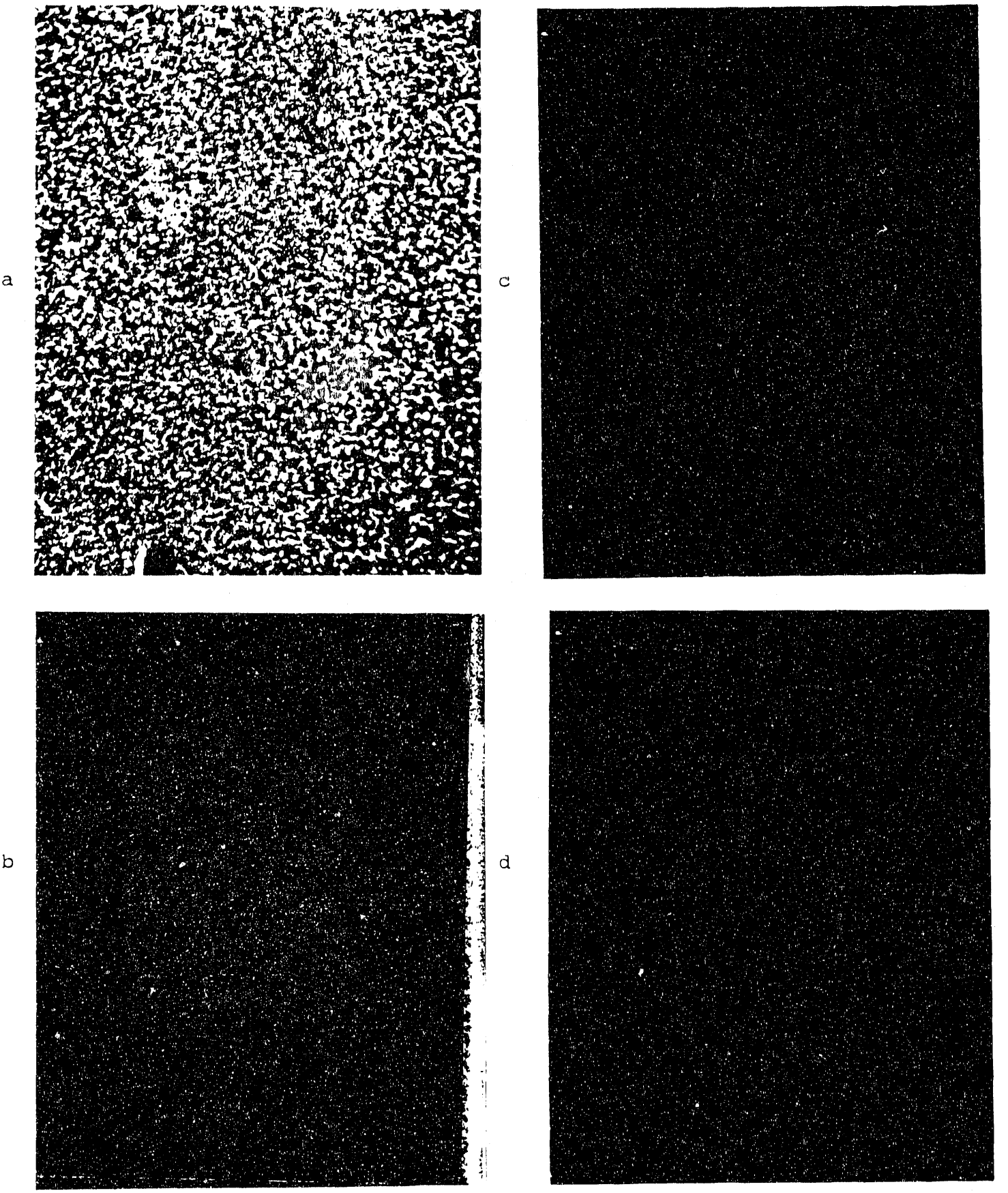

Figure 2. Sample B-3-L-OX(BOTTOM), center, 1000X
a. Secondary electron image c. Zinc(Zn) x-ray map
b. Iron(Fe) x-ray map d. Sulfur(S) x-ray map

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