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The smelting of lead drosses

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THE SMELTING OF LEAD DROSSES

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ABSTRACT

The constitution of the matte and bullion obtained by the smelting of lead drosses coming from the cooling of lead blast furnace bullion was investigated by metallographic, chemical, electron-microprobe, and X-ray means. At smelting temperatures (1200°C to 1300°C) two liquid phases are in equilibrium. A liquid lead phase with low concentrations of copper and sulfur, and a lighter liquid matte phase containing a high concentration of copper and sulfur with some dissolved lead. On cooling to room temperature the matte precipitates cuprous sulfide, a eutectic mixture of cuprous sulfide and lead sulfide with a deficiency of sulfur, and metallic lead rich in copper and sulfur. Simultaneously the lead bullion precipitates some metallic copper which reacts with the sulfur going out of solution to form particles of copper surrounded by $Cu_{2+x}S$ which remain entrapped in the metallic lead. The lead showed small amounts of copper in solution.

Samples of dross and matte from industrial practice were also studied by metallographic and X-ray diffraction methods.

The influences of time and temperature of smelting upon matte formation were studied. A holding time of two hours at 1200° - 1250°C was found to give the most fluid matte formation with a minimum of losses due to volatilization.

Silica sand was found to increase the fluidity of dross fusions when used up to 2% by weight of the total dross fused. Additions of soda ash above 2% by weight did not show any improvement in the matte or bullion formed. Increased amounts of soda additions resulted in a decrease of the lead content of the slags. A slight decrease of copper in the bullion was also noted.

Sulfur additions to dross fusions were investigated. The copper content of the bullion formed by dross smelting can be lowered from 13% Cu to about 4% Cu by the use of 2 to 3% by weight sulfur. Additions of sulfur over 3% were detrimental, because the matte formed contained a considerable amount of lead as lead sulfide (31% Pb). The effects of PbO and FeS_2 additions were also investigated. Although it was not possible to measure the efficiency of sulfur additions, it is believed that a considerable amount of sulfur was volatilized before having time to react.

ACKNOWLEDGEMENTS

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I. INTRODUCTION

The first metallic product obtained in extracting lead from its ore is called bullion. The base bullion from the blast furnace contains varying amounts of impurities, depending on both the processing conditions and the purity of the initial concentrate. These impurities may be held in the bullion in part by mechanical suspension, as well as being in solution in the liquid lead. This material is delivered to the drossing kettles, which are containers of 200 - 240 tons capacity heated by natural gas.

The temperature of the bullion coming from the blast furnace is approximately 1000°C. On cooling, the appearance of a dross is noted. A mechanical stirrer "dries" this dross, which eliminates a major portion of the entrapped liquid lead and mixes it with the caustic soda, granulated coke, and sand that have been previously added to the kettles. The removal of the dross constitutes the first step in the refining of the lead blast furnace bullion. The drosses, because of their contents of lead and copper sulfides, oxides of these materials, nickel sulfide, metallic copper, and a great amount of entrapped metallic lead, are valuable materials.

These values are recovered by smelting the dross in a reverberatory furnace, to produce a layer of slag, a layer of sulfides, called matte, and a lead bullion.

The bullion is separated and returned to the drossing kettles in batch type operations or by a continuous process.

The matte and the slag are granulated separately in water, or they are poured into slag molds, solidified, and mechanically separated.

The fluxes used for smelting are of such composition and quantity as to be capable of combining with all the silicates still entrapped in the dross, and form a slag of suitable fluidity and composition. When the dross contains iron compounds, generally siliceous materials are added to eliminate the iron which will go to the slag. The extent of this and similar additions, and their nature, differ with the kind of dross treated. Scrap iron could be added for the purpose of lowering the lead content of the slag and matte. This practice, however, is sometimes avoided because magnetite and spinels may form. Other fluxing agents often used are: borax, calcium carbonate, coke, soda ash, and sulfur.

A typical analysis of products in the reverberatory furnace is given in Table I.

The slag produced in this operation is usually recirculated into the blast furnace, for this reason specific limits for lead and copper contents have not been set. This is not the situation with the mattes, where it is desirable to have a high copper and low lead content in the matte, but at the same time maintaining a low copper content in the bullion.

TABLE I

TYPICAL ANALYSIS OF DROSS FURNACE PRODUCTS

Product	% Pb	% Cu	% Fe	% S	% As	% SiO_2	% Co	% Ni
Slag*	16-30	5- 8	11	-	-	30-40	1.1	0.2
Matte*	20-30	40-45	1	14-17	-	-	0.8	3.8
Bullion*	98	0.5	-	-	-	-	-	-
Slag**	38	6- 8	11	-	-	16	-	-
Matte**	32	47-50	1	16	-	-	-	-
Bullion**	98	0.08	-	0.23	-	-	-	-
Slag***	6	2- 3	25	-	1-2	15-25	-	-
Matte***	25	30-55	9	8-15	3-9	0.5-3	-	-
Bullion***	97	1- 3	-	-	0.5	-	-	-

* St. Joseph Lead Co., Herculaneum, Missouri.

** Broken Hill Associated Smelters, Port Pirie, Australia.

*** Silica Process.

Average compositions of 8 - 10% Pb; 45 - 60% Cu; 10 - 19% S would comprise good mattes.

Control of the smelting of drosses is important in this step of lead refining as a closed circuit of high impurity levels is generally the cause of high refinery costs.

The purpose of this investigation was to study the phases present in the matte and the bullion produced when dross is smelted in a reverberatory furnace, and the effects of original composition, the influence of addition reagents, holding time and temperature on the final chemical composition.

II. REVIEW OF THE LITERATURE

Some of the earliest work on the smelting of lead drosses was done by Fulton and Goodner[1] in 1908, which showed the mattes to be a conglomerate of sulfides with metallic lead and copper as inclusions. Meisner[2] studied the system Cu - Pb - S in 1921; Dice, Oldright and Brighton[3] established the alkemade triangles by slow cooling synthetic mixtures of lead, copper and sulfur from $1300^{\circ}C$ to room temperature and studied the resulting microstructures. These results are shown in Figure 1. The three phase regions present were found to contain lead, copper, copper sulfide (Cu_2S); lead, lead sulfide (PbS), copper sulfide (Cu_2S); and lead sulfide (PbS), copper sulfide (Cu_2S), and sulfur.

Krysko[4] investigated the metallic phases entrapped in the dross by hot pressing or centrifuging drosses at 400° C. An X-ray diffraction investigation of the products showed the matte phase to be composed of mainly PbS, Cu_2S, Sb_2S_3, Cu_3As, Cu_2Sb as positively identified phases together with lead and copper inclusions.

Tables II and III show Krysko's results. The compounds marked positive were compounds which were clearly identified; the compounds marked negative had diffraction lines that could not be determined with the required accuracy and clarity to justify a conclusion.
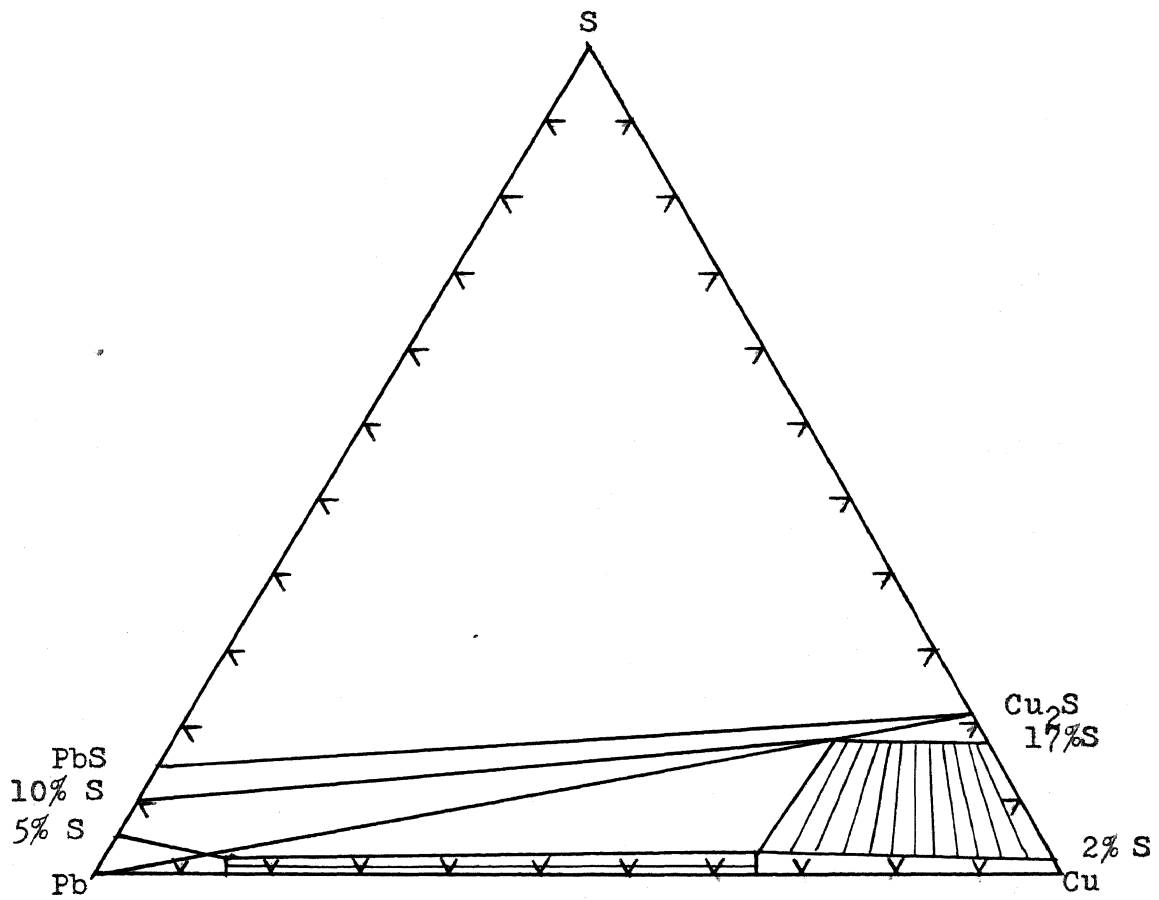
Figure 1. Lead - Copper - Sulfur system. (After Meisner)

TABLE II

X-RAY DIFFRACTION ANALYSIS OF COPPER CONTAINING LEAD DROSS*

		d Spacing Å			Source
Metals:					
Pb	(+)	2.86	2.48	1.49	ASTM
		(100)	(50)	(32)	I
		2.83	2.45	1.49	Observed
Cu	(+)	2.09	1.81	1.28	ASTM
		(100)	(46)	(20)	I
		2.08	1.81	1.23	Observed
Oxides:					
PbO Yellow	(−)	3.07	2.95	2.74	ASTM
PbO Red	(−)	3.12	2.81	1.87	ASTM
Pb_2O_3 (Probable)		3.18	1.95	1.66	ASTM
		(100)	(100)	(100)	I
		3.09-3.31	1.95	1.66	Observed
Pb_3O_4		3.38	2.90	2.79	ASTM
		(100)	(98)	(45)	I
		3.38	2.93	2.79	Observed
Sulfides:					
PbS (Probable)		2.97	3.43	2.10	ASTM
		(100)	(84)	(57)	I
		2.93-3.02	3.38-3.50	2.08-2.20	Observed
Cu_2S (Probable)		2.03	1.73	2.87	ASTM
		(100)	(60)	(50)	I
		2.03	1.73	2.83-2.93	Observed
Sb_2S_3 (Probable)		2.76	3.05	3.56	ASTM
		(100)	(95)	(72)	I
		2.61-2.79	3.02-3.09	3.50	Observed
SnS (Probable)		2.83	3.42	3.24	ASTM
		(100)	(40)	(40)	I
		2.83	3.31-3.50	3.09-3.3	Observed
Intermetallic Compounds:					
Cu_3As	(+)	2.05	1.89	1.97	ASTM
		(100)	(70)	(50)	I
		2.04	1.90	1.99	Observed
Cu_2Sb	(+)	2.07	2.00	1.43	ASTM
		(100)	(100)	(100)	I
		2.08	1.98	1.43	Observed
Cu_3Sn (Probable)		2.08	2.16	2.25	ASTM
		(100)	(40)	(20)	I
		2.08	2.08-2.20	2.20-2.33	Observed

* After W. Krysko
(+) Phases clearly identified; (−) Phases identified without the required accuracy to justify a conclusion; (Probable) Phases that could be present but were not identified.

TABLE III

X-RAY DIFFRACTION ANALYSIS OF LEAD DROSS AFTER SULFUR TREATMENT*

		d Spacing $\overset{o}{A}$			Source
Metals:					
Pb	(+)	2.86	2.48	1.49	ASTM
		(100)	(50)	(32)	I
		2.86	2.49	1.48	Observed
Cu	(+)	2.09	1.81	1.28	ASTM
		(100)	(46)	(20)	I
		2.08	1.82	1.28	Observed
Oxides:					
PbO Yellow	(−)	3.07	2.95	2.74	ASTM
PbO Red	(−)	3.12	2.81	1.87	ASTM
Pb_2O_3	(+)	3.18	1.95	1.66	ASTM
		(100)	(100)	(100)	I
		3.07-3.27	1.94	1.66	Observed
Pb_3O_4	(+)	3.38	2.90	2.79	ASTM
		(100)	(48)	(45)	I
		3.39	2.90	2.79	Observed
Sulfides:					
PbS	(+)	2.97	3.43	2.10	ASTM
		(100)	(84)	(57)	I
		2.95	3.44	2.08	Observed
Cu_2S	(+)	2.03	1.73	2.87	ASTM
		(100)	(60)	(50)	I
		2.03	1.73	2.87	Observed
SnS (Probable)		2.83	3.42	3.24	ASTM
		(100)	(40)	(40)	I
		2.83	3.42	3.07-3.27	Observed
Sb_2S_3	(+)	2.76	3.05	3.56	ASTM
		(100)	(95)	(72)	I
		2.76	3.07	3.56	Observed
Intermetallic Compounds:					
Cu_3As	(+)	2.05	1.89	1.97	ASTM
		(100)	(70)	(50)	I
		2.04	1.88	1.97	Observed
Cu_2Sb	(+)	2.07	2.00	1.43	ASTM
		(100)	(100)	(100)	I
		2.07	1.99	1.43	Observed
Cu_3Sn (Probable)		2.08	2.16	1.24	ASTM
		(100)	(40)	(40)	I
		2.08	2.09-2.19	1.25	Observed
Cu_6As (Probable)		1.99	2.11	2.25	ASTM
		(100)	(40)	(20)	I
		1.99	2.08-2.20	2.25	Observed

*After W. Krysko
(+) Phases clearly identified; (−) Phases identified without the required accuracy to justify a conclusion; (Probable) Phases that could be present but were not identified.

Davey[5] states that the precipitates in the drossing operation comprise solid crystals of copper, cuprous sulfide (Cu_2S), Cu_3As, Cu_3Sn, SnS, and PbS, constituting at higher temperatures, mixtures of complex compositions.

No definite statement has been made on the phases existing in the bullion after cooling from high temperatures. It is accepted that the lead contains copper, antimony, tin, arsenic, zinc, silver, sulfur, oxygen; some in elemental form while others are present as compounds.

Metallic copper is fairly soluble in lead at high temperatures. Kleppa and Weil[6] determined a maximum solubility of 9.48% by weight copper in lead at temperature of $1000^{\circ}C$.

The phase diagram of Cu-Pb alloys has been extensively studied by several authors and it is shown in Figure 2, plotted from the values given by Hansen[7]. (Compositions are given in weight per cent, as will be the case in the remainder of this study.) Between 36% and 87% lead, Pb-Cu alloys separate into two liquid layers.

The critical temperature of liquation has been an object of dispute in earlier studies. Bernemann and Wagenmann[8] gave the critical temperature as $1500^{\circ}C$. Later, more reliable studies by Johnen and Wagner[9] gave the value of $990^{\circ}C$ at about 63% Pb.
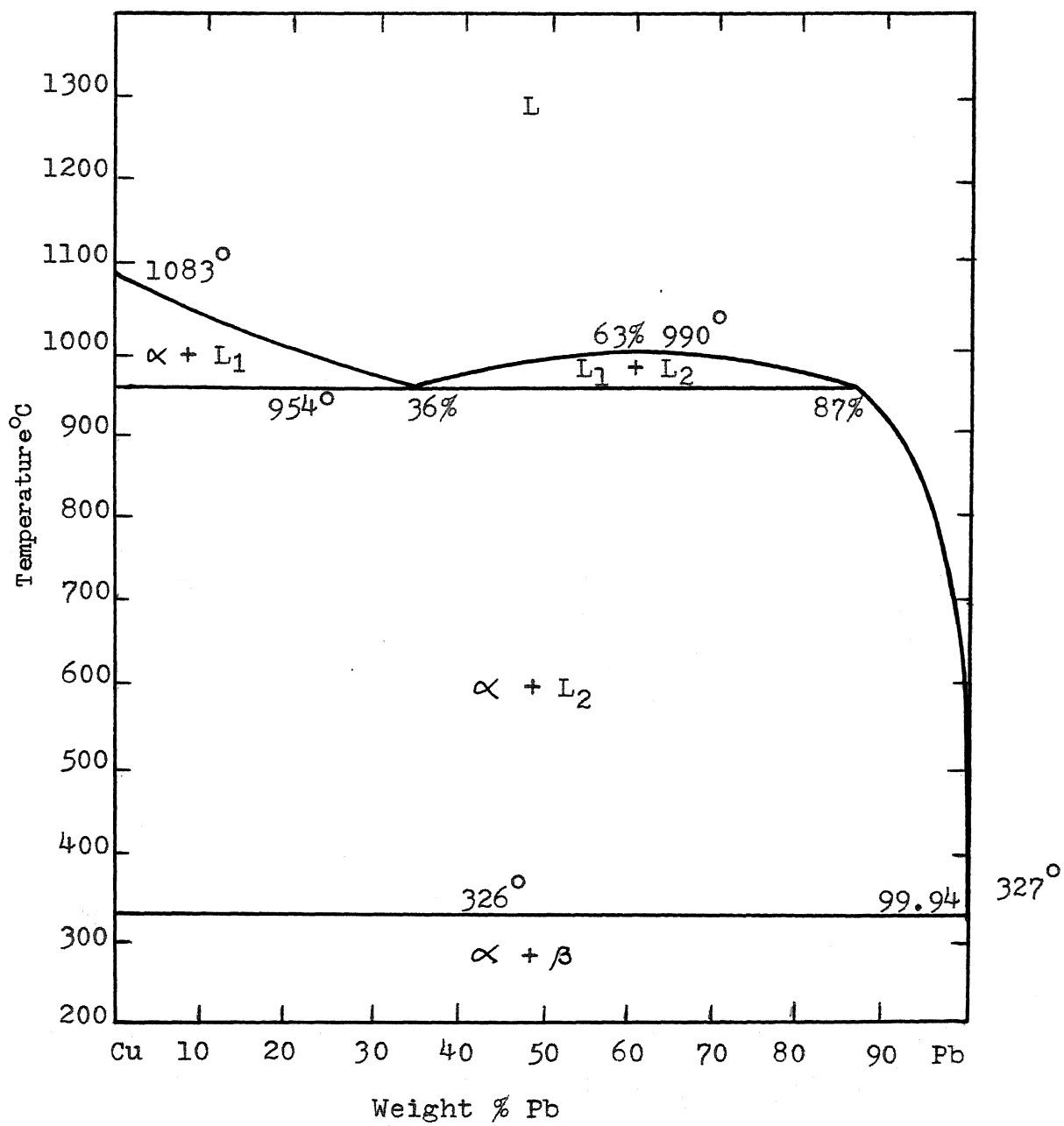
Figure 2. Copper - Lead Phase Diagram
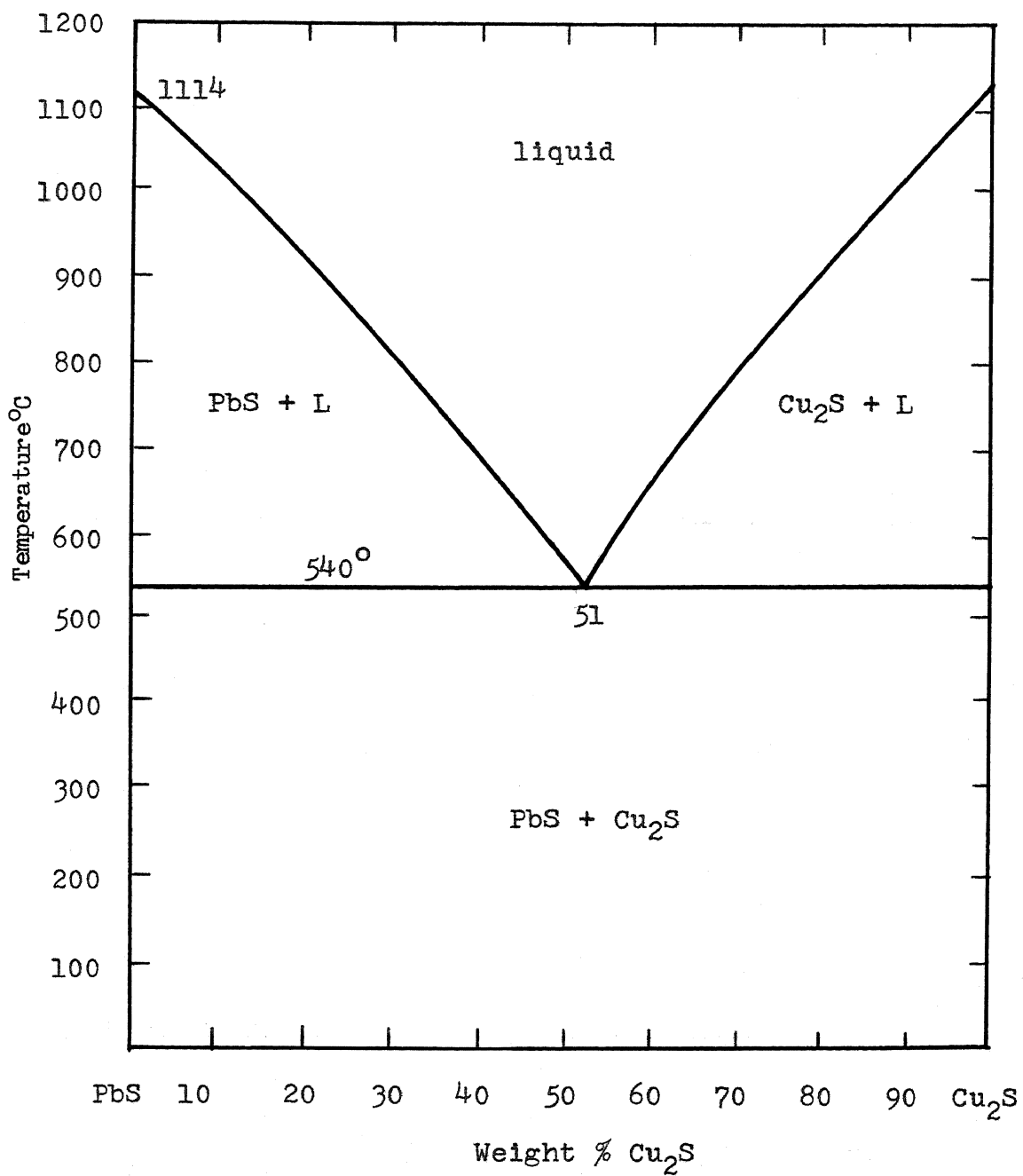
Figure 3. PbS – Cu$_2$S Constitution Diagram
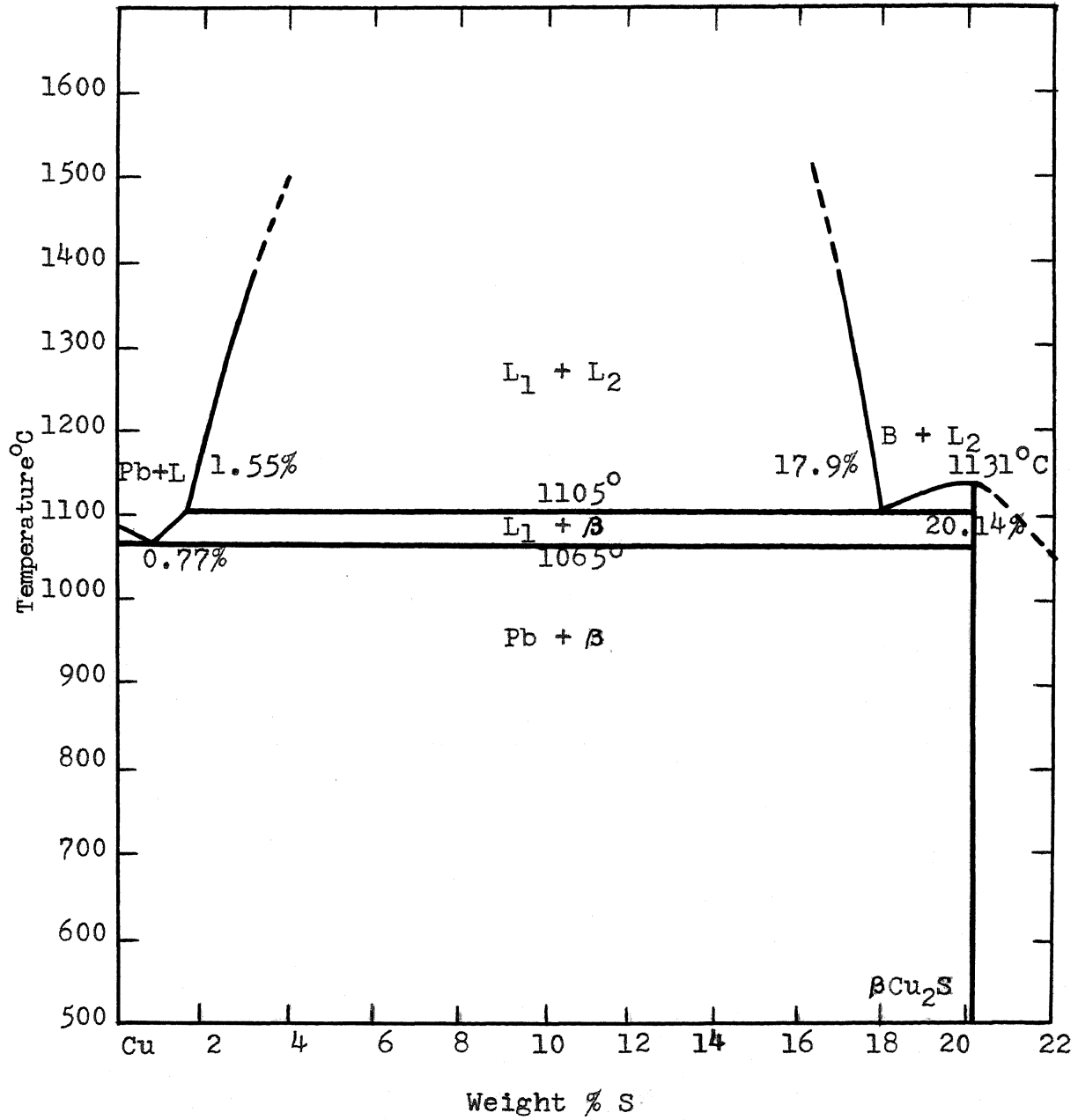
Figure 4. Cu - Cu_2S Constitution Diagram.
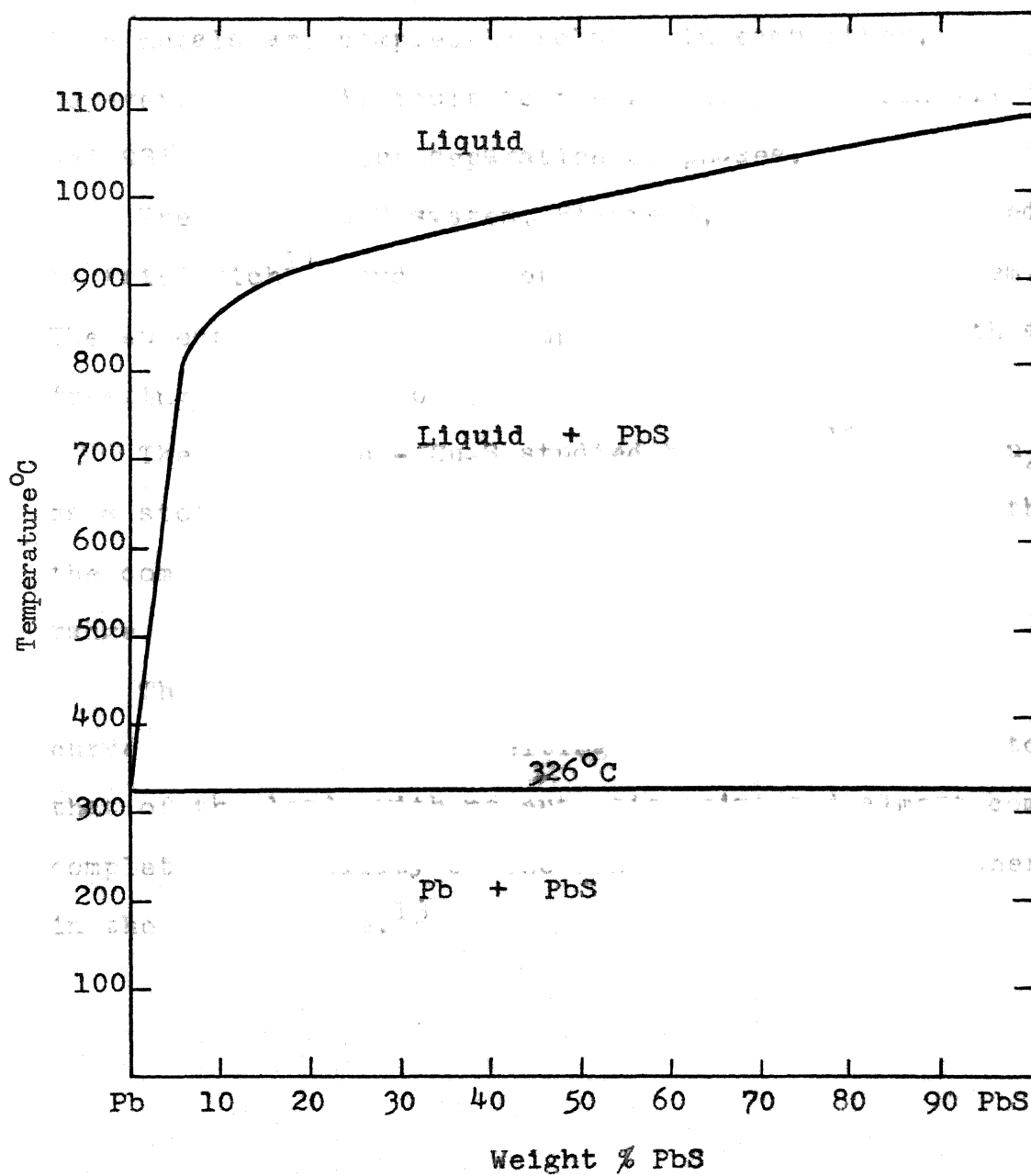
Figure 5.   Pb - PbS Phase Diagram.

The studies of Jacobs, Maes, and Strycker[10] show $980^{\circ}C$ as the critical temperature of this system.

According to the Pb - Cu phase diagram, at $1200^{\circ}C$ both metals are completely soluble in each other, however, it is difficult to freeze alloys between 41% and 93% lead without separation of phases.

The PbS - Cu_2S system, Figure 3, has been reported by Friederich[11], and it shows a simple eutectic system. The eutectic occurs at a composition of 51% Cu_2S with a freezing point at $540^{\circ}C$.

The binary Cu - Cu_2S studied by Rhines[12] shows Cu_2S as a stoichiometric compound, it is, however, likely that the compound can exist over quite a large composition range, as it is shown in Figure 4.

The binary Pb - PbS, Figure 5, shows a liquidus curve dropping from the melting point of the sulfide to that of the lead, with no eutectic point and almost com-complete insolubility of the constituents in each other in the solid state.[13]

III. EXPERIMENTAL

A. Statement of the Problem

This study included two types of experimental investigations. The object of the first was to determine the constitution of the reverberatory products (slag, matte, and bullion) upon lead dross smelting, by metallographic, chemical, electron-microprobe, and X-ray means. Both industrial melts provided by the St. Joseph Lead Company at Herculaneum, Missouri and synthetic melts made in the laboratory were used.

The second part involved determining the effects of various parameters on the resultant composition of the matte and bullion. Temperature, time, and additions to the lead dross charged to the furnace were the main parameters studied.

B. Determination of the Constitution of the Dross Furnace Products

Two types of matte samples were obtained from the smelter at Herculaneum, Missouri.

1. One product, called "good matte", had the following composition:

Pb 17.1%; Cu 46.4%; Ni 0.6%; Co 0.3%; S 14%.

This matte satisfies the grade requirements for commercial sale or further copper extraction. (Cu/Pb ratios of 2.0 or more are considered satisfactory.)

2. One product, called "bad matte", had the following composition:

Pb 42.3%; Cu 35.1%; Ni 5%; Co 0.3%; S 15%.

At the beginning it was observed that both materials contained some magnetic component, therefore, the samples were ground to -100 mesh and separated magnetically. The magnetic portion was composed mainly of spinels, predominantly Fe_3O_4. The lines obtained on the diffraction pattern is shown in Appendix 1.

The -100 mesh non-magnetic material was sized on a 170 mesh screen. The +170 mesh portion was fractioned at different intensities of current in a Frantz Isodynamic Separator to try to isolate the copper, iron, and lead compounds in order to obtain simpler diffraction patterns than the ones obtained with the whole material.

The X-ray diffraction patterns obtained using the material separated at intensities of 0.2 and 0.35 amperes showed no appreciable difference. The lines of the pattern accounted for cuprous sulfide (Cu_2S), metallic lead, and a probable lead sulfide (PbS) phase. The portion suceptible at 1.5 amperes contained the same material found in the portion suceptible at 0.35 amperes, but the intensity of the diffraction lines of metallic lead and lead sulfide were greater. (Appendix 2).

The phases identified in the matte at room temperature by X-ray diffraction are summarized in Table IV.

TABLE IV

PHASES IDENTIFIED IN THE MATTE AT ROOM
TEMPERATURE BY X-RAY DIFFRACTION

Compound	d Spacings $\overset{o}{A}$			Source
	2.85	2.47	1.49	ASTM
Lead	(100)	(50)	(32)	I
	2.85	2.47	1.49	Observed
	2.09	1.81	1.28	ASTM
Copper	(100)	(46)	(20)	I
	2.08	1.79	1.27	Observed
	1.96	1.86	2.72	Powder Fusion
Cu_2S	1.99	1.89	2.73	ASTM
	(100)	(100)	(50)	I
	1.98	1.88	2.73	Observed
	2.94	3.40	2.08	Powder Fusion
PbS	2.97	3.43	2.09	ASTM
	(100)	(84)	(57)	I
	2.95	3.40	2.09	Observed
	2.53	1.48	1.61	ASTM
Fe_3O_4	(100)	(80)	(64)	I
	2.51	1.48	1.61	Observed

In order to obtain a microstructure of the matte, the granulated sample containing the high lead content ("bad matte") was remelted in a graphite crucible at 1200°C. As a result an appreciable amount of metallic lead was separated (50% by weight). Microscopic examination of the products show a matte containing primary crystals of copper sulfide, some primary crystals of lead sulfide and a $PbS-Cu_2S$ eutectic as shown in Figure 6. Metallic lead inclusions were most numerous in the vicinity of the matte-bullion boundary. (See Figure 7.)

The bullion obtained by remelting the high lead matte contained dendrites of free copper and cuprous sulfide in a lead matrix as shown in Figure 8.

To identify more definitely the compounds resulting from the smelting of lead drosses, samples of this material were obtained from the first refining kettle, (prior to the addition of fluxes) in order to reproduce by fusion the smelting products obtained in the reverberatory furnace, namely slag, matte and bullion.

The dross sample used as starting material for the fusions had the following chemical composition:

Pb	66.0%	Fe	2.0%	Zn	3.0%
Cu	17.0%	S	4.5%	Insoluble	0.5%
Ni	3.0%	Co	0.3%		
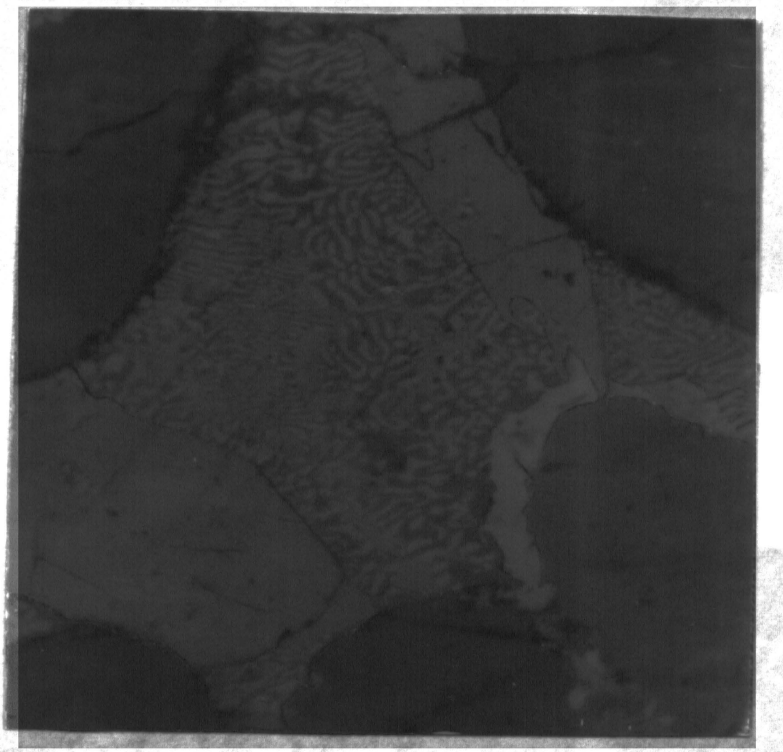
Figure 6.

Refused matte. (400X).

Dark: Cu_2S

Light: PbS

Eutectic: $PbS - Cu_2S$
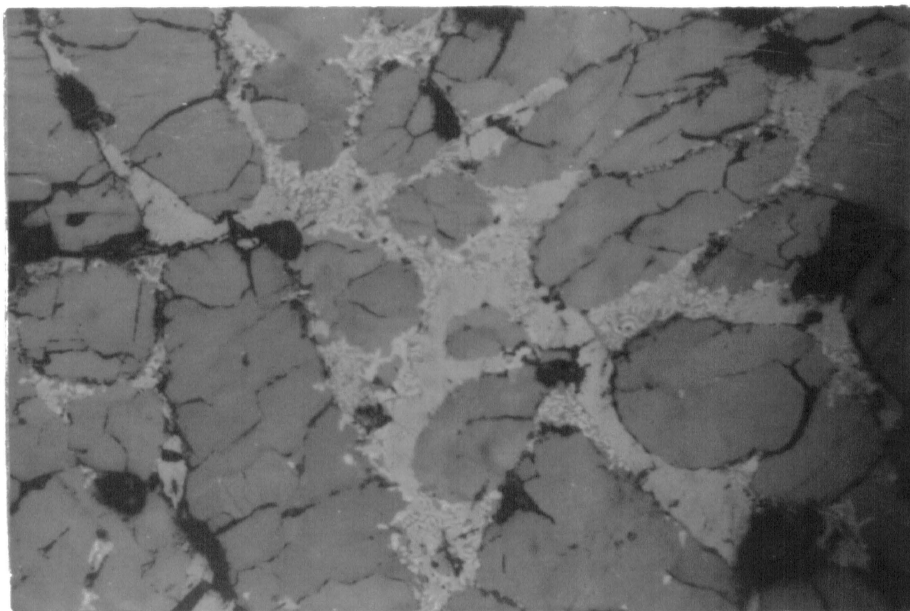
Figure 7

Refused matte (150 X).
Gray: Cu_2S; light: PbS; eutectic: $PbS-Cu_2S$;
dark: metallic lead inclusions.
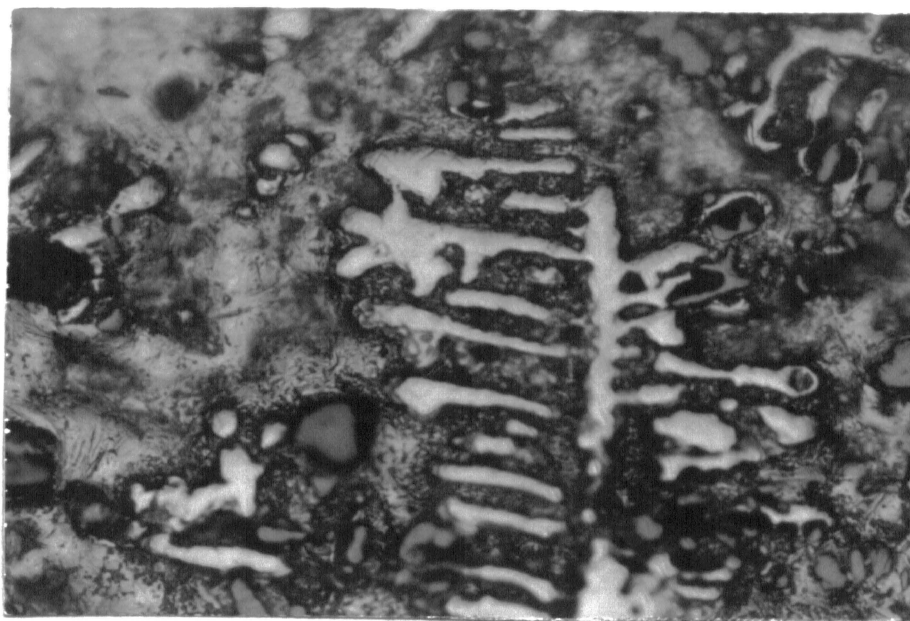
Figure 8

Lead bullion (150 X).
Copper dendrites in a lead matrix.
Gray particles are Cu_2S.

The lead content of this sample was due mainly to entrapped lead (50 to 60%), and lead oxides formed during the drossing operation.

The sulfur content is enough to tie up all the copper and some lead, forming copper and lead sulfides. Slag is also entrapped in the dross and contains most of the iron, zinc and cobalt.

The original ore treated by the smelter, from which the samples for this study were obtained, do not contain appreciable amounts of arsenic, therefore, no compounds of arsenic are present in the dross to make any appreciable quantities of speiss, frequently noticed in similar investigations. However, by careful control of the tapping cycles in the dross furnace it is possible to obtain an accumulation of a high nickel speiss assaying 20% Ni; 9% As, 25% Pb, 25% Cu.

The sample of dross obtained from the kettles was ground and screened. The -200 mesh product was X-rayed with the results shown in Table V.

With this dross as starting material, fusions were made in fireclay crucibles at 1200°C, and fast cooled in air after heating for two hours. Four layers were obtained after cooling: slag, matte, intermediate layer, and the metallic bullion.

The matte was about 20% to 25% by weight and the bullion 60 to 65% by weight of the charged dross.

TABLE V

<u>PHASES IDENTIFIED IN THE LEAD DROSS AT</u>
<u>ROOM TEMPERATURE BY X-RAY DIFFRACTION</u>

Compound	d Spacings Å			Source
	2.85	2.47	1.49	ASTM
Lead	(100)	(50)	(32)	I
	2.85	2.45	1.49	Observed
PbO	3.11	2.80	1.68	ASTM
(Litharge	(100)	(40)	(40)	I
tetragonal)	3.10	2.79	1.68	Observed
PbO	3.10	1.86	1.67	ASTM
(Lithargita	(100)	(80)	(80)	I
tetragonal)	3.10	1.86	1.68	Observed
	1.99	1.89	2.73	ASTM
Cu_2S	(100)	(100)	(50)	I
	1.97	1.86	2.79	Observed

The intermediate layer was included with the bullion due to the difficulty of separation. Samples of these products analyzed:

Product	% Weight	% Pb	% Cu	% Fe	% S	% Insoluble
Slag	15	35	3	5		40
Matte	20	17	63	0.3	15	
Bullion	65	86	13	0.1	0.1	

The matte, intermediate layer, and bullion were analyzed microscopically, by X-ray diffraction, and microprobe analysis.

Figures 9 and 10 show the matte phase. Gray bluish particles are primary Cu_2S surrounded by a light gray eutectic composed of Cu_2S and PbS, light grains are lead sulfide crystals PbS. Rounded globular inclusions are metallic lead and they are more numerous in the lower portion of the matte layer. Light pink crystals of an undetermined iron compound are also occasionally present.

The interface between matte and bullion is shown in Figure 11. Phases present are mainly metallic lead with a great concentration of Cu_2S and PbS. In this zone the lead is probably saturated with sulfur, forming PbS, which is believed to precipitate along with Cu_2S while the bullion is cooling.

The lead bullion is shown in Figure 12 and the presence of gray particles of Cu_2S are in close contact with light reddish particles of metallic copper. The background is metallic lead.
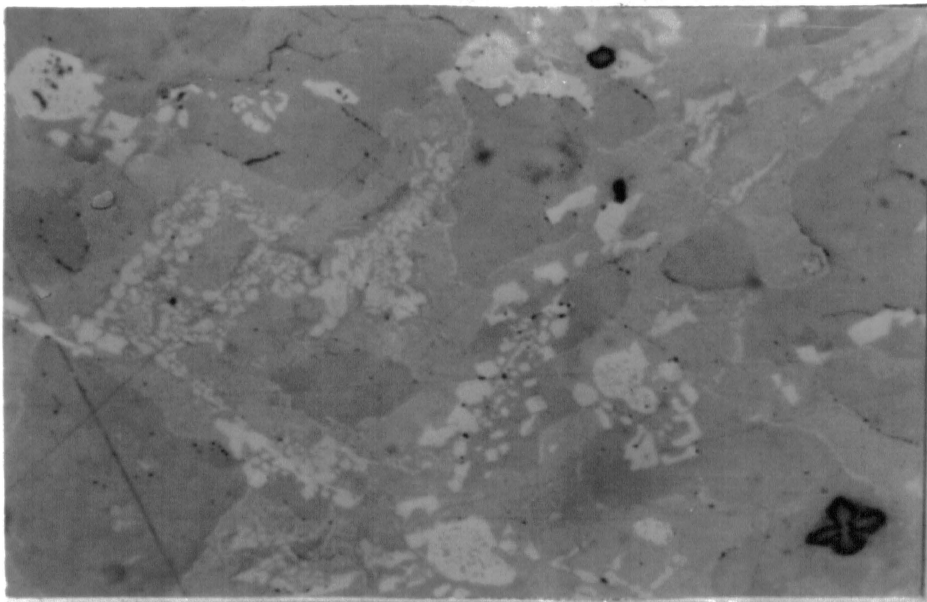
Figure 9

Upper portion of matte (150 X).
Gray dark grains are Cu_2S, surrounded by
eutectic PbS-Cu_2S; light grains are PbS.
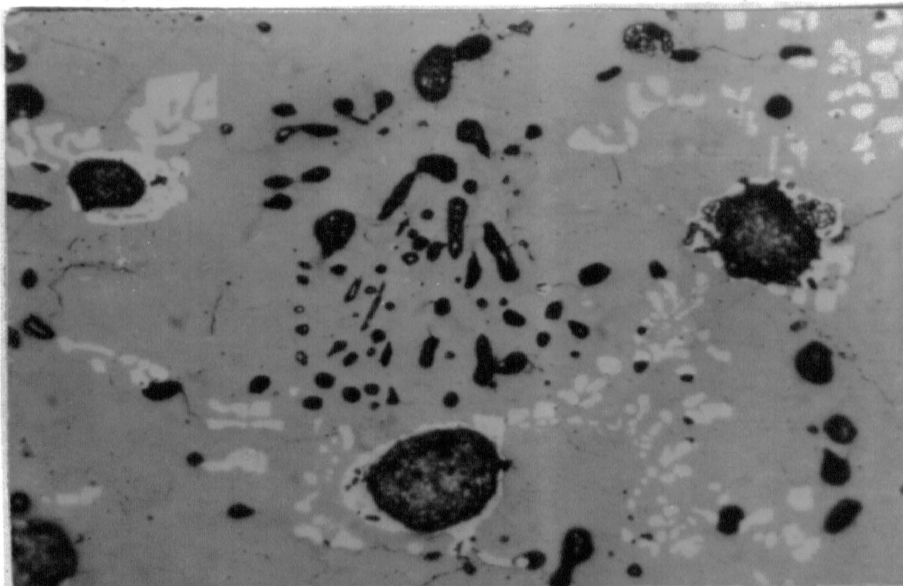
Figure 10
Lower portion of matte (150 X).
This portion shows a great number of
metallic inclusions surrounded by PbS
crystals; gray background is Cu_2S.
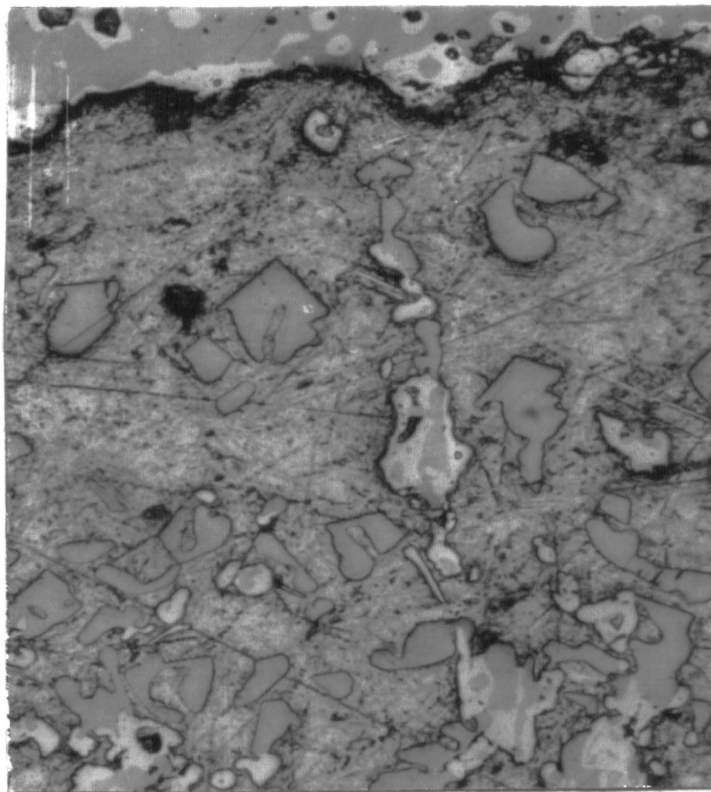
Figure 11.
Interface between matte and lead bullion.
(150 X). Mainly metallic lead. Matte
inclusions are gray Cu_2S and light PbS.
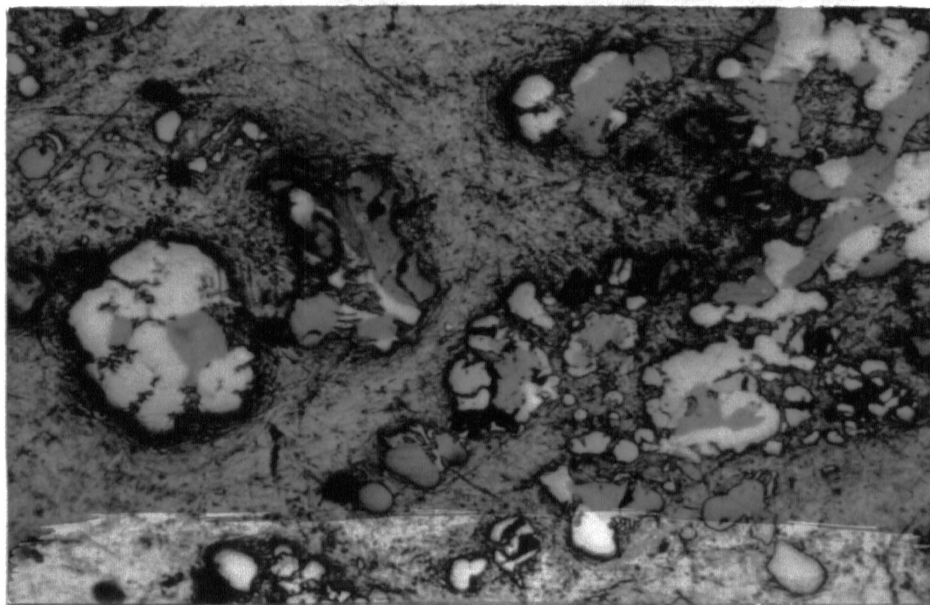
Figure 12.
Lead bullion (150 X).
Gray particles are Cu_2S; light (reddish)
particles are metallic copper; background
is metallic lead.
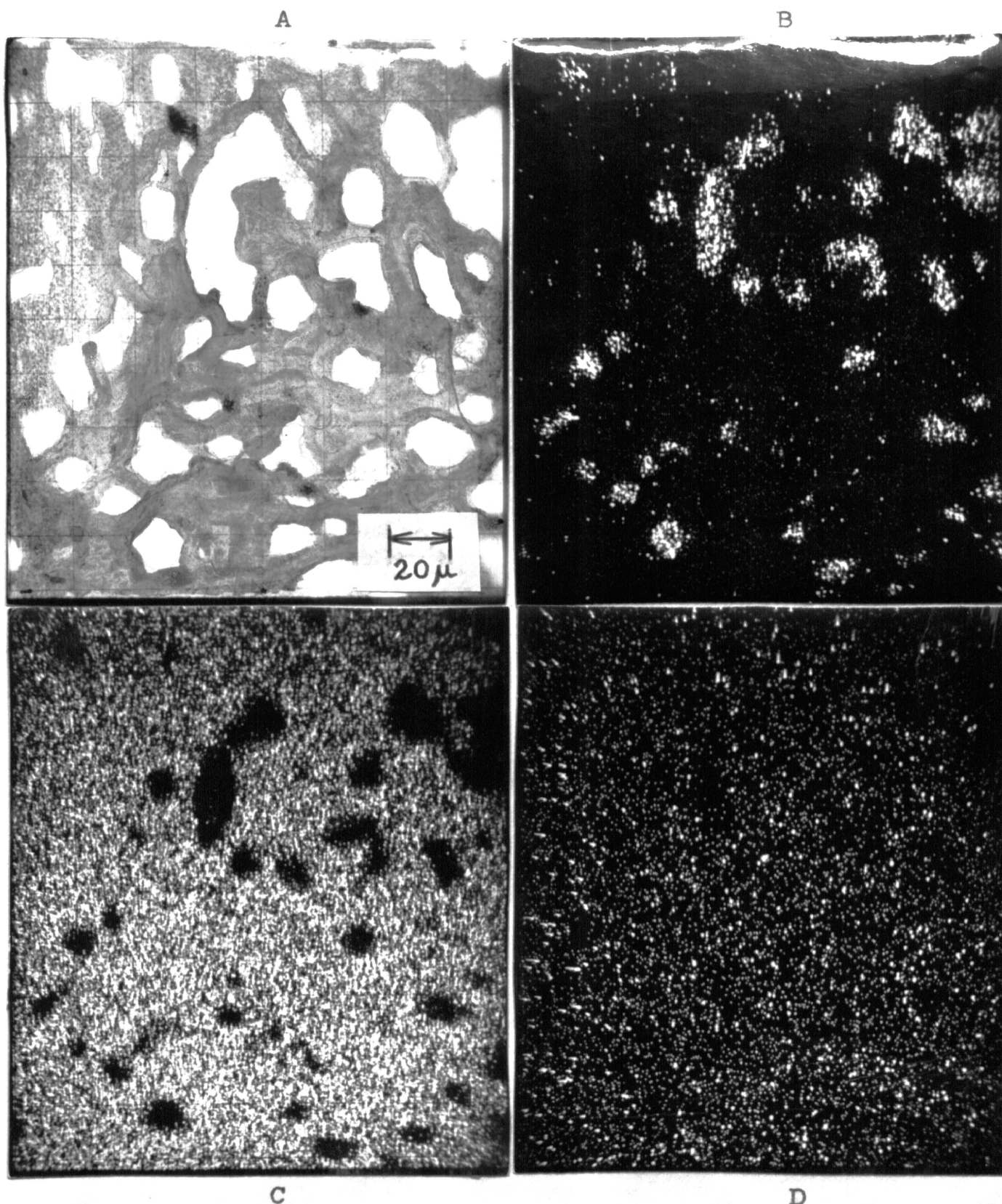
Figure 13. Back scattered electron and X-ray images
showing element distribution in the matte layer.
(A) Back scattered electron image; (B) Pb X-ray image;
(C) Cu X-ray image; (D) S X-ray image.
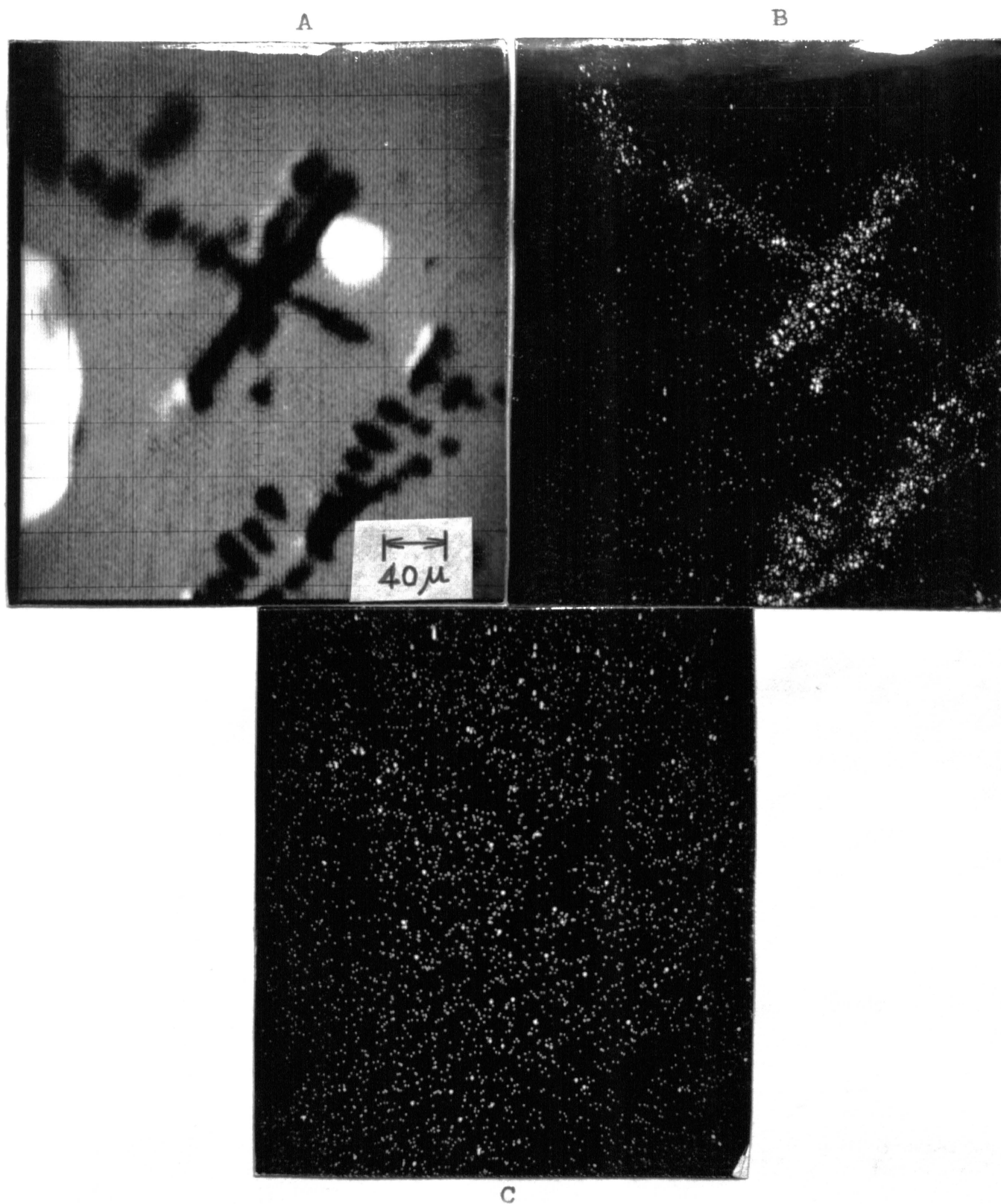
Figure 14. Back scattered electron and X-ray images of
dendritic iron compounds in the matte. (A) Back
scattered electron image; (B) Fe X-ray image; (C) S
X-ray image.
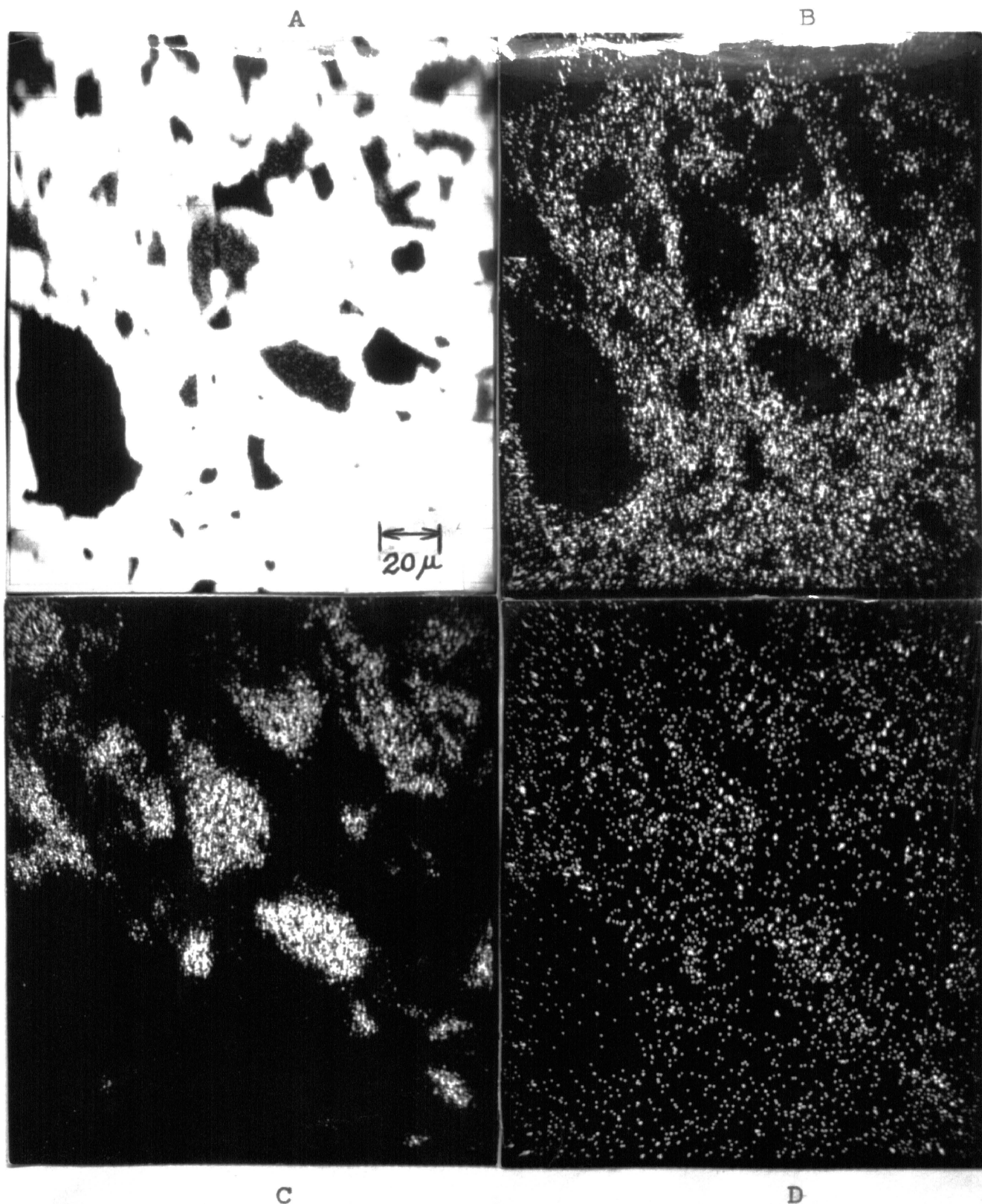
Figure 15. Back scattered electron and X-ray images showing element distribution in the interface matte-bullion. (A) Back scattered electron image; (B) Pb X-ray image; (C) Cu X-ray image; (D) S X-ray image; (E) Si X-ray image.
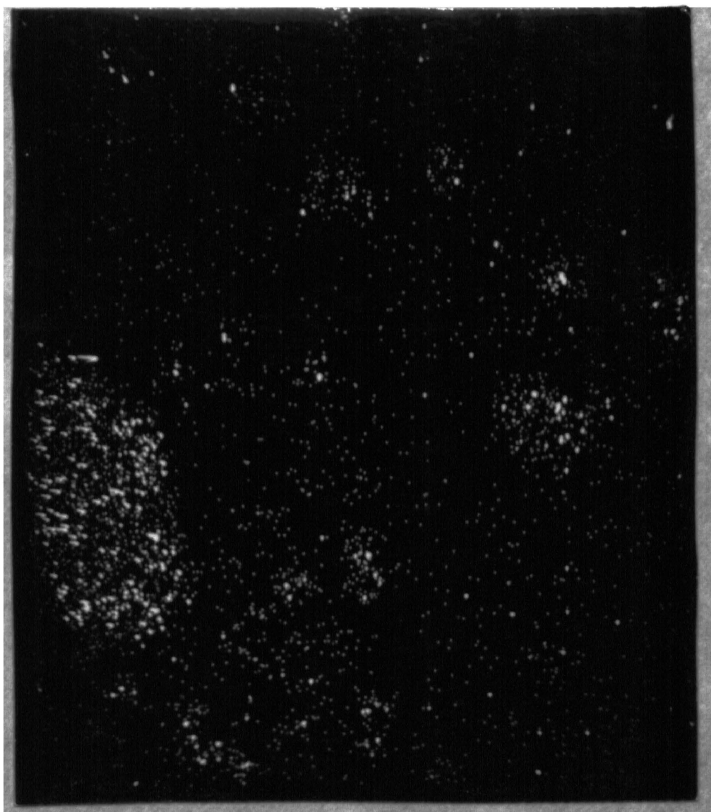
Figure 15. (Continuation) (E) Si X-ray image.
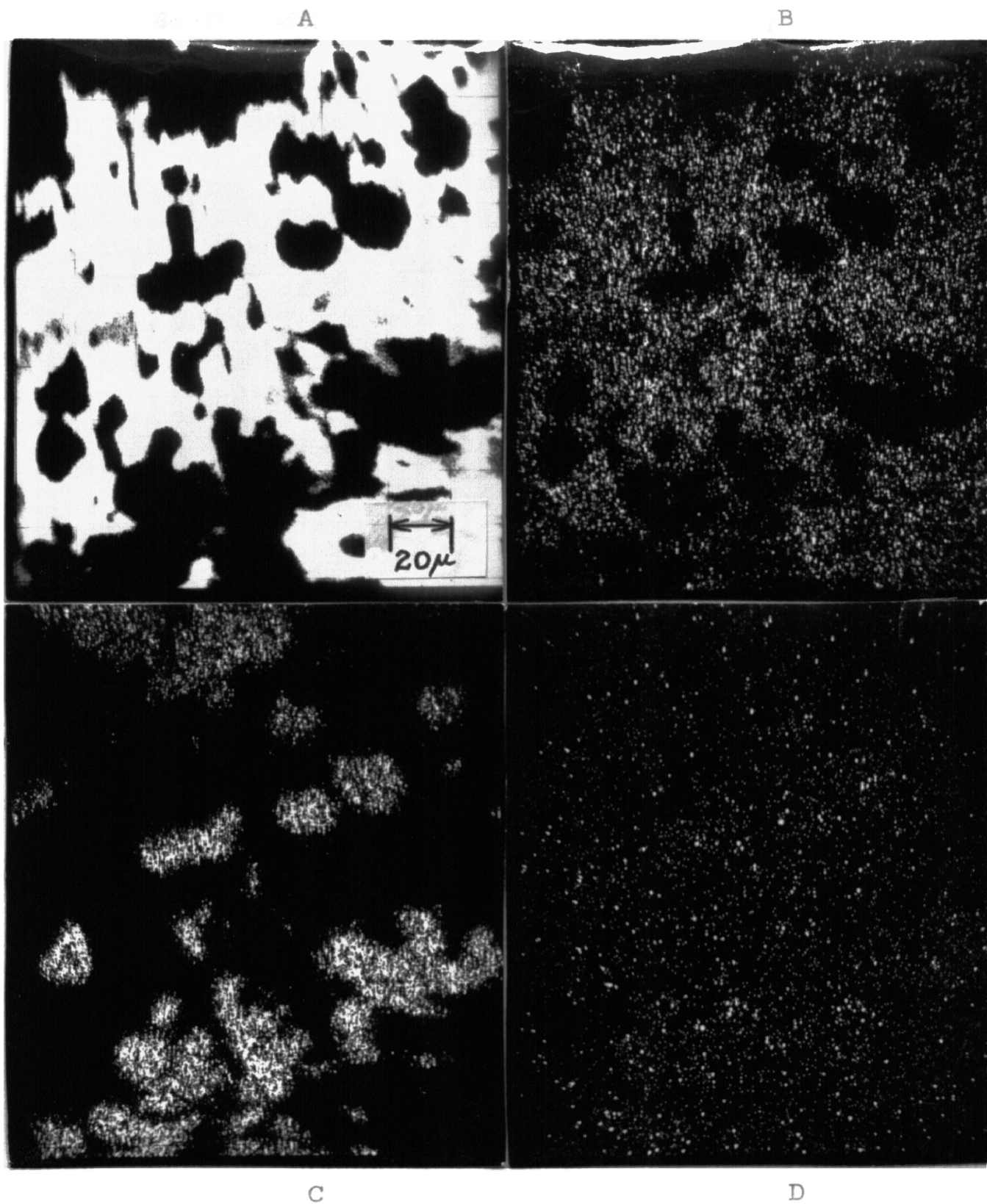
Figure 16. Back scattered electron and X-ray images
showing element distribution in the lead bullion.
(A) Back scattered electron image; (B) Pb X-ray image;
(C) Cu X-ray image; (D) S X-ray image.
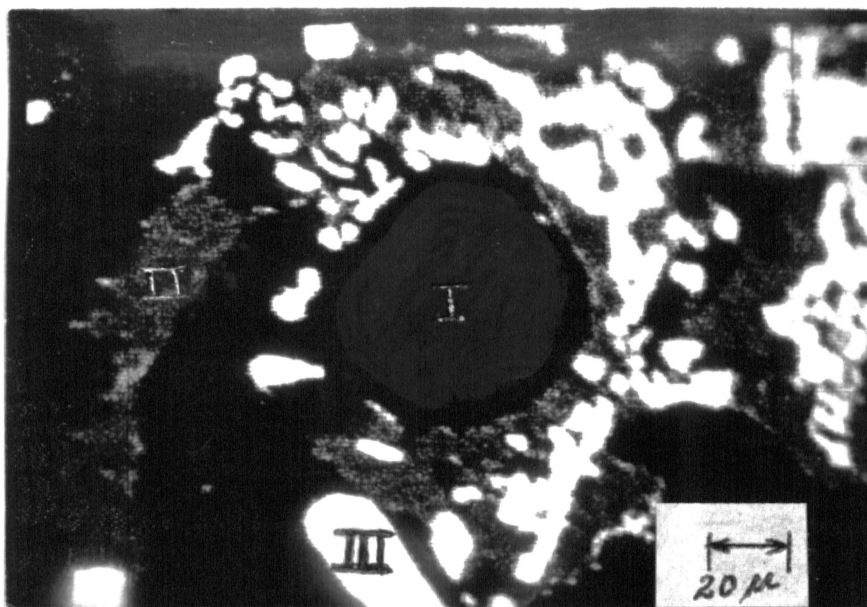
A
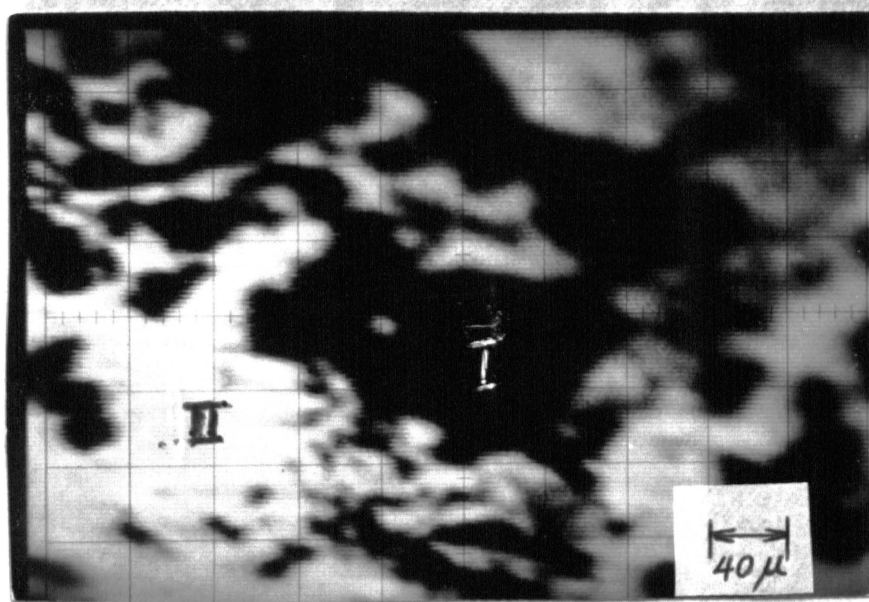
B

Figure 17. Back scattered electron images showing element distribution in: (A) Matte; (B) Interface between the matte layer and bullion.

C
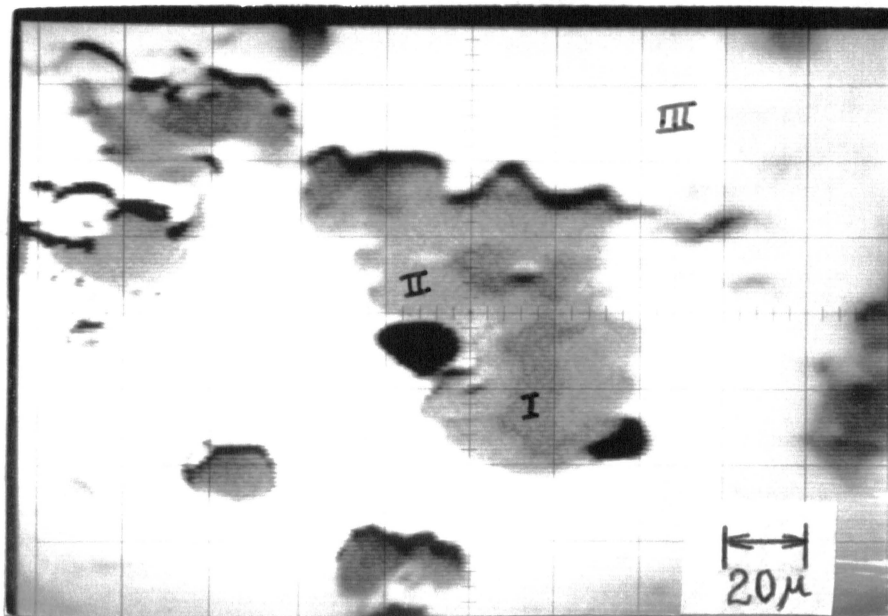
D

Figure 17. (Continuation). Back scattered electron images showing element distribution in: (C) Particles in the interface matte-bullion; (D) Lead bullion. See Table VI for microprobe analysis.

TABLE VI

ELECTRON PROBE MICROANALYSIS OF MATTE, MATTE-BULLION BOUNDARY, AND BULLION PARTICLES

Area	Counts per second			Compounds Identified
	Pb	Cu	S	
(A) Matte:*				
I	7.02	1976.99	117.86	Mostly $Cu_{2+x}S$.
II	311.08	1655.66	90.48	$Cu_{2-x}S$; PbS.
III	566.51	1060.75	19.29	Met. Cu; Met Pb; some Cu_2S.
(B) Matte-bullion boundary:**				
I	12.41	1365.84	183.45	Mostly pure $Cu_{2-x}S$.
II	243.00	1.20	–	Metallic lead.
(C) Particle in the interface between matte and bullion:**				
I	66.95	558.80	121.36	Mostly Cu_2S; some PbS.
II	99.36	39.68	93.00	Mostly PbS; little Cu_2S.
III	242.10	1.50	–	Metallic lead.
(D) Bullion:**				
I	6.79	1421.44	156.96	Mostly $Cu_{2-x}S$.
II	8.24	1250.24	37.59	Metallic Cu very little Cu_2S.
III	240.02	–	–	Metallic lead.

*Standards:

Cu_2S	20.40	1958.89	116.17
PbS	1194.60	2.56	100.94
Met. Cu	–	2149	–
Met. Pb	1416.87	–	–

**Standards:

Cu_2S	1.20	1365.81	185.33
PbS	232.60	1.22	127.86
Met. Cu	–	1791.21	–
Met. Pb	243.40	–	–

To complement the X-ray diffraction and microscopic
observations and to have an idea of the type of asso-
ciation existing among the lead, copper, and sulfur in
the matte, interface between matte and bullion, and
bullion, different areas of these three portions were
analyzed using an electron-microprobe. Figures 13, 14,
and 15 give a qualitative picture of the partitioning of
lead, copper, and sulfur between the primary phases and
eutectic, in the matte; and between the matrix and pri-
mary phases in the bullion.

Figure 16 and Table VI show the spots analyzed and
the phase identification of the compounds under the
beam of electrons. The counts of characteristic radia-
tion excited from the point of the specimen analyzed
were compared with the counts obtained from pure standards.

From the previous results it can be concluded that at
smelting temperatures (1200° - $1300^{\circ}C$), two liquid phases
are in equilibrium. A lead phase with dissolved copper
and sulfur in low concentrations; and a lighter matte
phase containing a high concentration of copper and sulfur,
and dissolved lead.

On cooling to room temperature the matte precipitates
cuprous sulfide, (gray areas); a eutectic mixture of lead
sulfide and cuprous sulfide with a deficiency of sulfur,
and metallic lead rich in copper and sulfur. Simultane-
ously, the lead bullion precipitates some metallic copper,
that reacts with the sulfur going out of solution. The

light reddish particles in the bullion gave counts corresponding to mostly pure copper with very little sulfur; while the bluish gray adjacent exterior area of the particles gave counts corresponding to Cu_2S with copper excess. The metallic lead showed very small amounts of copper in solution.

C. Matte Smelting

The main function of the reverberatory furnace is to smelt the charged drosses and permit the formation of a slag, matte, and lead bullion. This is achieved by charging the dross from the decoppering and refining circuits, with various fluxes (coke, sodium carbonate, silica sand, borax, sulfur, and some other reducing agents, depending on the nature of the drosses) and smelting the charge at a temperature between $1100^{\circ}C$ and $1300^{\circ}C$ for a certain time.

The variables mentioned above were investigated in a series of experimental fusions.

1. The effect of time and temperature.

The general test procedure consisted of combining selected proportions of synthetic samples resembling industrial mattes and smelting the blend in standard fireclay crucibles at the desired temperature. After remaining at temperature for either 2 or 3 hours, the crucible was removed from the furnace and allowed to cool in air to room temperature. The products were separated, weighed,

and chemically analyzed, according to the chemical pro-
cedures outlined in Appendix 3.

The temperature and holding time had to be high
enough to give a fluid slag, which promotes a rapid and
sharp separation of the matte layer and entrapped lead.

To determine the synthetic sample whose composition
was most similar to the mattes obtained from practice, a
series of mixtures of lead sulfide, cuprous sulfide, and
metallic lead were fused together using a graphite plus
sodium silicate cover to avoid oxidation. In all cases
a lead bullion was formed. The amount of lead formed de-
pended on the amount of lead originally present.

The results of these fusions are shown in Table VII.

The matte from the third fusion was found micro-
scopically and chemically to correspond to the mattes
obtained in practice as shown in Figure 18.

Phases present in the matte of Fusion 3 were deter-
mined by X-ray diffraction as Cu_2S, PbS, and metallic
lead.

The importance of temperature upon matte formation
was studied by fusing synthetic mixtures, of a composition
similar to Fusion 3 in Table VII, at different temperatures
in a globar furnace. The products were weighed and anal-
yzed for Cu and Pb.

The observations of this study are recorded in Table
VIII and plotted in Figure 19. Evolution of gases occurred
at all temperatures studied, but the high losses of weight

TABLE VII

PbS - Cu₂S - Pb SYNTHETIC MATTES

No	% PbS	% Cu₂S	% Pb	% Pb	% Cu	% Pb	% Cu
	% By Weight in Original Mixture			Before Fusion		After Fusion	
1	-	85.6	14.4	14.4	68.5	3.2	75.0
2	20.0	68.6	11.4	17.2	54.9	4.1	67.2
3	40.0	51.4	8.6	34.4	41.1	17.3	58.5
4	60.0	35.6	4.4	51.6	28.5	36.5	45.0
5	80.0	17.2	2.8	68.8	13.8	66.0	2.0
6	100.0	-	-	86.0	-	84.5	-
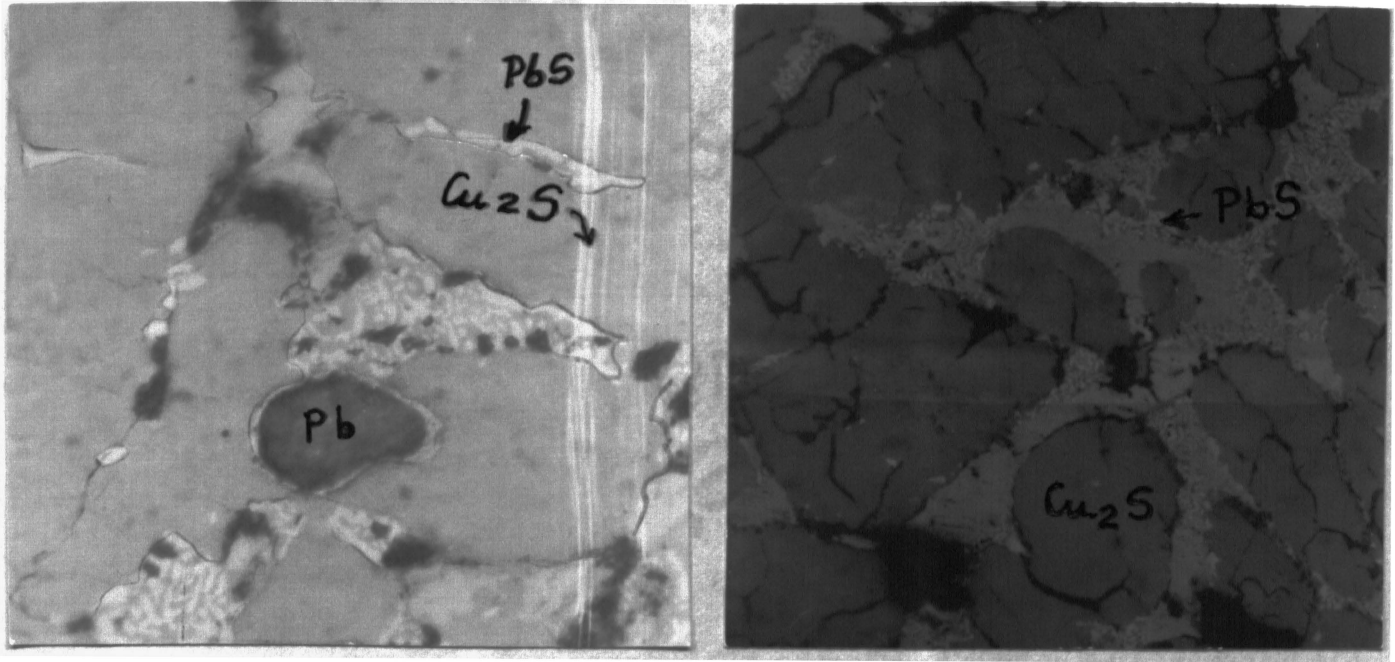
A   B

Figure 18.   Microstructures of a synthetic and industrial

matte.

(A)   Synthetic matte.   58.5% Cu, 17.3% Pb.   Gray is Cu_2S,

light is PbS, eutectic $PbS-Cu_2S$, and dark is a metallic

lead inclusion. (400 X.)

(B)   Industrial refused matte.   Gray is Cu_2S, light PbS,

eutectic $PbS-Cu_2S$, dark metallic lead inclusions. (150 X.)

TABLE VIII

THE INFLUENCE OF TEMPERATURE UPON MATTE FORMATION

Temp.	Weight of sample g.			% Cu in matte		% Pb in matte	
°C	before	after	% loss	before	after	before	after
1100	50	48.7	2.5	48	36.4	36	31.1
1100	50	48.4	3.1	48	46.0	36	26.8
1100	50	47.8	4.4	48	44.0	36	23.1
1150	50	43.9	12.1	48	46.5	36	25.7
1150	50	45.5	9.1	48	46.8	36	20.9
1200	50	47.9	4.2	48	49.0	36	14.5
1200	50	47.3	5.4	48	52.5	36	14.2
1250	50	47.5	5.0	48	54.0	36	8.0
1250	50	48.3	3.4	48	57.6	36	9.6
1300	50	47.3	5.4	48	53.5	36	10.7
1300	50	47.9	4.2	48	49.8	36	12.5
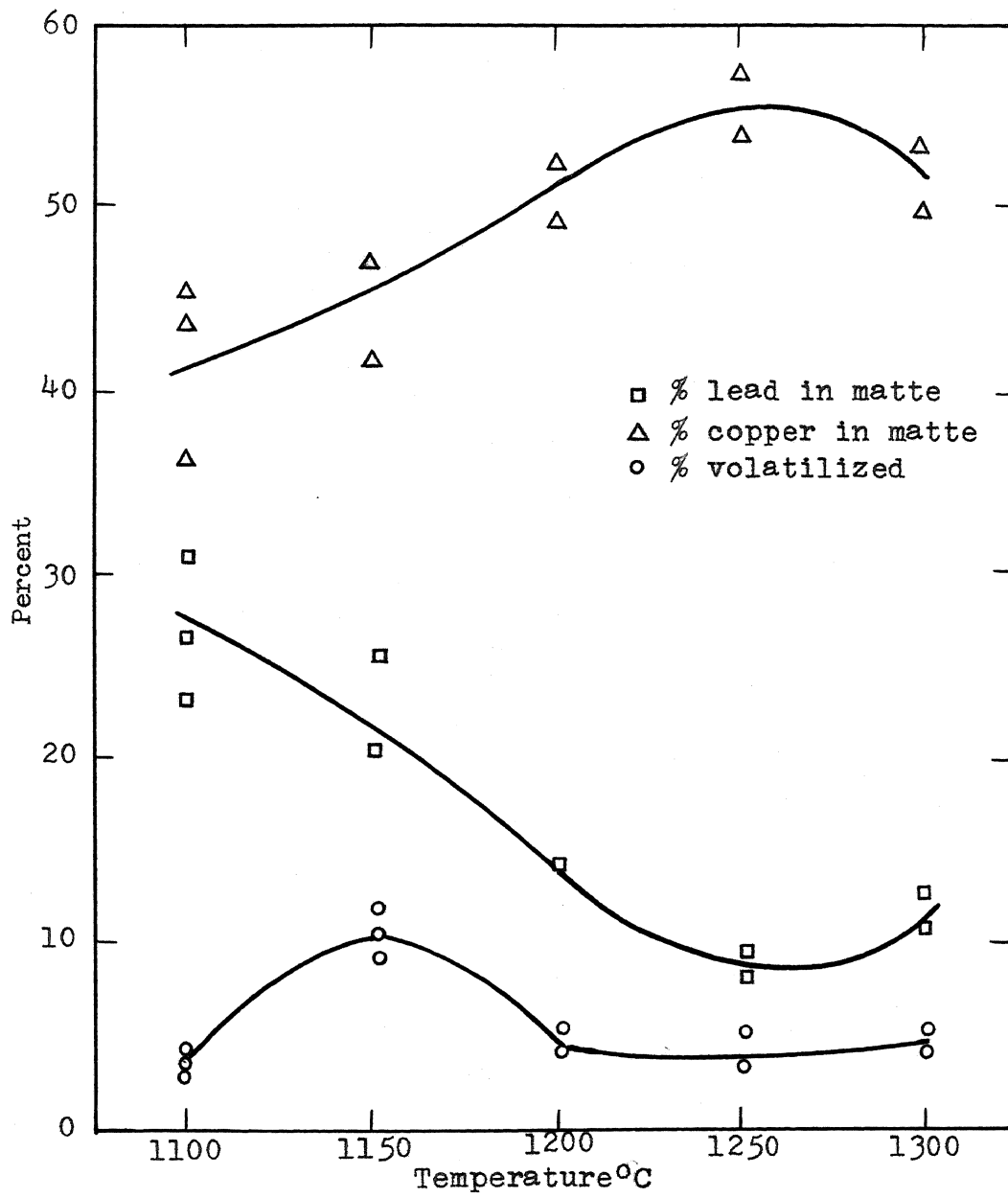
Figure 19. The effect of temperature upon matte formation.

from $1100^{\circ}C$ to $1150^{\circ}C$ decreased at higher temperatures, $1200^{\circ}C$ to $1300^{\circ}C$. This trend is probably the result of the formation of a completely liquid matte phase.

The best Cu/Pb ratios were obtained at temperatures between $1200^{\circ}C$ and $1300^{\circ}C$.

The influence of holding time was studied using the same ratio of sulfides in Fusion 3, Table VII. The mixtures were smelted at $1200^{\circ}C$ and times of 1, 2, 6, 9, and 12 hours. The samples were covered with a layer of sodium silicate. (Duplicate samples were run each time.)

Table IX and Figure 20 show the results of these fusions. The weight loss due to volatilization was determined by weighing the crucible and charge before and after the reaction. The weight losses increase sharply in the first hour of fusion and they remain about the same for samples held longer times. The trend of the slag to gain weight as time increases, shows that after twelve hours the reactions between the slag and matte constituents were still occurring.

A study of the volatilized material from the above fusions was accomplished by condensing the vapor phase on the walls of a vycor tube and analyzing it by X-ray diffraction. The predominate phase was PbS with very little Cu_2S, and PbO. (See Appendix 4.)

The holding time of two hours in the furnace was found to be adequate for matte fusions, because after this time the changes in weight seemed to be small, particularly when a slag cover was formed which prevented further sul-

TABLE IX

THE INFLUENCE OF TIME UPON MATTE SMELTING

TEST	Time hrs.	Wt. of sample grams	Wt. loss grams	% loss by volatil- ization	Wt. matte + lead	Wt. loss to the slag
1-a	1	50	0.69	1.38	40.10	19.80
1-b	1	50	0.59	1.18	43.20	13.60
2-a	2	50	2.20	4.40	35.24	29.52
2-b	2	50	2.39	4.78	35.56	28.88
3-a	6	50	3.40	6.80	-	-
3-b	6	50	2.90	5.80	32.49	35.02
4-a	9	50	2.35	4.70	35.71	28.58
4-b	9	50	3.78	7.56	-	-
5-a	12	50	2.58	5.16	31.15	37.70
5-b	12	50	2.73	5.46	34.68	30.64

Sample calculation:

Wt. of sample - final wt. (matte + lead) = X

$$\frac{X}{50} \cdot 100 = \% \text{ wt. loss to slag}$$

$$\text{Wt. loss} = \begin{array}{l} \text{(Wt. of crucible + charge before fusion)} \\ - \text{(Wt. of crucible + charge after fusion)} \end{array}$$

$$\frac{\text{Wt. loss}}{50} \cdot 100 = \% \text{ wt. loss by volatilization}$$
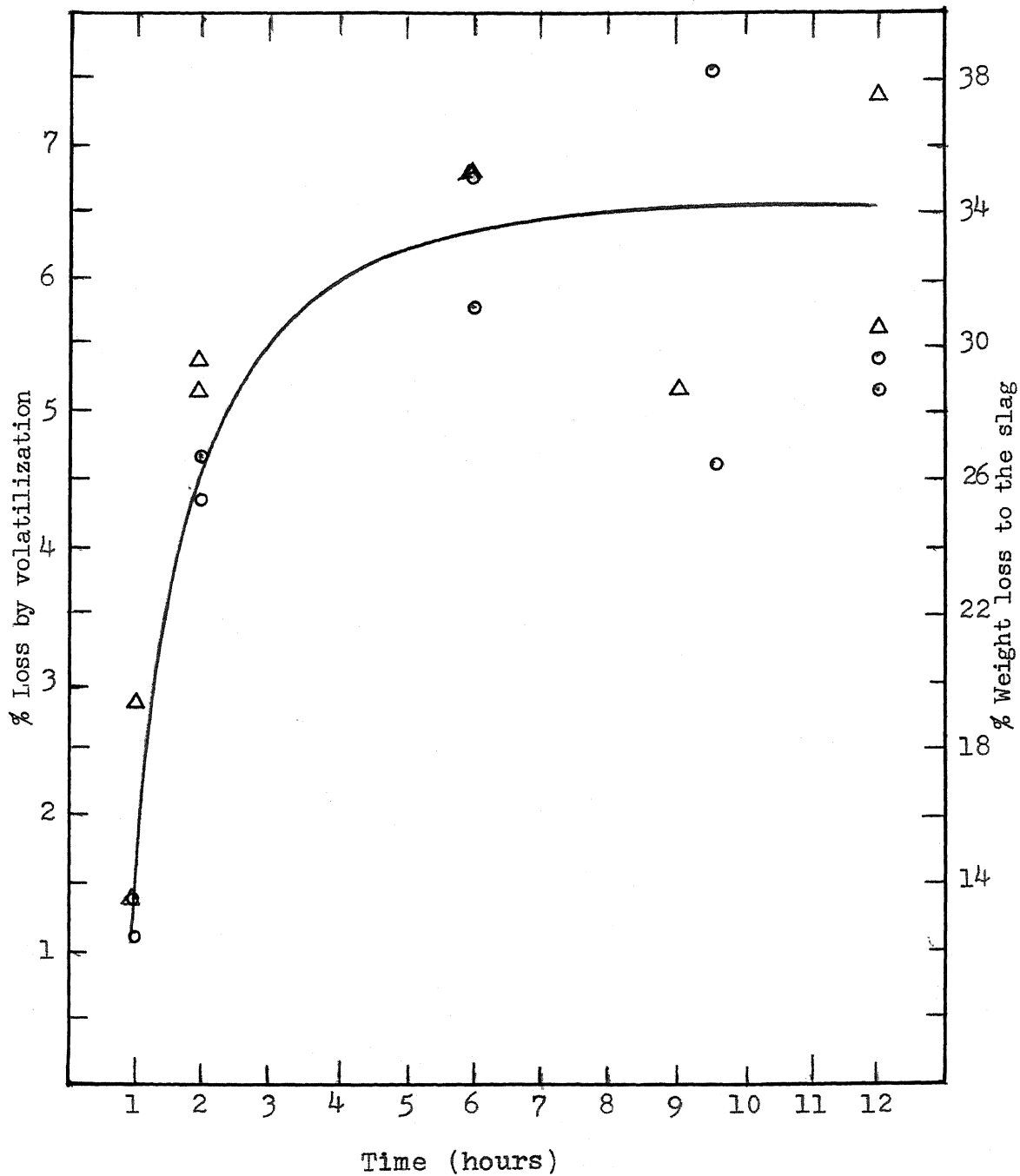
Figure 20. The influence of time upon matte smelting at 1200°C.

    o % weight of material loss by volatilization

    △ % weight of material loss to the slag

fide volatilization from the matte layer.

2. The effect of SiO_2 additions.

Silica sand is added to the dross furnace to aid in the formation of a fluid slag, by combining with the Fe, Zn, Al, and other impurities initially present in the dross as oxides. As a solvent, the slag absorbs all the FeO formed by reactions such as:

$$FeS_2 + 5Fe_2O_3 = 11FeO + 2SO_2$$

Some of the ferrous oxide may be further oxidized to magnetite, together with other oxides, (ZnO, Al_2O_3, PbO, MgO, etc.) which forms a floating "mush" of spinels very difficult to melt down. The removal of the FeO is aided by the addition of silica sand which ties up the FeO to form $FeO \cdot SiO_2$ (Fayalite).

To observe the effect of silica additions upon dross smelting, a series of fusions with different amounts of silica sand additions were performed on industrial drosses.

The dross used as starting material had the following composition:

66% Pb

17% Cu

2% Fe

4.5% S

3.0% Zn

2.0% Ni

0.5% Co

0.5% Insoluble materials.

TABLE X

<u>THE EFFECT OF SILICA SAND (SiO_2) ADDITIONS UPON
DROSS SMELTING</u>

% SiO_2 added	SLAG			MATTE			BULLION		
	% wt	% Pb	% Cu	% wt	% Pb	% Cu	% wt	% Pb	% Cu
-	8	35	4	32	22	56	60	86	9
0.5	11	40	2	30	28	52	59	94	3
2.0	10	28	3	28	32	52	62	90	2
4.0	18	29	3	24	24	56	58	89	4
8.0	22	31	7	26	25	51	52	91	4

200 gram portions of this dross were mixed with silica sand and fired in fireclay crucibles in a muffle furnace at 1200°C for two hours.

The results of these fusions are shown in Table X. Not surprisingly, the fusions without silica additions were the least fluid and a clear separation of layers was not always accomplished. The fluidity of the slags increased with sand additions. Slight decrease of the lead in the slag takes place with increased amounts of SiO_2. This is probably due to the easier segregation of layers. No appreciable advantage was noticed when additions higher than 4% silica were made.

The influence of silica sand on the matte and bullion Pb and Cu grades was not definite.

3. The effect of soda ash (Na_2CO_3) additions.

When sodium carbonate is added for the smelting of dross, high copper to lead ratios can be consistently attained, the lead content of the slag is decreased, and the copper in the bullion is lowered.[14]

Fusions of dross containing different amounts of sodium carbonate were made to observe these variations.

Standard fireclay crucibles were charged with 200 grams of dross mixed with various amounts of soda ash. The composition of the dross used in the experiments was the same as that described in the paragraph of silica additions.

TABLE XI

THE EFFECT OF SODA (Na$_2$CO$_3$) ADDITIONS UPON DROSS SMELTING

% Na$_2$CO$_3$ added	SLAG			MATTE			BULLION		
	% wt	% Pb	% Cu	% wt	% Pb	% Cu	% wt	% Pb	% Cu
-	11	36	4	29	18	59	60	88	9
0.5	10	21	3	30	20	51	60	89	5
1.0	9	20	6	30	23	58	61	90	3
2.0	9	13	10	31	17	52	60	94	4
4.0	12	18	6	31	24	55	57	91	5
8.0	11	12	8	34	22	59	55	92	7

The crucibles were placed in a muffle furnace and heated to $1200^{\circ}C$ for two hours, after which they were removed and allowed to cool rapidly. The crucibles were then broken away from their contents, which in all cases were found to be in layers that could easily be separated from one another.

The results of the experiments are shown in Table XI. Increased amounts of soda additions resulted in a decrease of the lead content of the slags. A slight decrease of copper in the bullion was also noted. The Cu/Pb ratio in the mattes remained practically the same.

Additions above 2% soda ash seem to be unnecessary; only causing larger amounts of slag.

The decrease of lead in the slag was explained as being the result of the following reactions:[12]

$$PbS + 2PbO = 3Pb + SO_2 \qquad \Delta F^{o}_{1200^{o}C} = -7 \text{ Kcal/mole}^{o}C$$

$$Na_2CO_3 + SO_2 = Na_2SO_4 + CO \qquad \Delta F^{o}_{1200^{o}C} = -8.4 \text{ Kcal/mole}^{o}C$$

$$Na_2SO + 4CO = Na_2S + 4CO_2 \qquad \Delta F^{o}_{1200^{o}C} = -194 \text{ Kcal/mole}^{o}C$$

$$Na_2S + Cu_2O = Cu_2S + Na_2O \qquad \Delta F^{o}_{1200^{o}C} = -12.5 \text{ Kcal/mole}^{o}C$$
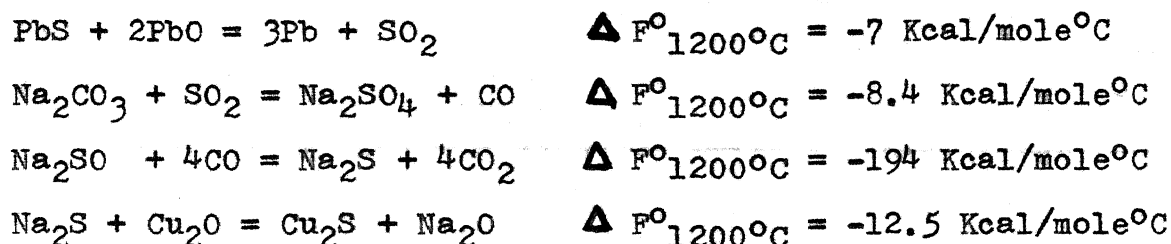
The Na_2O formed will eventually end up in the slag together with the impurities and entrapped slag originally present in the dross. It is evident that if sodium sulfate is formed in an intermediate stage, the addition of coke or coal should assist the efficiency of the dross smelting as:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2 \qquad \Delta F^{o}_{1200^{o}C} = -326 \text{ Kcal/mole}^{o}C$$

With the above idea in mind a series of fusions were made, using Na_2S and Na_2SO_4 as addition agents for dross

TABLE XII

THE EFFECT OF Na_2S AND Na_2SO_4 ADDITIONS UPON DROSS SMELTING

% Addition	SLAG			MATTE			BULLION		
	% wt	% Pb	% Cu	% wt	% Pb	% Cu	% wt	% Pb	% Cu
1% Na_2S	12	34	4	26	34	46	62	87	9
5% Na_2S	16	25	8	29	34	41	55	91	6
1% Na_2SO_4	15	39	4	30	33	44	55	92	7
5% Na_2SO_4	18	35	2	32	33	47	50	90	7
1% Na_2SO_4 1% Coke	17	17	1	31	25	52	52	89	9
4% Na_2SO_4 1% Coke 2% Sulfur 0.5% Borax	29	29	2	31	32	48	40	97	2

smelting. Results of these fusions are shown in Table XII.
Although a clear separation of layers was obtained, no def-
inite trend could be observed to indicate that the above
reactions are occurring during dross smelting and matte
formation. It does seem possible from the experimental
results that the following type reactions might take place:

$Na_2CO_3 = Na_2O + CO_2$ $\Delta F^O_{1200^OC} = +8.5$ Kcal/mole^{O}C

$Na_2O + PbSiO_3 = PbO + Na_2O \cdot SiO_2$ $\Delta F^O_{1200^OC} = -296$ Kcal/mole^{O}C

$2PbO + PbS = Pb + SO_2$ $\Delta F^O_{1200^OC} = -7.0$ Kcal/mole^{O}C
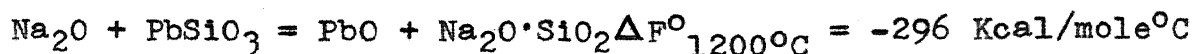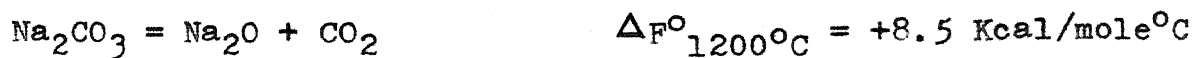
4. The effect of sulfur additions upon dross smelting.

To observe the effect of sulfur additions upon dross
smelting, a series of fusions was made using the previously
described industrial dross as starting material.

200 gram portions of dross were thoroughly blended
with 1.47 g. Na_2CO_3, 1.17 g. coke, 1.17 g. borax, 0.88 g.
silica sand, and varying amounts of elemental sulfur. The
mixtures were placed in fireclay crucibles and fused at
1200°C for two hours. The crucibles were cooled to room
temperature afterwards, and the products were separated,
weighed, and chemically analyzed.

The results of the fusions are shown in Table XIII and
the chemical assays are plotted in Figures 21 and 22.

The chemical reactions that take place when sulfur
is added during dross smelting are:

$2 Cu + S = Cu_2S$ $\Delta F^O_{1200^OC} = -40$ Kcal/mole^{O}C

$Pb + S = PbS$ $\Delta F^O_{1200^OC} = -18$ Kcal/mole^{O}C
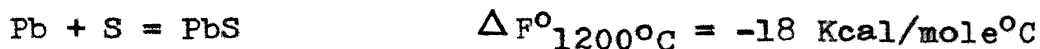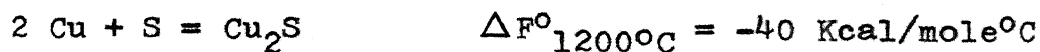
TABLE XIII

THE EFFECT OF SULFUR ADDITIONS UPON DROSS SMELTING

% sulfur added	MATTE				BULLION		
	% wt	% Pb	% Cu	Cu/Pb	% wt	% Pb	% Cu
-	25	17	63	3.70	65	86	13
0.5	34	24	56	2.34	66	88	8
1.0	37	25	52	2.08	63	90	7
2.0	45	28	51	1.82	55	94	4
3.0	49	31	47	1.52	51	98	2
4.0	58	37	43	1.16	42	98	1
5.0	60	42	37	0.88	40	99	1
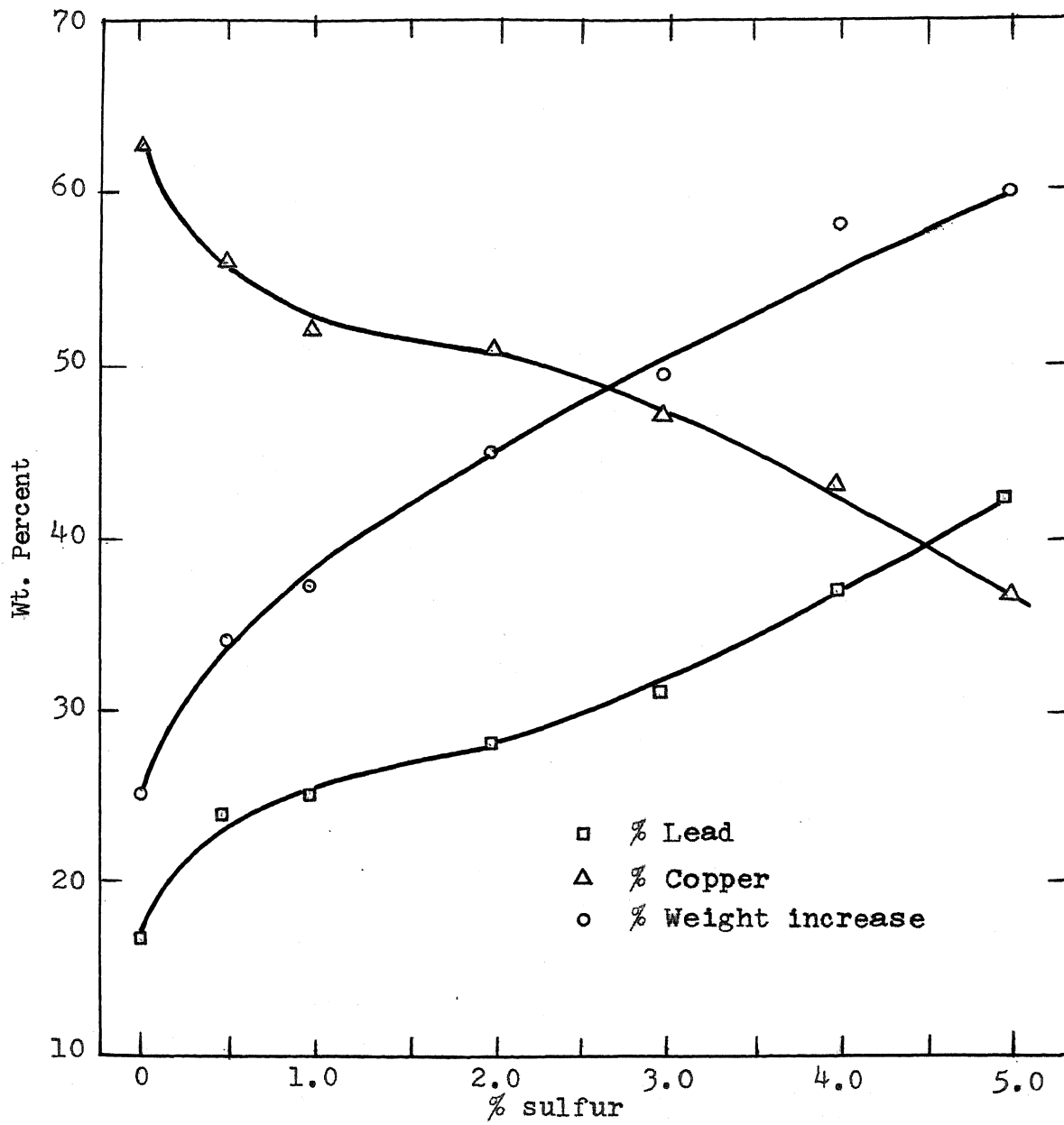
Figure 21. Effect of sulfur additions upon matte composition.
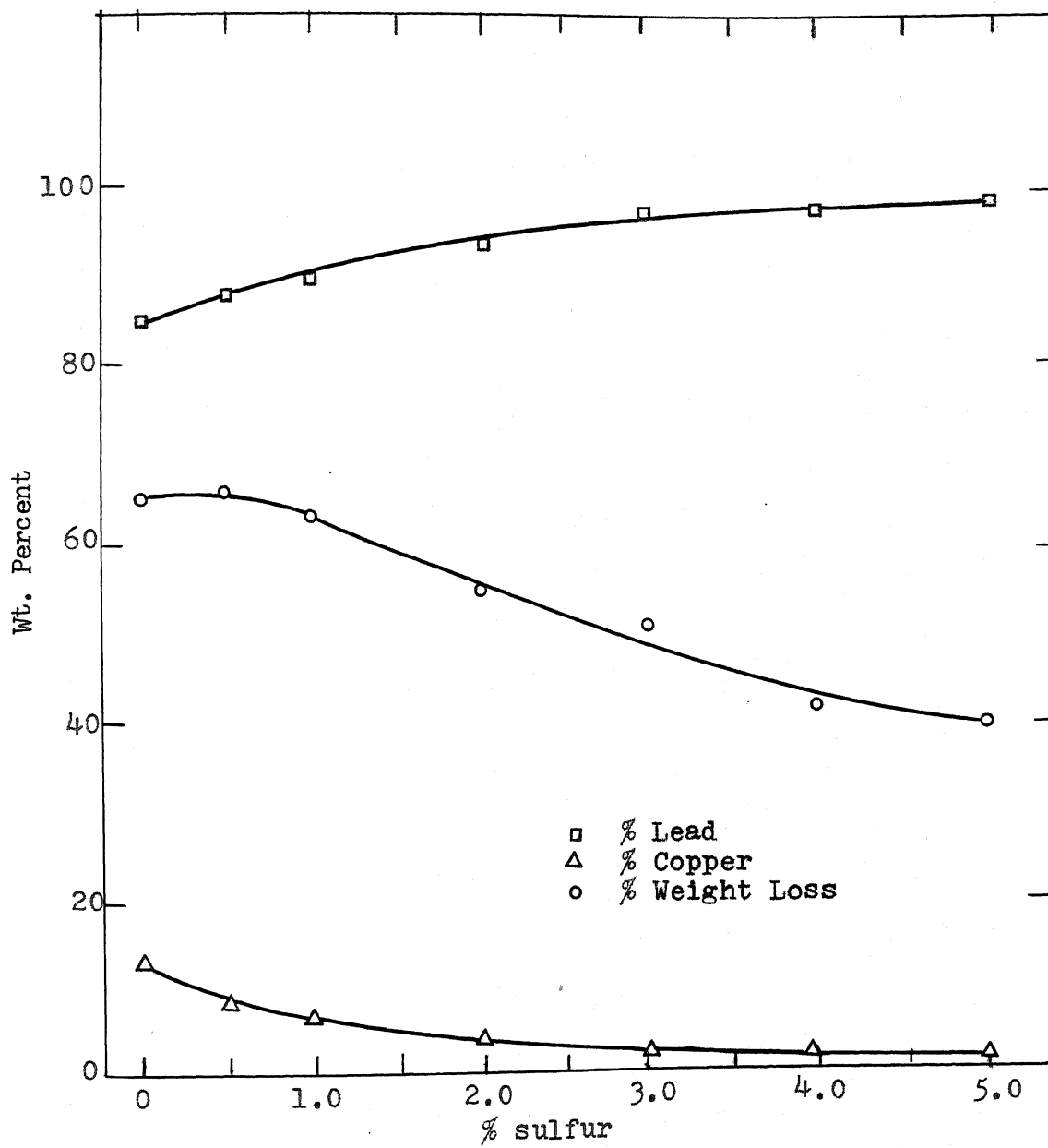
Figure 22. Effect of sulfur additions upon bullion
composition.

The free energies[15] indicate that sulfur reacts preferentially with copper to form Cu_2S. However, the increase of weight in the matte together with its increased lead content give an indication that the second reaction takes place simultaneously.

From the results it can be seen that the copper content of the bullion can be lowered from 13% Cu to about 4% Cu by the use of 2% to 3% by weight sulfur. Additions of sulfur over 3% were detrimental, because the matte formed contained a considerable amount of lead (31% Pb.).

Cu/Pb ratios in the matte are the general rule used to decide which grade of matte is the most desirable. The matte with the highest Cu/Pb ratio would be considered to be the best.

The fusion with no sulfur additions gave the highest Cu/Pb ratio (3.7); but at the same time the copper content of the bullion was high (13% Cu). The fusions to which 2% by weight sulfur were added seemed to give a high Cu/Pb ratio (1.82) together with low copper in the bullion (4% Cu).

Evolution of SO_2 was strong at all times when sulfur fusions were made. Although it was not possible to measure the efficiency of sulfur additions, it is believed that a considerable amount of the initial sulfur was volatilized before having time to react.

5. The effect of pyrite (FeS$_2$) additions upon matte smelting.

Pyrite is known to be a matte forming material. Because of this property and its excess sulfur, an attempt was made to use it as a source of sulfur to reduce the copper content of the bullion in the dross furnace. Therefore, before using pyrite as a reagent, it was necessary to know its effects upon matte formation. With this idea in mind, mixtures of synthetic mattes with metallic lead were fused in fireclay crucibles together with different amounts of pyrite concentrate. The fusions were made at 1250°C and they were kept in the furnace for only 30 minutes, because of the high tendency of the melt to corrode the crucibles.

The products of the fusions were slag and matte which were separated mechanically after freezing the melts to room temperature. The mattes were chemically analyzed and the results of these analyses are shown in Figure 23 and Table XIV.

As the amount of pyrite increased, the lead content of the matte increased considerably up to values as high as 43.7% Pb. At the same time the copper content in the matte decreased to the lower value of 27.2% Cu when 20% pyrite was added.

Another important disadvantage of the pyrite additions was the tendency to form "mushy" matte melts. Additions above 3% by weight of pyrite were not completely

TABLE XIV

THE EFFECT OF PYRITE (FeS_2) ADDITIONS UPON MATTE SMELTING

No	Synthetic mixture			% FeS_2	Matte formed		
	% Pb	% PbS	% Cu_2S	added	% Pb	% Cu	% Fe
1	40	20	40	-	21.0	57.0	-
2	40	20	40	2	23.6	59.5	0.8
3	40	20	40	4	23.4	57.5	0.5
4	40	20	40	8	34.0	51.0	0.8
5	40	20	40	12	40.4	34.8	5.8
6	40	20	40	16	43.0	28.0	5.8
7	40	20	40	20	43.7	27.2	2.0
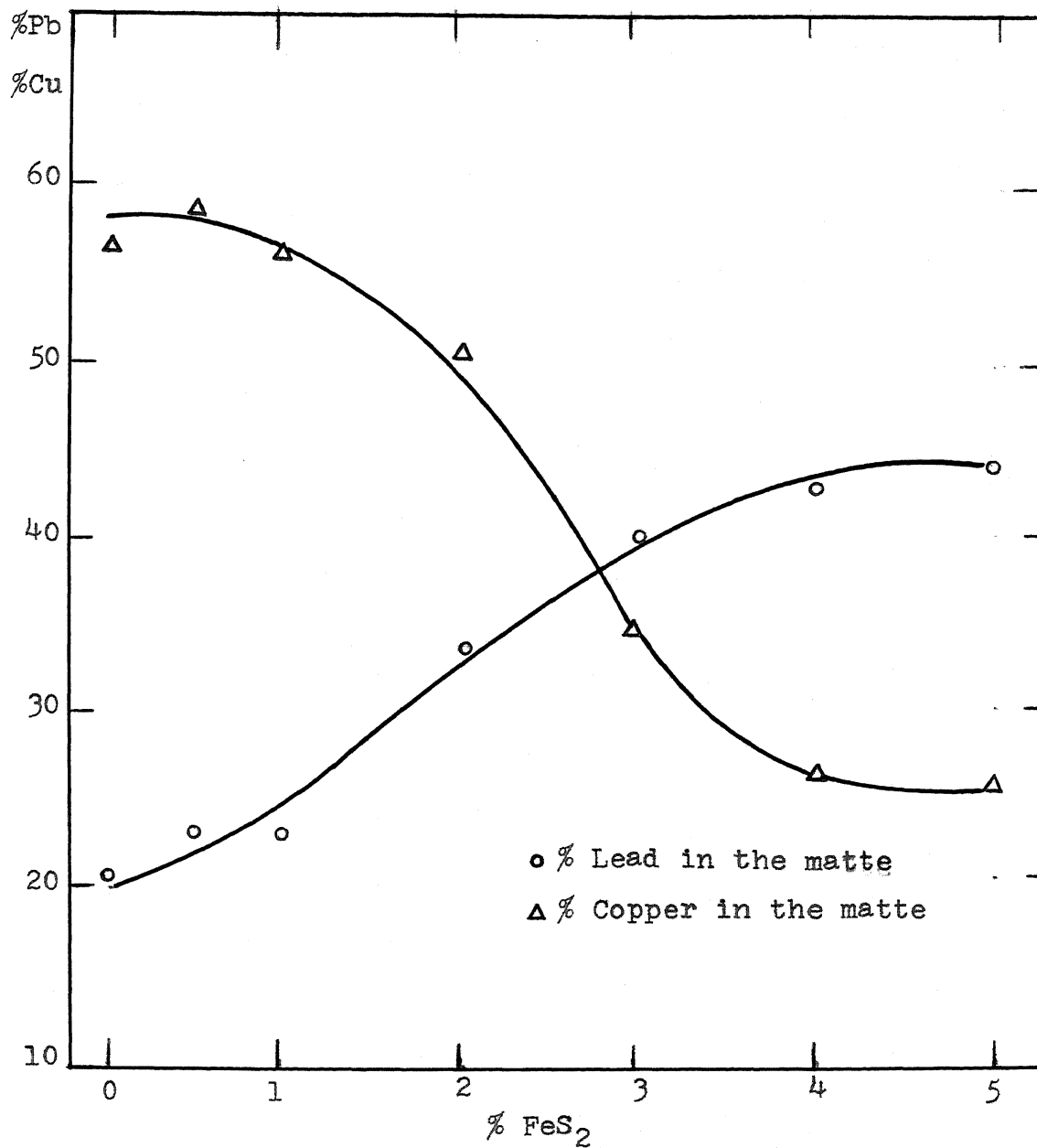
Figure 23. The effect of pyrite additions upon matte smelting.

fluid, which could have led to part of the difficulty.
Results would indicate that the effect of iron should be
investigated further, as a relatively small quantity pres-
ent in the matte caused a major decrease in the matte grade.

As far as the use of pyrite as a high temperature de-
copperizing agent for the bullion at $1200^{\circ}C$, its action
was investigated in separate fusions of Pb-Cu alloys. Mi-
croscopic examination of air cooled melts indicated that
copper remained in the bullion, and that the reaction of
pyrite with the metallic lead was predominant.

6. The effect of litharge (PbO) upon dross smelting.

Litharge is known to be an excellent fluxing agent.
When heated to bright redness with lead sulfide in the
stoichiometric ratio of two to one, all the lead in both
compounds is reduced to metal, and sulfur dioxide is
evolved according to the equation:

$$PbS + 2PbO = 3Pb + SO_2$$

With this idea in mind a series of fusions was made
using a mixture of dross and litharge as starting materi-
als. The temperature was about $1200^{\circ}C$. Results of these
fusions are shown in Table XV..

No appreciable advantage was found, but there are
definite indications that the PbO additions have no major
detrimental effects while helping to increase in matte
grade. Also the PbO would be readily available and attrac-
tive from an economic point of view. The PbS in the matte
remained the same as it would be for a straight fusion of

TABLE XV

THE EFFECT OF LITHARGE (PbO) ADDITIONS UPON DROSS SMELTING

% PbO Added	Product	% Weight	% Pb	% Cu
1	Slag	8	20	6
1	Matte	39	33	38
1	Bullion	53	97	2
3	Slag	8	16	3
3	Matte	39	33	40
3	Bullion	53	95	2
5	Slag	8	13	1
5	Matte	37	31	43
5	Bullion	55	97	2

dross. This was due to the incomplete decomposition of PbS and it remained in solution in the PbS-Cu_2S matte. Another cause for the high lead mattes was the fluxing mixture used together with the oxide PbO, i.e. sulfur 2%, coke 2%, and borax 1%.

Some more investigation should be done using oxides of lead as an addition to the dross furnace, since lead oxides are produced in the refining of lead and they would be a handy product to use as a fluxing agent.

IV. SUMMARY AND CONCLUSIONS

The following summary is presented in two parts:
(A) Phase determinations, and (B) The influence of addition agents upon matte formation.

A. Phase Determinations

Matte products of the reverberatory lead dross furnace were studied and their components determined by microscopic, X-ray diffraction and microprobe analysis.

An initial magnetic separation indicated the presence of spinels, predominantly magnetite, Fe_3O_4. The nonmagnetic portion was separated in a Frantz Isodynamic Separator at different current intensities. The products of this separation were analyzed by X-ray diffraction.

As a result of these studies the matte was found to be composed of Cu_2S, PbS, metallic lead, metallic copper, and magnetite as positively identified phases and FeS, Pb_3O_4, and Ni_2S_3, as phases that could be present but not proven conclusively by X-ray diffraction techniques.

The above observations were corroborated by the analysis made on the products obtained by fusing industrial drosses as starting materials. The drosses were studied first by X-ray diffraction. They were composed of mainly PbO tetragonal, alpha Cu_2S, and metallic lead. Probable phases for which identification was not possible by X-ray diffraction, were Pb_3O_4, PbS, metallic Cu, and FeS.

The lead dross was then smelted at $1200^{\circ}C$. A separation of slag, matte, an intermediate, and bullion layers occurred at this temperature.

The phase determinations made with the products of the dross fusions coincide with the determinations made with the industrial mattes. At smelting temperatures the liquid matte and bullion phases are present. The matte phase is lighter than the bullion phase and contains a high concentration of copper and sulfur (liquid sulfides), and dissolved lead. The bullion phase at the bottom contains lead with a low concentration of copper and sulfur. When the matte and bullion are cooled to room temperature, the matte precipitates cuprous sulfide, and a eutectic mixture of cuprous sulfide and lead sulfide. The cuprous sulfide in the eutectic mixture has a deficiency of sulfur.

Metallic lead in the matte goes out of solution forming lead dropplets rich in copper and sulfur.

Simultaneously, metallic copper precipitates from the lead bullion on cooling. This reacts with the sulfur going out of solution to form cuprous sulfide, which surrounds the high copper grains. The metallic lead solidifies with some copper and other impurities in solution.

The interphase between the bullion and matte consists of a layer that contains a greater concentration of lead sulfide and a small amount of copper sulfide in a matrix of metallic lead. Copper is also present. This layer is present in the furnace together with the accumulated speiss.

B.   The Influence of Addition Agents Upon Matte Formation

As a preliminary investigation, the influence of temperature and time of smelting upon matte formation was studied. The sulfide melts evolved gases at all temperatures investigated; but the mattes formed at 1200°C to 1300°C gave the most fluid liquid melts, and the losses due to volatilization decreased considerably.

Time studies indicated that when holding is of at least two hours duration, the formation of the layers is complete. Very small changes were noticed at longer holding times, however, reactions between slag, matte, and bullion were still occurring. Equilibrium was not attained even when holding times were up twelve hours.

By using the conditions of temperature and smelting time best suited for matte formation, a series of fusions using industrial drosses and different addition agents were tried.

Silica sand was found to increase the fluidity of the melt and a clear separation of layers was obtained when using 2% by weight silica sand. The lead grade of the slag decreased slightly when using 2% silica, but the matte and the bullion were not affected by these additions.

The lead content of the slag decreased with additions of soda ash up to 2% by weight. The use of soda above 2% did not show any improvement in the matte or the bullion. It was believed that Na_2CO_3 would react with the SO_2 in the furnace to form a Na_2S or Na_2SO_4 which would act as the

sulfur provider for collecting copper in the matte. Although the reactions are thermodynamically possible, this was not proved true, since fusions using pure Na_2S and Na_2SO_4 did not show the advantages obtained by using Na_2CO_3. Soda ash seems to be more a fluxing agent which lowers the melting point of the dross and insures a better layer separation. Other possible reactions could be the decomposition of Na_2CO_3 to form Na_2O which reacts with the $PbSiO_3$ in the slag to give a PbO. The PbO is then reduced to metallic lead by the PbS in the matte.

Sulfur additions gave the most interesting results. The copper grade in the bullion decreased considerably, maintaining at the same time good Cu/Pb ratios in the matte when additions up to 2% sulfur were made.

Additions of 3 to 4% sulfur gave 2 to 1% Cu in the bullion, however, the lead content in the matte increased considerably (31 to 37% Pb).

Evolution of SO_2 gas occurred during smelting, and would be the principal disadvantage for using sulfur as a regular addition to the dross furnace.

Pyrite was found to be detrimental to the grade of the matte, as it increases the lead content and decreases the copper content. A definite advantage of pyrite as a high temperature decopperizer of the lead bullion was not evident. Indications were that the Fe content of the charge might be important in determining matte grade and

should probably be checked more closely.

Litharge additions did not affect the bullion but did improve the slag and matte. Additional work would be required to verify these results.

V. RECOMMENDATIONS

The forms of lead in the matte are lead sulfide and metallic lead; the "bad matte" samples when refused gave 50% by weight metallic lead separated from a matte comprised mostly of Cu_2S and a eutectic $PbS-Cu_2S$. This indicates the possibility of reclaiming the lead from the non-satisfactory mattes by the use of an additional smelting step. At the same time the copper grade of the matte is raised and a better Cu/Pb ratio is obtained.

Since the dross coming from the cooling of blast furnace bullion contains Cu_2S and some PbS as entrapped matte, the best smelting temperatures are in the range $1200^{o}C$ to 1250°. Below this range an intermixing of layers occurs with no definite separation of liquid phases. After two hours of holding at $1200^{o}C$ the separation of layers was accomplished; additional time did not prove to be beneficial. Shorter times show considerably less volatilized material, but equilibrium was not attained.

A good fluxing mixture for the dross studied would be silica sand, Na_2CO_3, sulfur, coke in a proportion of 1 : 2 : 2 : 1 respectively per each hundred by weight of dross smelted. Some more investigation should be done in this regard to find a most economical mixture.

Even though the study of slags is out of the scope of this study a brief investigation was necessary to understand the nature of a "mushy" material encountered in the interface slag-matte. Appendix 5 shows a typical chemical composition of a slag obtained at the dross furnace and the "infusible material" which floated on it.

A complete study of the structural composition of the dross furnace slags is definitely necessary since no available references exist on the subject.

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APPENDIX 1

X-RAY DIFFRACTION PATTERN OF THE MAGNETIC -100 MESH PORTION
OF THE "GOOD MATTE"

Fe Radiation

Magnetic -100		Fe_3O_4		PbS		Unaccounted	
d	I	d	I	d	I	d	I
				3.40	M		
2.95	M	2.96	M	2.94	S		
2.85	W					2.85	W
2.71	VW					2.71	VW
2.60	VW					2.60	VW
2.51	S	2.52	S				
2.29	W					2.29	W
2.06	S	2.09	M	2.08	S		
1.80	W			1.78	M		
1.705	W	1.708	W	1.70	M		
1.61	S	1.61	M				
1.48	S	1.48	S	1.475	W		
				1.32	M		
1.275	W	1.275	W				
				1.205	M		
1.09	M	1.089	S				

X-RAY DIFFRACTION OF PRODUCTS OBTAINED AT DIFFERENT INTENSITIES OF CURRENT IN A FRANTZ ISODYNAMIC SEPARATOR

Fe Radiation

Orig.		Sample 0.2 Amp.		0.35 Amp.		1.5 Amp.		Met. Pb		Cu_2S		PbS		Pb_3O_4	
d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I
				3.9	VW										
3.4	W	3.40	W	3.4	W	3.40	W			3.37	50	3.40	M	3.38	100
3.0	VW	3.0	W	3.0	W	3.00	VW							2.90	48
		2.92	W	2.92	W	2.94	W					2.94	S		
2.84	M	2.85	W	2.82	W	2.85	S	2.85	100	2.85	50				
2.80	W			2.75	W										
2.71	S	2.71	S	2.71	S	2.71	S							2.72	45
2.46	W	2.46	W	2.45	W	2.45	W	2.47	50						
2.40	M	2.40	W	2.39	W					2.38	90				
2.30	S	2.29	S	2.28	S	2.30	S								
2.08	W	2.06	VW	2.07	W	2.08	W			2.06	30	2.00	S		
2.00	M	2.00	M	2.00	W	2.00	W								
1.98	W	1.98	W				W								
1.96	M	1.96	W				W			1.95	100				
1.88	VW	1.89	M				M			1.87	100				
1.75	M	1.76	W	1.74	W	1.74	VW	1.75	31			1.78	M		
1.71	M	1.71	M	1.70		1.70	VW			1.69	70	1.70	W		
1.61	M	1.61	M				W			1.64	50				
1.49	M	1.49	W	1.48	W	1.48	S	1.49	32			1.48	W		
1.40	W	1.40	W		VW			1.42	9						
1.33	W	1.328	VW		VW					1.28	50				
1.198	VW	1.195	VW												
1.14	VW	1.14	VW	1.14		1.14	W	1.159	10						
1.09	VW	1.089	W	1.10		1.10	W								
1.01	VW	1.011	W	1.009		1.009	VW								

APPENDIX 3

DETERMINATION OF LEAD BY THE TITRATION METHOD USING EDTA

Reagents:

Buffer solution 1 lb. ammonium acetate is dissolved in distilled water, 60 ml of acetic acid is added and the solution is made up to 2 L with distilled water. Xylenol orange solution 0.2% in distilled water. EDTA solution 8.93 g of disodium ethylenediaminetetracetate to 1 liter of distilled water. 1 ml of this solution is equal to 5 mg of Pb.

Method:

Using 400 ml beakers follow the normal routine in the dissolution of the sample, precipitation of the lead sulfate up to the point where it has been filtered and washed well; then wash the precipitate back into the original beaker adding the filter paper. Add 30 ml of the buffer solution, dilute to 150 - 250 ml with distilled water and boil for 10 minutes. Remove from the heat and beat up the filter paper. Titrate when desired, hot, warm, or cold. Titrate with the EDTA solution using 8 - 10 drops of indicator. The color change will be from purple through orange to lemon yellow.

DETERMINATION OF COPPER (Cu)

Bring the filtrate of the Pb to a boil and add 15 ml
of Hypo. Boil until precipitate settles and then
filter. Wash once. Burn with HNO_3 and H_2SO_4. When
clean remove cover and bake dry. Cool and add 10cc
of H_2O and 1 cc of Hac. Boil and then cool for
titration. Titrate with Hypo using 10 cc of KI and
5 cc of starch as indicator. (1 cc is 1% Cu.)

APPENDIX 4

X-RAY DIFFRACTION PATTERN OF THE MATERIAL VOLATILIZED FROM MATTE FUSIONS

Volatilized		Lead sulfide		Cuprous sulfide		Unidentified	
d	I	d	I	d	I	d	I
4.50	VW					4.50	VW
4.20	VW			4.20	W		
3.90	W					3.90	W
3.80	W			3.75	W		
3.60	M			3.60	W		
3.40		3.40	M				
2.94	S	2.94	S	2.94	W		
2.80	S					2.80	S
2.71	W			2.72	M		
2.51	S			2.51	S		
2.40	W			2.45	S		
2.26	M			2.31	S		
2.21	M					2.21	M
2.15	W					2.15	W
2.09	S	2.08	S				
2.06	W					2.06	W
1.96	M			1.96	W		
1.90	W			1.87	S		
1.79	S	1.78	M				
1.72	M	1.70	W				
1.69	W			1.69	W		
1.58	W			1.51	M		
1.48	W	1.48	W				
1.41	W			1.41	W		
1.36	W	1.36	W	1.38	W		
1.33	S	1.32	M				
1.21	M	1.21	M				
1.14	M	1.14	W				
1.05	W	1.05	W				
0.99	W	0.99	W				
0.94	W					0.94	W

APPENDIX 5

Chemical Composition

A study of the structural composition of the slags is out of the scope of this study and only some points are indicated here. When the slag is high in zinc and iron it is necessary to charge silica sand, Na_2CO_3, borax, and some coke to flux the zinc and iron oxides and reduce oxidized lead and copper. Following is a typical slag composition.

Pb	3 - 10%
Cu	4 - 20%
FeO	20 - 25%
Si	1 - 5%
Ni	0.3%
Co	5.0%
CaO	5 - 10%
SiO_2	20 - 25%

The above slag was formed by fusing a dross with sand, Na_2CO_3, coke, borax and sulfur in a ratio of 1/2 : 3/4 : 1/2 : 1/2 for each 100 parts of dross charged to the furnace. This slag is fluid at about $1200^{o}C$. The iron after slagging is largely in the ferrous condition; which is indicative that the main silicate is FeO SiO_2. The formation temperatures of ferric silicates are far above the temperatures reached in the dross furnace ($1470^{o}C$).

Spinels were found to accompany the slag from time to time in the form of accretions that float at slag matte interface as an "infusible slag". Samples of accretions or "infusible slag" were taken from the dross furnace and analyzed:

Pb	Cu	Fe	S	Ni	Co	Insoluble
4%	12%	35%	1%	2%	5%	18%

Probable phases present are:

Pb 4%; Cu 7%; Cu_2S 5%; FeO SiO_2 44%; Fe_3O_4 21%; Others 12%; Insoluble (Fe_3O_4) 5%; SiO 13%.

With the above product, crucible fusions were made to find the best combination of fluxing agent which will give a "good fluid" slag i.e. to make the "infusible slag" fusible at the temperature of $1200^{O}C$. The flux studied was a combination of silica sand, borax, soda ash with the additions of coke.

For the mixture:

Slag	20
Infusible slag	20
Bullion	60

The best combination of fluxing material found was:

Sand	10
Soda ash	2
Borax	10
Coke	2

Fluidity was the only factor for judging a good fusion from a bad fusion.

Since the bullion separated from the mixture without difficulty the remaining tests were made using only the "infusible material" mixed with the fluxing mixture.

The effect of borax in fusing accretions:

"Infusible" Slag	Sand	Borax	Soda ash	Coke	Observations
20	5	5	1	1	good fusion
20	5	6	1	1	good fusion
20	5	4	1	1	good fusion
20	5	2	1	1	bad or in-
20	5	0	1	1	complete fusions

Additions of sulfur to form a matte from the insoluble slag:

Insoluble Slag	Sand	Borax	Soda ash	Coke	Sulfur
20	10	4	2	2	2
20	10	4	2	2	4
20	10	4	2	2	6
60	30	8	2	4	8

PbS concentrate additions to provide the sulfur to aid matte formation:

Insoluble Slag	Sand	Borax	Soda ash	Coke	PbS Concentrate
20	10	4	2	2	4
20	10	4	2	2	8
20	10	4	2	2	12
60	30	8	2	4	30

Volume of lead bullion increases with the increase of PbS concentrate (which means we have reducing conditions in the furnace).

	% Pb	% Cu	% Fe	% S	Insoluble
Slag	1	0.5	12	-	76
Matte	29	33	9	17	-
Bullion	75	11	-	-	-

Copper concentrate additions as sulfur provider for the matte formation were also tried for smelting the "accretions".

"Infusible" Slag	Sand	Borax	Coke	Copper Concentrate
60	30	10	2	30
60	30	10	2	20
60	30	10	2	10
60	30	10	2	5

The first fusions gave the following assays:

	% Pb	% Cu	% Fe	% S	Insoluble
Slag	0.5	1	12	-	85
Matte	8	41	19	29	-

The products obtained with the higher copper concentrate additions assayed:

	% Pb	% Cu	% Fe	% S	Insoluble
Slag	0.5	1	19	-	59
Matte	10	61	3	17	-

Results: The spinels could be reduced by adding any of sulfur carrier materials above mentioned. Pb concentrates would be preferred; if copper concentrates are available would be the best addition.

APPENDIX 6

"INFUSIBLE" MATERIAL: 4.0% Pb — 12% Cu — 35% Fe — 1% S
2.0% Ni — 5% Co — 18% Insoluble

Fe

UNKNOWN d	UNKNOWN I	Fe$_3$O$_4$ d	Fe$_3$O$_4$ I	Na Al Si O$_4$ d	Na Al Si O$_4$ I
4.60	W	4.7	60		
4.25	M			4.29	100
3.21	W				
2.96	M	2.96	80		
2.87	W				
2.76	W	2.61	90		
2.59	M				
2.525	S	2.53	100		
2.41	VW	2.41	40		
2.1	W	2.09	80		
1.71	W	1.71	60	1.69	40
1.62	M	1.60	80		
1.49	M+	1.49	100	1.50	60
1.33	W	1.33	40		
1.28	W	1.28	70		
1.12	VW	1.13	50		
1.092	M	1.10	100		
1.05	W	1.05	70		
0.99	VW	0.99	40		

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VIII. VITA

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