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THE INFLUENCE OF ADDITIVE ELEMENTS
ON THE DECOPPERIZING OF LEAD

by

Richard Joseph McClincy

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Metallurgical Engineering.

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ABSTRACT

Laboratory-scale decopperizing experiments were conducted on ternary lead-copper alloys containing as the third element, Sn, Ag, As, Sb, Bi, Zn, and Au (common impurities in lead blast furnace bullion). Sulfur, hydrogen sulfide, and lead sulfide were used independently as sources of sulfur. In the decopperizing with sulfur, copper removal as a function of individual added elements is observed to decrease in the order Sn, Ag, As, Sb, no element added, Zn, Au, Bi.

A possible mechanism for the decopperizing of lead is suggested. Based upon experimental evidence, a calculation has been made to determine the limiting copper concentration in lead as 1.26×10^{-6} weight percent.

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INTRODUCTION

The removal of copper from lead blast-furnace bullion is accomplished in two operations. A hot drossing operation is first performed at a temperature near 400°C. When the bullion is cooled to this temperature, sulfides and arsenides of various impurities separate from the melt as a solid dross according to their solubility limits. The copper concentration normally decreases to about 0.05 w/o (weight percent) during this operation. Since copper greatly increases zinc consumption during the desilverizing process and interferes with the subsequent treatment of the silver-zinc crusts, it is desirable to lower the copper concentration even further. This decopperizing is accomplished in the cold drossing operation in which the lead bullion is cooled to about 330°C, at which temperature elemental sulfur is stirred into the bath in the amount of 1 to 2 pounds per ton of bullion. The residual copper concentration in the bullion is normally between 0.001 w/o and 0.005 w/o after cold drossing. The

calculable equilibrium copper concentration is an order of magnitude greater than the values obtained in commercial practice as described above.

Purpose of Investigation

This study of lead decopperizing was undertaken in order to gain some information as to why very low copper concentrations are achieved in commercial practice. This investigation qualitatively determines the effect of additive elements on the degree to which copper can be removed from liquid lead by successive sulfur treatments using sulfur and hydrogen sulfide as the sources of sulfur. The impurity elements were added singly to prepared lead-copper alloys; no attempt was made to study their effects in combination. A second purpose of this investigation was to analyze the suggestions that have been proposed to account for the mechanism of decopperizing.

Survey of the Literature

Most investigators have suggested that the various impurities in the lead bullion are responsible for the lower copper concentrations observed in practice. There is little agreement, however, as to which of the impurities are helpful and which are not. Haig (1950, p. 316) insists that tin must be present in amounts above 0.15 w/o in order to achieve a

copper concentration below 0.04 w/o. Haney (1950, p. 321), on the other hand, states that tin need not be present in any amount. Gallagher (1951, p. 42) proposes that the copper content after sulfur treatment falls to 0.003 w/o as the arsenic content rises to 0.08 w/o. Dennis (1954, p. 244) and Blanderer (1959, p. 662) require that antimony be present in order to reach copper concentrations of from 0.002 w/o to 0.010 w/o. Willis and Blanks (1959, p. 1007) find that silver must be present. Gahkaishi (1964, p. 601) reports that antimony, arsenic, and tin hinder the removal of copper from lead, and that silver aids copper removal to a small extent at temperatures between 500°C and 800°C. Kunchev and Nikolov (1964, p. 19) declare just the opposite; antimony, arsenic, and tin aid in the removal of copper from lead bullion.

The empirical studies outlined above make no attempt to establish the nature of the effects described. Few investigators have sought to explain the mechanism responsible for the removal of copper to very low concentrations. Willis and Blanks (1959, p. 1012) proposed that a non-stoichiometric copper-deficient copper sulphide formed in place of the supposed Cu_2S . Being copper-deficient, this sulphide phase would possess a low copper activity, and the diffusion of copper dissolved in the liquid lead into this phase would

be greatly facilitated.

Pin and Wagner (1963, p. 1275) investigated the removal of copper from liquid lead by studying the effect of impurity-doped lead sulphide on decopperizing pure lead-copper alloys. It was found that copper removal decreased in the order bismuth-, antimony-, tin-, and silver-doped lead sulphide. In this case, it was found that the addition of silver to the lead sulphide resulted in slightly less copper removal than when pure lead sulphide was used.

APPARATUS AND EXPERIMENTAL PROCEDUREApparatus

The decopperizing experiments were carried out in a reaction tube which was constructed of pyrex tubing (25-mm-O.D., 375-mm-long) sealed at one end. This tube was mounted vertically in a resistance-heated hinge-type tube furnace. The furnace was equipped with two chromel-alumel thermocouples. One was mounted on the outside of the reaction tube and controlled the furnace temperature by means of a Barber-Coleman Model C293 controller. The second thermocouple was placed in a pyrex tube (6-mm-O.D., 500-mm-long) and lowered into the liquid metal alloy to measure its temperature by means of a potentiometer. Control of the liquid alloy temperature was within $\pm 1^{\circ}\text{C}$.

In order to add as little equipment as possible to the inside of the reaction tube, the tube containing the measuring thermocouple was used as a stirring rod. The sealed end of the tube was flattened for a distance of 1 cm from the

end and bent at an angle of 90° to the remainder of the tube. The stirring rod thus formed was used with a plunging as well as a rotary action and was operated manually.

To convert the apparatus to use with a $\text{H}_2\text{S}/\text{H}_2$ gas mixture as the source of sulfur, two separate gas trains were constructed of 9-mm-O.D. pyrex tubing. The use of two gas trains enabled the gas ratio to be varied over a range of desired values. Due to the high purity of the gases used, it was decided not to include drying chambers or gettering furnaces in the gas trains. A mercury pressure-relief bubbler was located between the furnace and the confluence of the two gas trains to protect the system against a blockage of the gas stream within the furnace.

The gas mixture was admitted to the liquid metal alloys by a pyrex lance (6-mm-O.D.). The measuring thermocouple was simply placed in a pyrex tube (6-mm-O.D., 500-mm-long) sealed at one end.

The gas-flow apparatus is shown schematically in Figure 1.

Experimental Procedure

Sulfur, hydrogen sulphide, and lead sulphide were each used as a source of sulfur for decopperizing lead in this study. The removal of copper was presumed to take place according to the reactions:

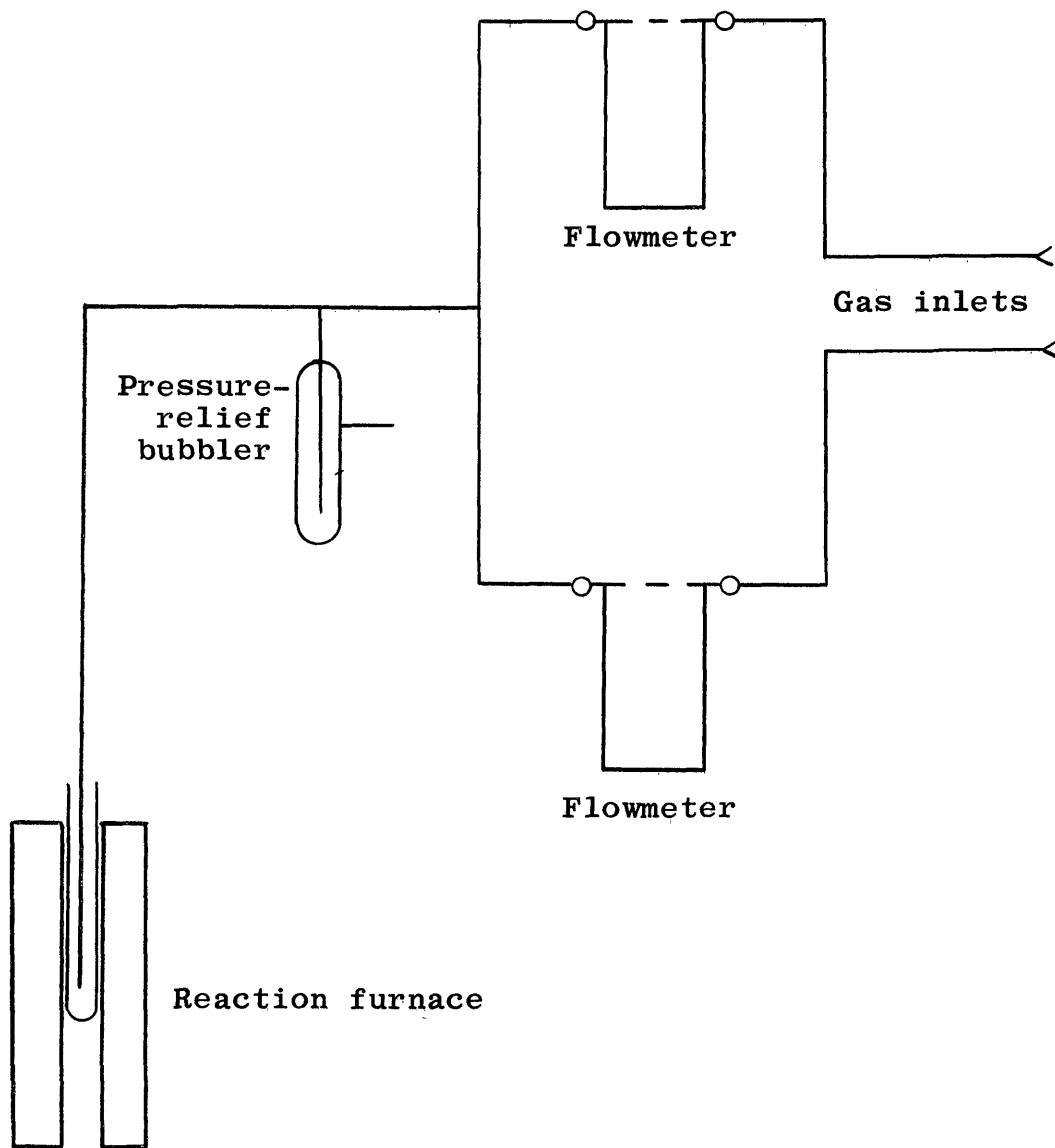
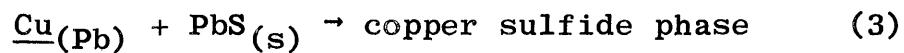
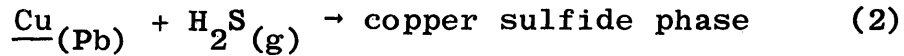
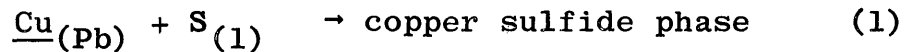


Figure 1. Schematic diagram of the gas-flow system.



In order to determine the effect of additive elements on these reactions, it was necessary to first establish the limit of copper removal from lead when no impurities were present. Various impurities were then added to the lead-copper alloy, and the decopperizing experiments were repeated. When the residual copper concentration of the lead alloys containing additive elements were compared with the values obtained for the pure lead copper alloy, the effect of the additive element could be determined.

Preparation of the Test Alloys. The various alloys prepared for the experimental study consisted of 1 binary and 7 ternary alloys. The constituent elements were all American Smelting and Refining Company research-grade materials of 99.999% purity, with the exception of the Sb, Sn, and Zn, which were of 99.99% purity, and the As, which was 98-99% pure. (Spectrographic analysis for each of the elements Pb, Cu, Ag, Sb, Au, and Bi is given in Appendix I.)

The elements Pb and Cu were mixed in the desired proportions and placed in a plumbago crucible for melting

after the crucible had been first washed several times by melting pure lead in it. The charge was then covered with a 1-in.-thick layer of carbon powder and placed in a resistance-heated furnace heated to 600°C. The alloy was stirred with a graphite rod at half-hour intervals for a period of 2 hours. At the end of this period, the alloy was poured into cold tap water to produce lead alloy shot. The shot was then dried and packed in air-tight containers until it was used.

Representative samples were collected from each batch of starting alloy and analyzed for exact copper concentration by means of the A.S.T.M. Standard Test Designation: E87-58, Copper by the Cupric Bromide Method. (The stepwise analytical procedure is given in Appendix II.)

The ternary alloy was prepared by first diluting the lead copper alloy to a constant reference copper concentration using high purity lead. The particular additive element was then weighed to yield the desired concentration and mixed with the lead-copper alloy. The ternary alloy thus prepared was melted at a temperature of 450°C and homogenized for 15 minutes with frequent stirring. The temperature was then lowered to the operating temperature and stabilized before beginning the experiment.

Decopperizing with Sulfur. A sample of 100 grams of the test alloy containing 0.05 w/o Cu and a small concentration of one of the additive elements was melted and homogenized as described in the preceding section. Because the efficiency of copper removal increases as the temperature approaches the melting point of lead, a temperature of 330°C was selected for the experiments.

Once thermal equilibrium had been attained at the operating temperature, 0.2 w/o (0.2 gm.) of solid sulfur was added to the bath and vigorously stirred in. Stirring was continued for a period of 3 minutes, discontinued for 5 minutes, and resumed for the remaining 2 minutes of a 10-minute cycle. This cycle was repeated for as many sulfur additions as desired.

Upon completion of the last cycle, the reaction tube was removed from the furnace, and the molten alloy was solidified as rapidly as possible by quenching in a strong blast of cold air. Representative samples were collected from the center of the resulting lead alloy slug and weighed and analyzed for residual copper concentration, as described in Appendix II.

Decopperizing with H₂S. A sample of 100 grams of the test alloy containing 0.075 w/o copper, plus a small concentration of one of the additive elements, was melted and

homogenized as described earlier. Stirring of the liquid alloy during homogenization was accomplished by means of a stream of hydrogen (@300 cc/min.) admitted through a 6-mm-O.D. pyrex lance. The lance was positioned so that the gas entered the liquid alloy at a point 15 mm above the center of the bottom of the reaction tube.

When the homogenization of the alloy was complete, the furnace controller was set at 350°C, and the alloy was allowed to come to thermal equilibrium. A temperature of 350°C was used in these experiments because the entering stream of gas caused slight temperature fluctuations which often resulted in solidification of the alloy at lower temperatures. When thermal equilibrium had been achieved, H₂S was admitted to the alloy at 100 cc/min. This flow-rate resulted in a gas ratio of 0.33 H₂S/H₂. The H₂S/H₂ gas mixture was then reacted with the sample alloy for times up to 120 min.

When the desired reaction time had elapsed, the lance was withdrawn from the liquid alloy, and the reaction tube was removed from the furnace. The liquid alloy was quenched in a blast of cold air as described in the preceding section. Elapsed time between removal of the gas supply and complete solidification was less than 1 min. Samples were collected for analysis to determine the residual copper concentration.

Decopperizing with PbS. Several experiments were performed with PbS as the source of sulfur. A pure lead-copper alloy containing 0.05 w/o copper was prepared and homogenized at 330°C. Additions of 1.00 gm of PbS were made to 100 gm of the alloy and manually stirred into the liquid alloy for a period of 15 min. Samples were collected and analyzed for residual copper concentration, as described in Appendix II.

Equilibria Studies. Willis and Blanks (1959, p. 1014) have pointed out that the formation of a non-stoichiometric copper-deficient copper sulphide may be formed wherever a high sulphur potential is maintained. If this phase had a sufficiently low copper potential, it would appear that copper concentrations well below the equilibrium value for Cu_2S could be expected in lead bullion if the kinetics of the reactions involved were fast enough. In order to investigate this possibility, two-phase mixtures consisting of Cu and Cu_2S , and " Cu_2S " and PbS were equilibrated with pure lead to determine the equilibrium copper concentration when a high copper potential prevailed and when a low copper potential prevailed.

Pure copper and sulfur were mixed in stoichiometric quantities to yield a total of 2 grams of the two-phase mixture. The Cu- Cu_2S mixture contained 18.00 w/o sulphur.

The mixture was placed in a Vycor glass tube (9-mm-O.D.) sealed at one end. The tube was necked down approximately 3 in. above the sample mixture. Small pieces of titanium sponge were placed in the tube, and a second necking operation was performed. The resulting tube was approximately 10 in. long and consisted of three separate chambers; the first contained the copper and sulfur mixture, the second contained Ti sponge, and the third was left open to the atmosphere. The capsule was then evacuated for 1 hour by means of a Welsh Duo Seal vacuum pump (Model 1405 B) and sealed off at the neck above the Ti sponge. The chamber containing the sponge was then placed in a tube furnace and heated at 750°C for 24 hours. This gettering operation removed any residual traces of oxygen and nitrogen. When gettering was complete, the chamber containing the Ti sponge was sealed off and removed from the capsule.

The remaining chamber containing the sample mixture was placed in a tube furnace at 450°C for 48 hours to insure equilibrium conditions and then rapidly quenched in cold tap water. The resulting two-phase mixture was removed from the capsule and finely ground.

In order to insure that the desired phases were present, each sample was qualitatively analyzed with an x-ray diffractometer. (A.S.T.M. values for "d" spacings

and 2θ angles for PbS, CuS, and Cu₂S are given in Appendix IV.)

The Cu-Cu₂S mixture was added to the top of approximately 10 gm of 99.999+% purity lead in a 9-mm-O.D. Vycor glass tube sealed at one end. The tube was prepared as before with three separate chambers; the first contained the mixture to be equilibrated, the second contained Ti sponge, and the third was left open to the atmosphere. Evacuation and gettering were accomplished as described before. The resulting sample chamber was placed vertically in a resistance-heated tube furnace and heated at 330°C for times up to 14 days to insure equilibrium conditions.

At the completion of the experiment, the two-phase mixture remaining above the lead phase was removed from the capsule and qualitatively analyzed by x-ray diffraction a second time to insure that no phase changes had taken place during the equilibration which would have changed the constant value of the copper potential set by the phases present at the start of the experiment. The lead phase was cleaned and sampled for copper analysis by the procedure discussed in Appendix II.

In order to define the limit of copper removal from lead by the use of PbS as a source of sulfur, samples of a lead-copper alloy (0.05 w/o Cu) were equilibrated with a

large excess of lead sulfide. Capsules were prepared by the method outlined in the preceding discussion, and the decopperizing experiments were conducted under equilibrium conditions. The samples were held at 330°C for 120 hours in order to determine the approximate equilibrium copper concentration of liquid lead coexisting with PbS.

Another set of samples were prepared in capsules to determine the equilibrium copper concentration in liquid lead at 330°C. A pure lead-copper alloy containing 0.100 w/o copper was equilibrated for 336 hours. In addition, samples of pure lead in contact with an excess of pure copper were equilibrated for 115 hours and 336 hours. By approaching the equilibrium concentration from both directions one could determine the true value.

RESULTS OF EXPERIMENTS

The experimental results for decopperizing lead alloys with elemental sulfur are illustrated by Figures 2 to 11. The data represented by these curves are summarized in Table I. The results for decopperizing lead alloys with H_2S are presented graphically in Figure 12.

Decopperizing with Sulfur

Industrial practice utilizes elemental sulfur as the source of sulfur in the decopperizing of blast-furnace lead bullion, and for this reason the present study investigated the system Pb-Cu-M-S in some detail. The alloys studied consisted of a basic lead-copper alloy containing 0.05 w/o Cu plus a small concentration of one of the elements Sn, Ag, Sb, As, Bi, Au, and Zn.

Sulfur additions consisting of 0.20 gm (0.20 w/o) were made to 100-gm samples of the binary lead-copper alloy as well as to the above-mentioned series of ternary alloys.

The results for each of the alloys studied are presented graphically in Figures 2 to 11 and are summarized in Table I. For purposes of comparison, the experimental curve obtained for the pure lead-copper alloy is included in the figures for each of the ternary alloys.

It can be seen in Figure 2 that a pure lead-copper alloy can be quite successfully decopperized with sulfur if a sufficient number of treatments are performed. It is also apparent that this curve has no limiting value in the range of concentrations shown. Further sulfur additions could not be made to determine the limiting value due to the small size of the test sample.

Of all the alloys studied, a lead-copper alloy containing 0.50 w/o Sn resulted in the lowest residual copper concentration after 1 sulfur addition. Figure 3 illustrates that the copper concentration continued to decrease with repeated sulfur treatments until it was beyond the limits of the analytical procedure (25 ppm) after 5 sulfur additions.

The addition of 0.20 w/o Ag to the basic lead-copper alloy also resulted in very low copper concentrations following several sulfur additions. A limiting copper concentration was found to be approximately 0.00035 w/o Cu after 3 sulfur treatments, as shown in Figure 4.

A ternary alloy containing 0.15 w/o As was also found

Table I. Summary of experimental results of decopperizing lead alloys with sulfur as a function of sulfur additions at 330°C.

Alloy	Sulfur Additions	Residual % Cu	Alloy	Sulfur Additions	Residual % Cu	
0.05% Cu	1	0.0375	0.05% Cu 0.05% Zn	1	0.0347	
	1	0.0377		1	0.0346	
	2	0.0252		3	0.0161	
	3	0.0175		3	0.0247	
	5	0.00984		5	0.0140	
	7	0.00384		7	0.0109	
	9	0.00162				
				0.05% Cu	1	0.0335
				0.002% Au	1	0.0333
0.05% Cu	1	0.00832				
0.05% Sn	1	0.0131		3	0.0206	
	3	0.00692		3	0.0214	
	3	0.00375		5	0.0210	
	5	0.00589		7	0.00836	
	7	0.00495				
			0.05% Cu	1	0.0174	
0.05% Cu 0.50% Sn	1	0.00343	0.20% Ag	1	0.0162	
	1	0.00206		2	0.00035	
	2	0.00066		2	0.00082	
	3	0.00019		3	0.00050	
	3	0.00018		3	0.00038	
	5	0.0000		5	0.00033	
0.05% Cu 5.00% Sn	1	0.00270	0.05% Cu 0.80% Sb	1	0.0337	
	1	0.00165		1	0.0323	
	3	0.00046		3	0.0146	
	3	0.00046		3	0.0165	
	5	0.00052		5	0.00890	
	7	0.00014		7	0.00164	
0.05% Cu 0.15% As	1	0.0192	0.05% Cu 0.20% Bi	1	0.0355	
	1	0.0171		1	0.0408	
	3	0.0148		3	0.0264	
	3	0.0138		3	0.0190	
	5	0.00928		5	0.0236	
	7	0.00973		5	0.0107	
				7	0.0232	
0.05% Cu* 0.50% Sn	1	0.0397				
	1	0.0389				
	3	0.0278				
	3	0.0314				
	5	0.0202				
	7	0.0207				

*Experiments made at 430°C.

to respond more rapidly to sulfur treatment than the pure lead-copper alloy. A limiting value was soon reached, however, which virtually stopped the removal of copper. This limiting value was quite high and was found to be approximately 0.009 w/o Cu after 7 sulfur treatments.

An alloy addition of 0.80 w/o Sb resulted in no effect on the decrease in copper concentration of the pure lead-copper alloy when less than 7 sulfur additions were made. The experimental results for this alloy are shown in Figure 6.

Alloy additions of 0.20 w/o Bi, 0.05 w/o Zn, and 0.002 w/o Au resulted in little or no effect on the copper removal obtained with the pure lead-copper alloy. In most of the experiments in which more than one sulfur addition was made, the influence of the additive element was in a negative sense; i.e., copper removal was hindered. The influence of these three additive elements are shown graphically in Figures 7 to 9.

Due to the very pronounced effect of tin on the de-copperizing of lead alloys, additional experiments were made to determine the effect of a variable tin concentration and the effect of an elevated temperature on the rate of copper removal. Alloys were prepared in which the concentration of tin was changed from 0.50 w/o to 0.05 w/o and 5.00 w/o. The results of these experiments are illustrated

in Figure 10.

It is seen that the higher concentration of tin resulted in much the same effect for the first two sulfur additions but became significantly less pronounced with continued sulfur treatments. The lower tin concentration also resulted in a very definite positive effect on the removal of copper but to a lesser extent than with the higher concentrations.

A series of alloys containing 0.50 w/o Sn were decopperized at an elevated temperature of 430°C rather than 330°C, as were all of the other alloys decopperized with sulfur. The results of these experiments are illustrated in Figure 11, together with the curve obtained for this alloy at 330°C. It is readily apparent that the beneficial effect of tin is completely nullified at this elevated temperature.

Decopperizing with H₂S

In the experiments in which lead alloys were decopperized with H₂S, the reference alloy to which the additions were made contained 0.075 w/o Cu. An H₂S-H₂ gas mixture was used as the source of sulfur at a composition corresponding to H₂S/H₂ = 0.33. Due to small temperature fluctuations caused by the incoming gas stream, the operating temperature was raised to 350°C. Reaction times were increased until

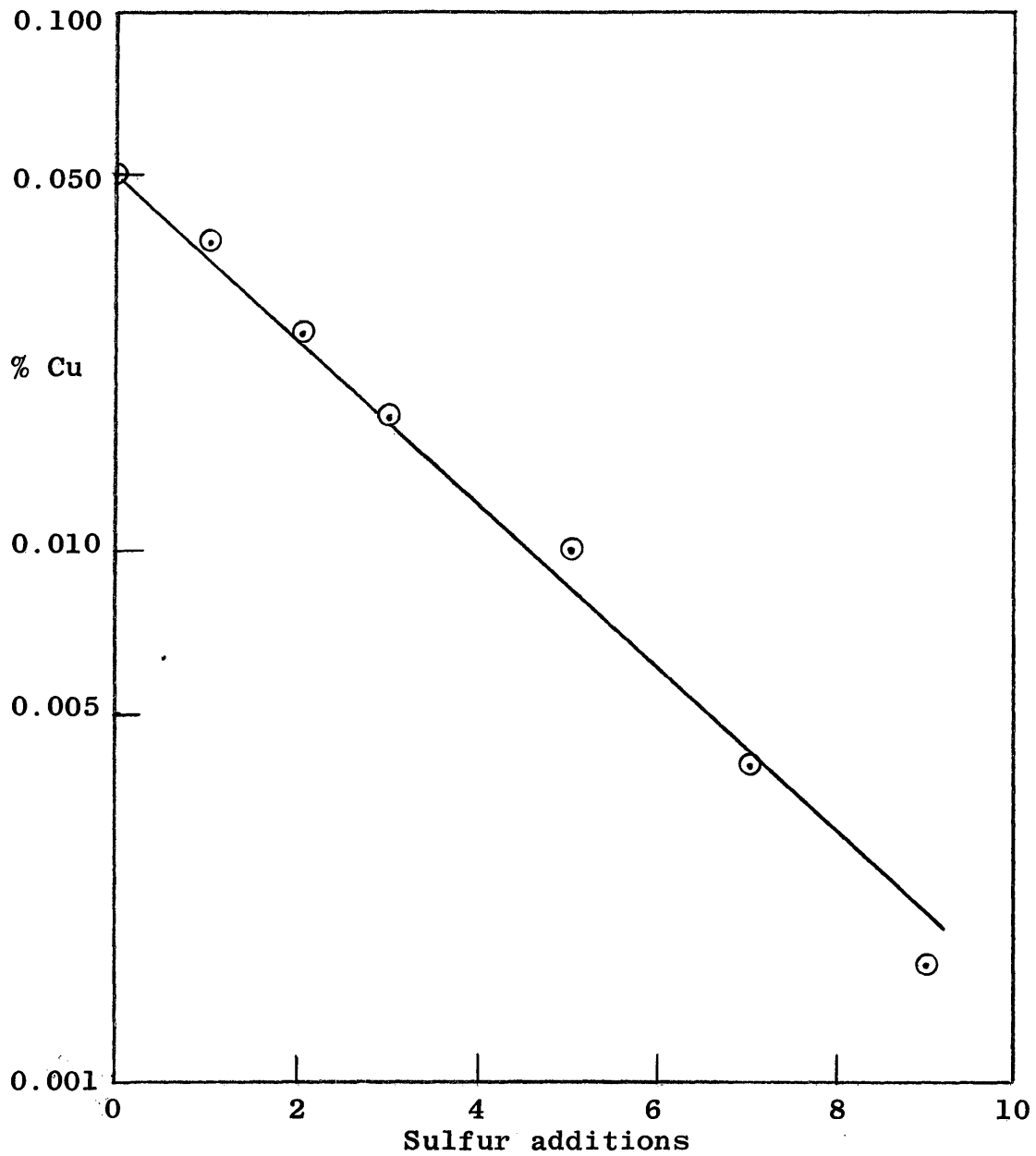


Figure 2. Residual copper concentration versus sulfur additions for a lead-copper alloy.

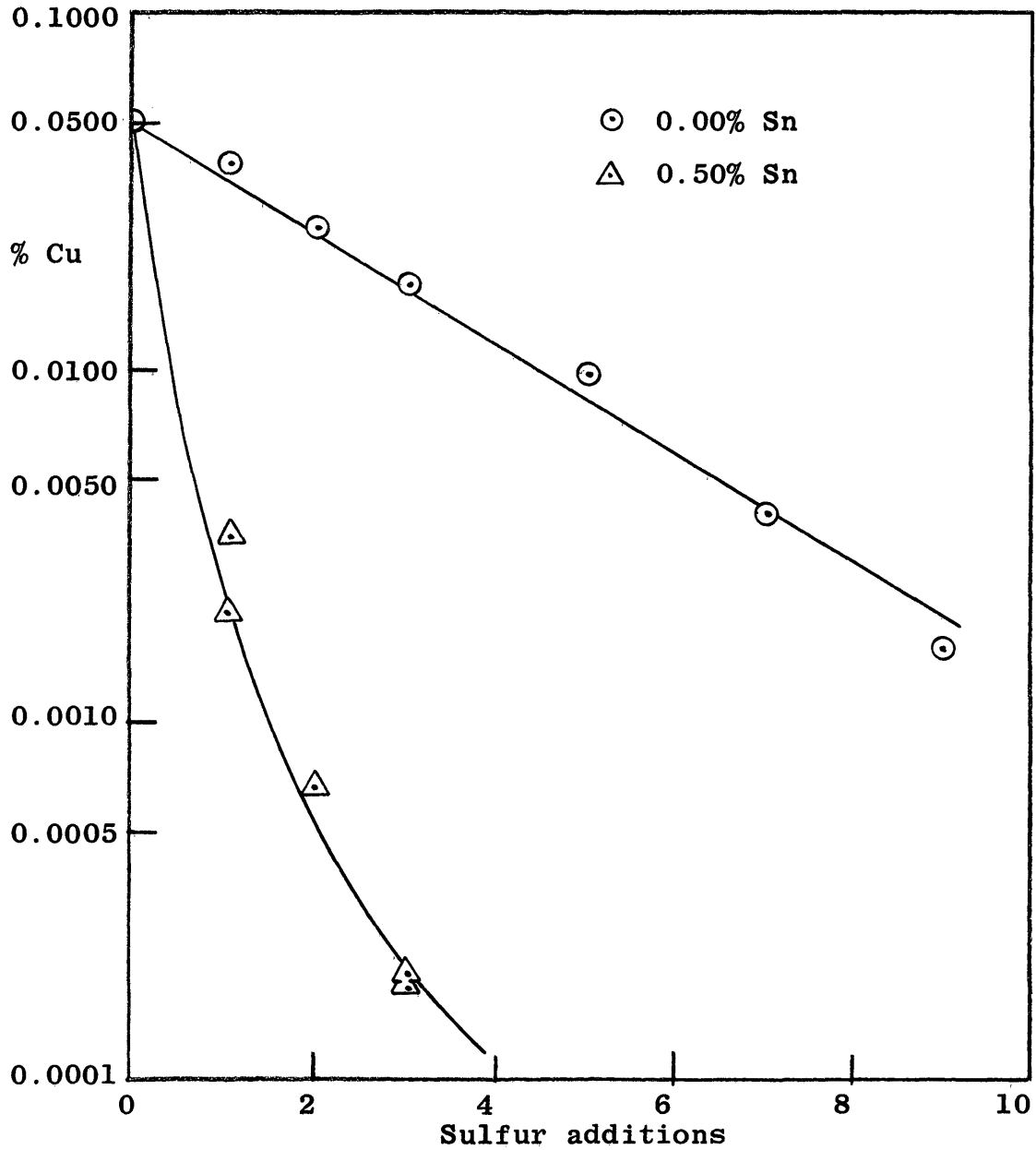


Figure 3. Residual copper concentration versus sulfur additions for a lead-copper-tin alloy.

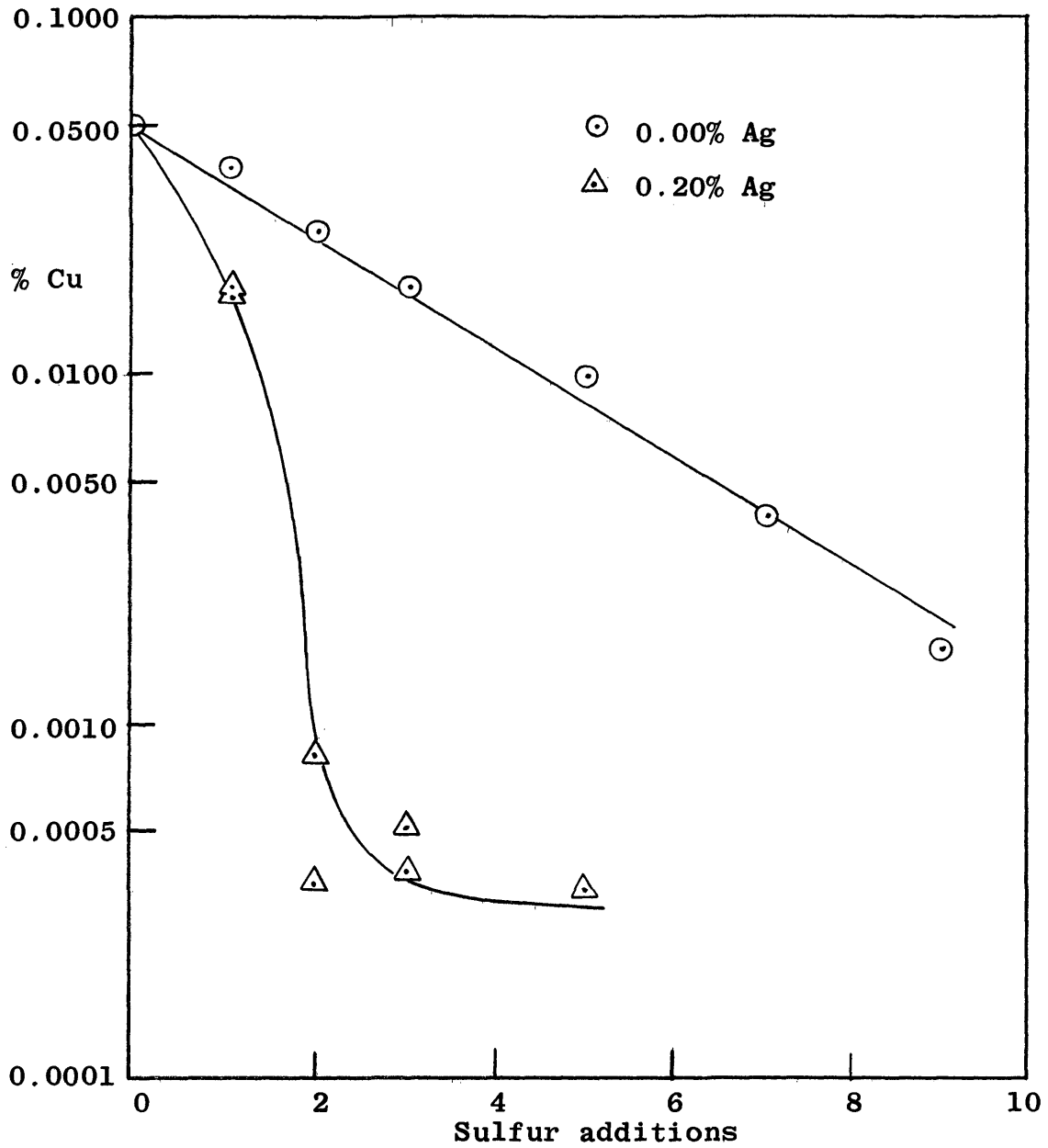


Figure 4. Residual copper concentration versus sulfur additions for a lead-copper-silver alloy.

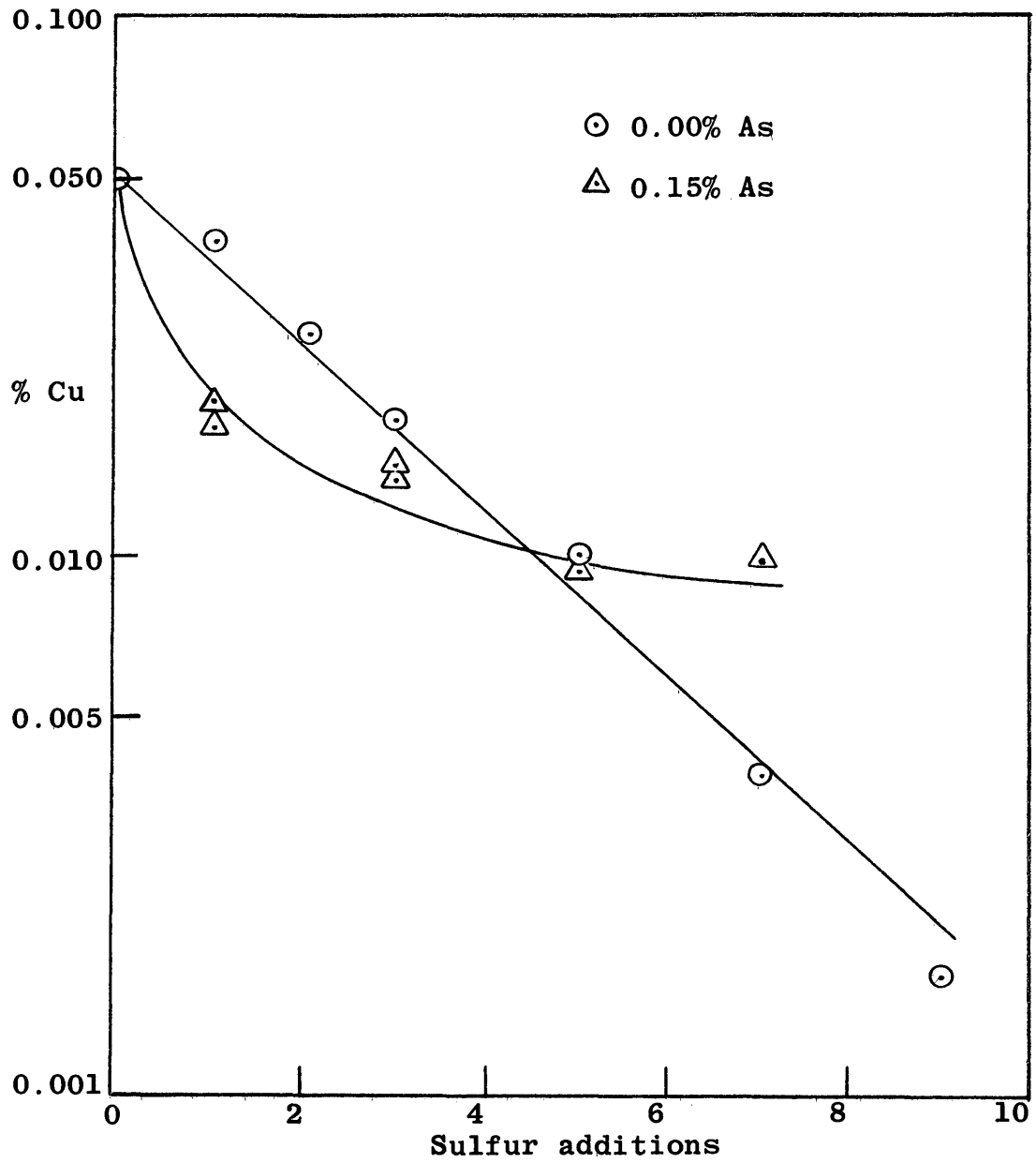


Figure 5. Residual copper concentration versus sulfur additions for a lead-copper-arsenic alloy.

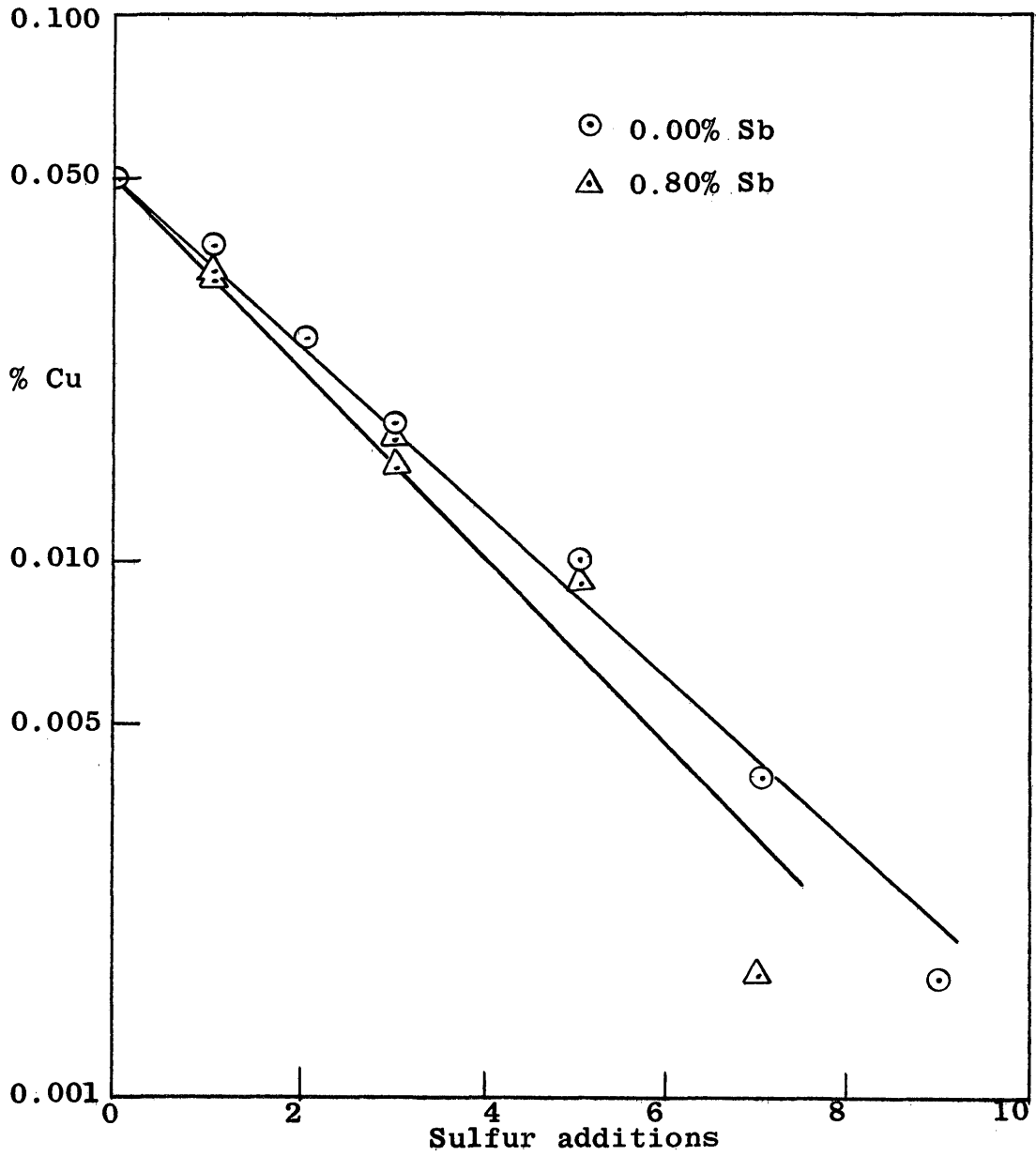


Figure 6. Residual copper concentration versus sulfur additions for a lead-copper-antimony alloy.

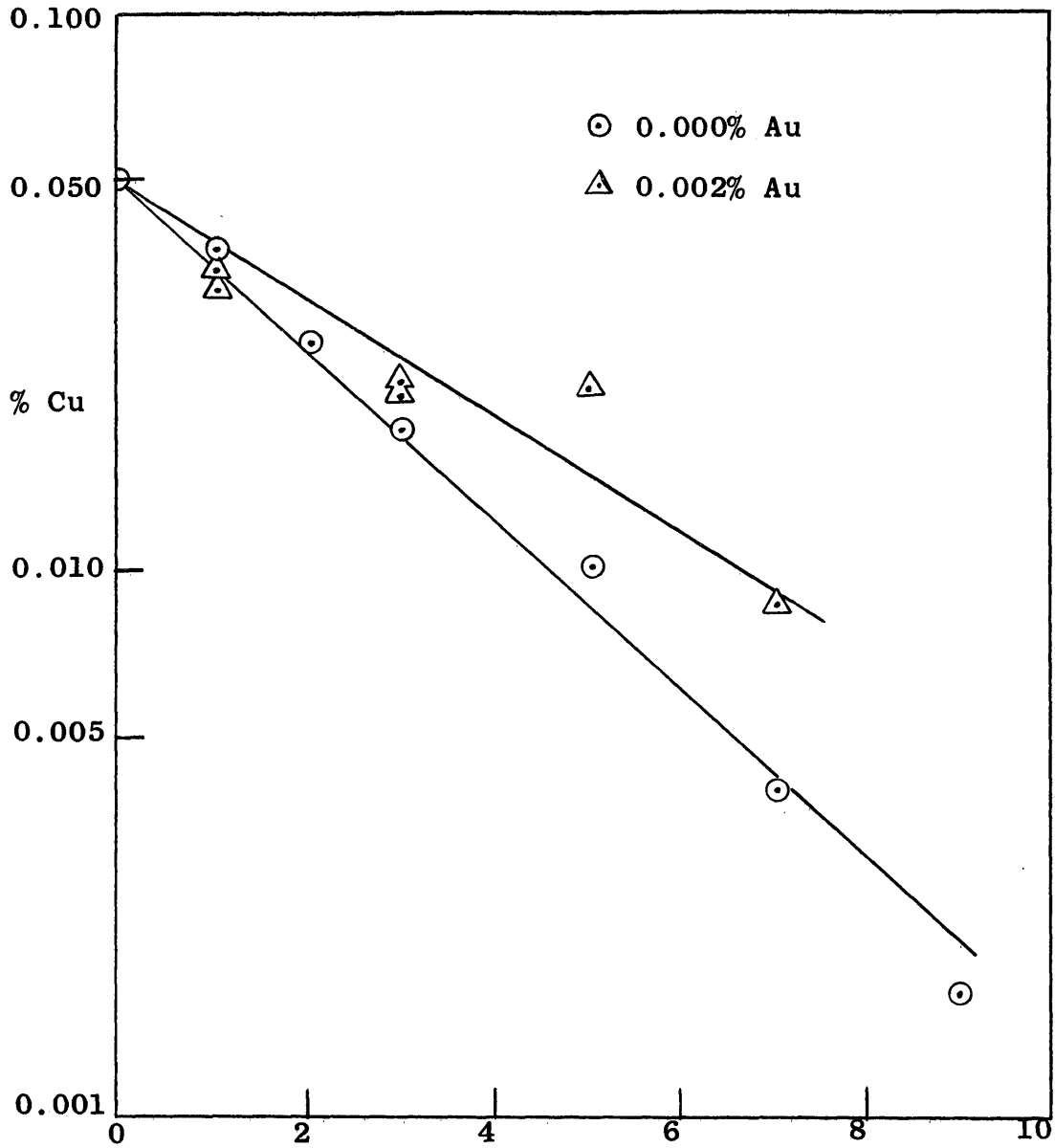


Figure 7. Residual copper concentration versus sulfur additions for a lead-copper-gold alloy.

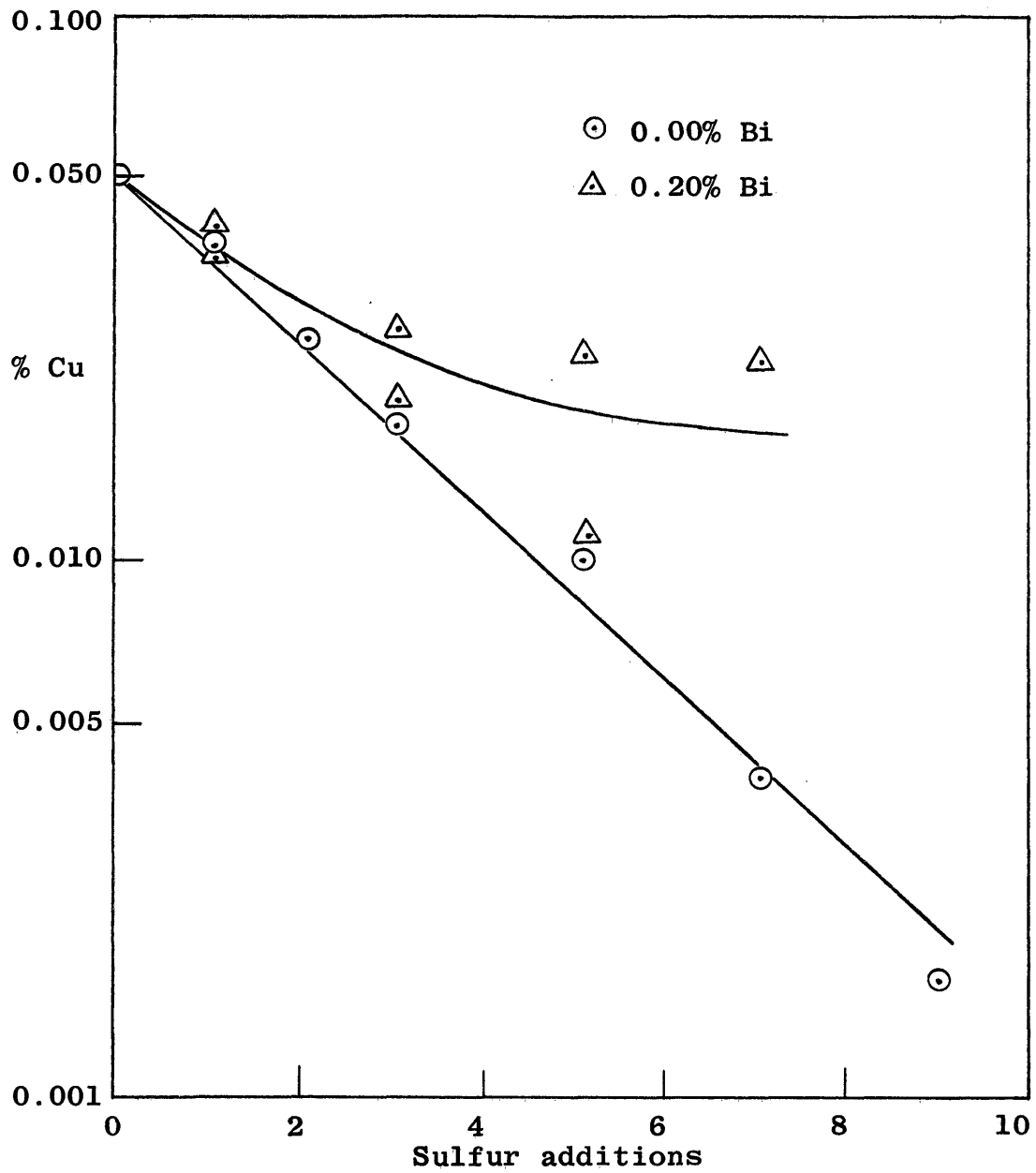


Figure 8. Residual copper concentration versus sulfur additions for a lead-copper-bismuth alloy.

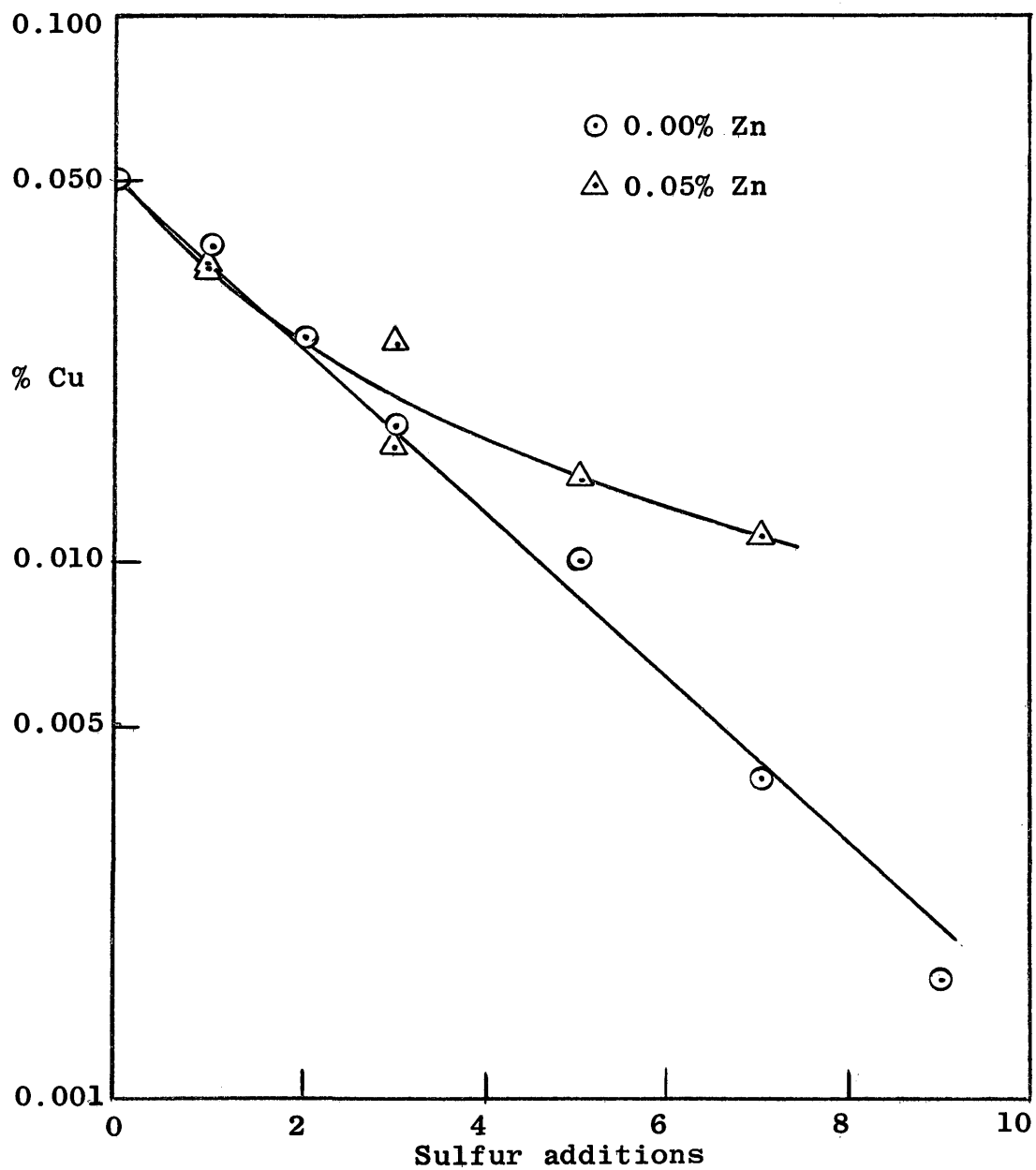


Figure 9. Residual copper concentration versus sulfur additions for a lead-copper-zinc alloy.

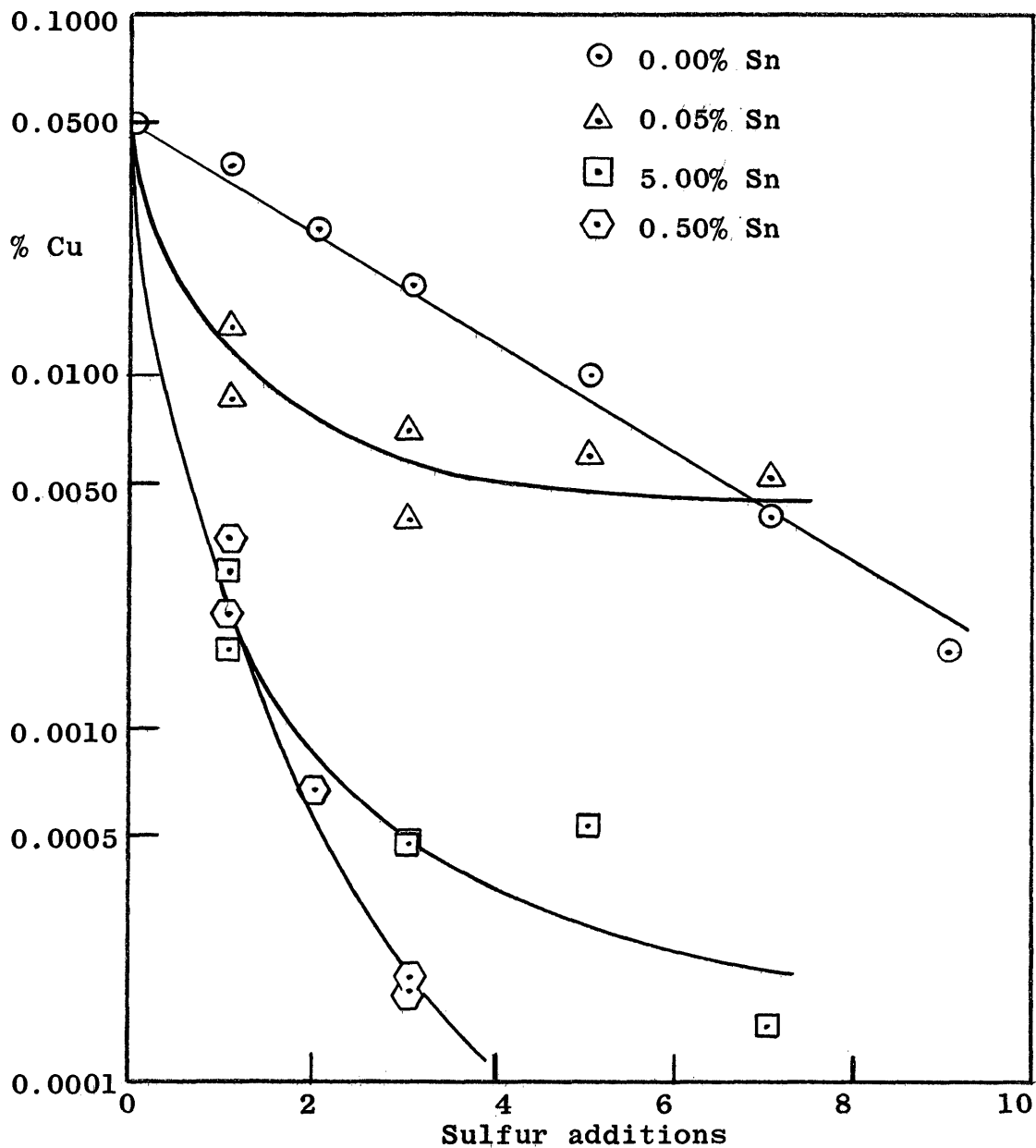


Figure 10. Residual copper concentration versus sulfur additions for lead-copper-tin alloys.

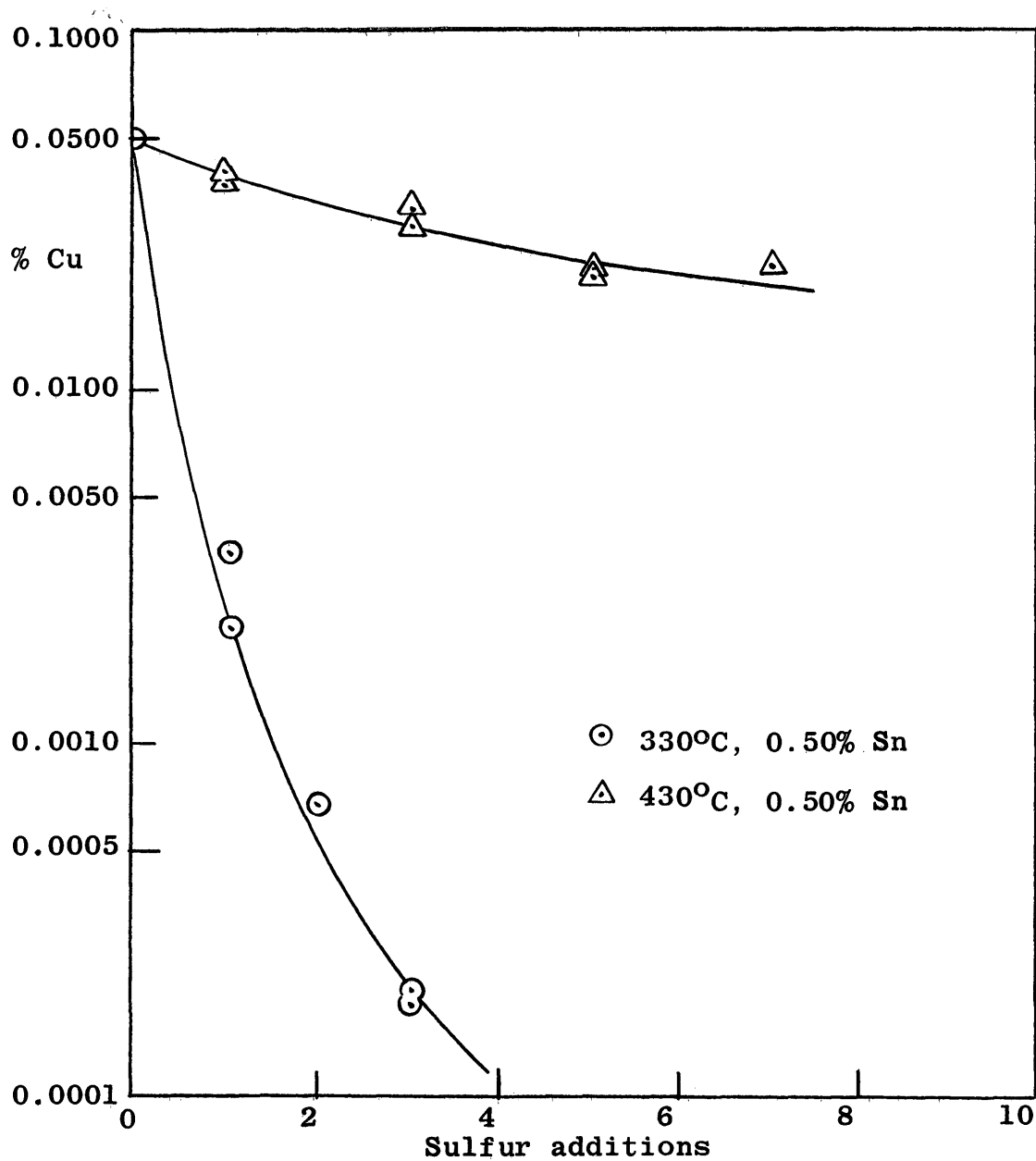


Figure 11. Residual copper concentration versus sulfur additions for a lead-copper-tin alloy at two different temperatures.

a steady-state value of copper concentration was achieved. The value obtained in this study was 0.006 w/o Cu at a reaction time of 120 minutes. The experimental data are presented graphically in Figure 12.

Alloys were prepared that contained 0.20 w/o Ag and 0.50 w/o Sn and decopperized with the same H_2S/H_2 gas mixture to determine any effect on the limiting value of copper concentration obtained with the pure lead-copper alloy. It was observed that silver had no effect on the limiting copper concentration and that tin appeared to have interfered with the copper removal. The results of these experiments are presented in Figure 12.

It was expected that silver and/or tin would show the greatest effect on the decopperizing of lead. Since preliminary experiments indicated that silver and tin had no positive effect on the reactions or the rates of the reactions involved, the study of H_2S as the source of sulfur for decopperizing was discontinued.

Decopperizing with PbS

Two 100-gm samples of a pure lead-copper alloy containing 0.05 w/o Cu were decopperized with reagent grade PbS in the amount of 1 gm (1 w/o). One addition of PbS was stirred into the liquid alloy at 330°C for 15 minutes

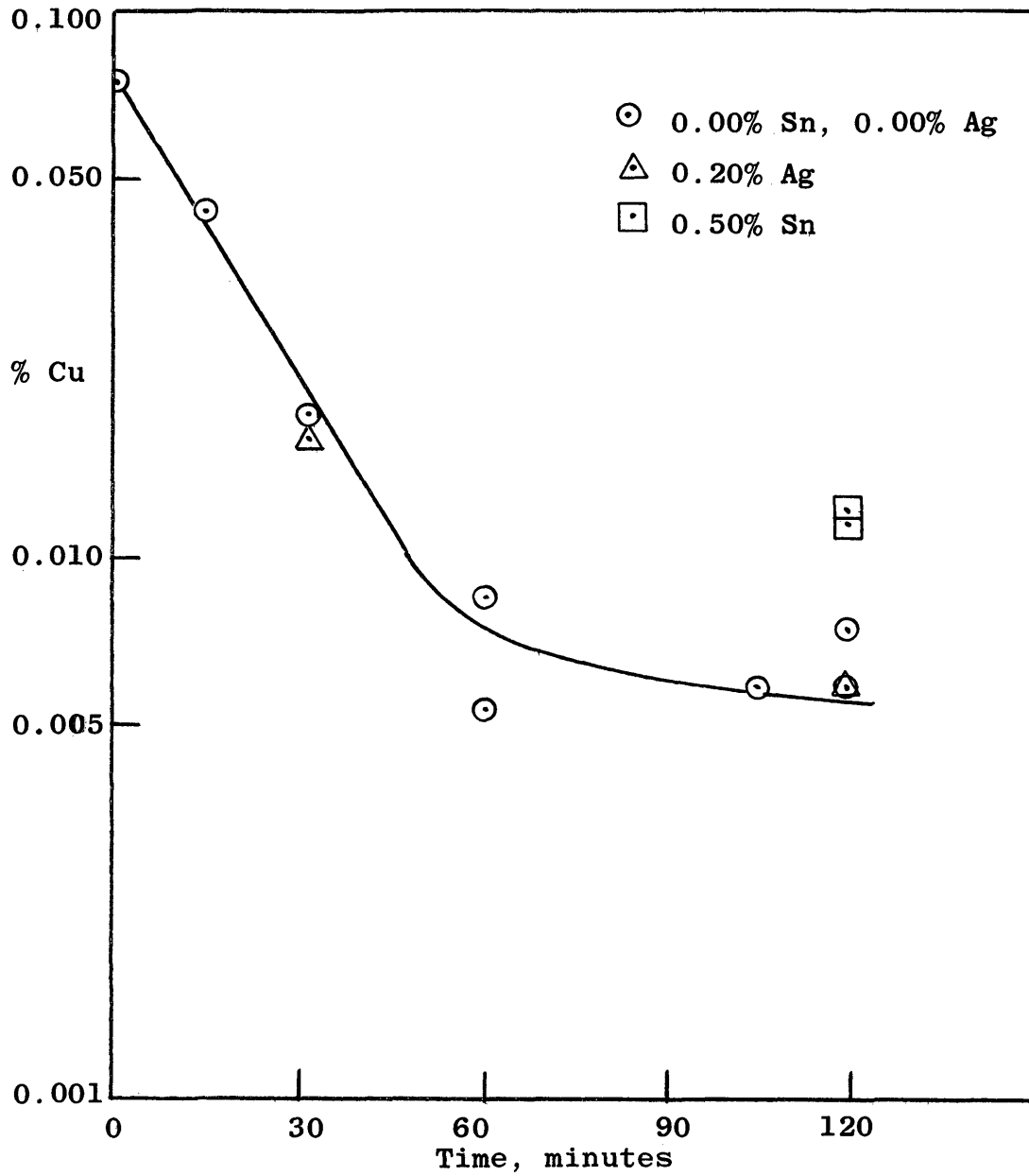


Figure 12. Residual copper concentration versus time for decopperizing Pb-Cu, Pb-Cu-Ag, and Pb-Cu-Sn alloys with H_2S .

before the alloy was quenched and sampled. The two alloys were found to decrease in copper concentration from 0.05 w/o Cu to 0.0486 w/o and 0.0485 w/o. Due to the very poor copper removal observed, the study of PbS as a source of sulfur for the decopperization of lead alloys was not continued further.

Equilibria Studies

Various mixtures of copper, cuprous sulfide, and lead sulfide were equilibrated with lead and lead-copper alloys. The results of these experiments determine the equilibrium copper concentrations of lead in equilibrium with Cu and Cu_2S , and " Cu_2S " and PbS.

The experimental results are presented in Table 2.

Many of the data of Table 2 are somewhat incomplete. The rate of attaining equilibrium in some of the experiments was prohibitively long from one of the two directions attempted. In such instances the equilibrium condition was approached from only one direction. Thus, the results are meant to be only an approximation and do not necessarily represent the true equilibrium concentration.

It was observed that the solubility limit of copper in lead at 330°C was slightly above the starting concentration for the decopperizing experiments. A value of 0.062 w/o Cu was determined.

Table 2. Experimental results for various equilibria in the lead-copper-sulfur system,

Phases	Initial % Cu in Pb	Final % Cu in Pb	Temperature (°C)	Reaction Time (hrs)
Pb-Cu-Cu ₂ S	0.0000	0.0305	330	48
Pb-Cu-Cu ₂ S	0.0000	0.0341	330	115
Pb-Cu-Cu ₂ S	0.0500	0.0429	330	120
Pb-Cu-Cu ₂ S	0.0500	0.0480	330	336
Pb-Cu	0.0000	0.0580	330	115
Pb-Cu	0.0000	0.0591	330	115
Pb-Cu	0.0000	0.0616	330	336
Pb-PbS	0.0500	0.0196*	330	120
Pb-PbS	0.0500	0.0213*	330	120
Pb-"Cu ₂ S"-PbS	0.0000	0.0225	330	120
Pb-"Cu ₂ S"-PbS	0.0000	0.0358	330	240

*Value depends on sulfur content of lead (see Figure 13).

When stoichiometric cuprous sulfide was equilibrated with pure copper and lead, a residual copper concentration of 0.0480 w/o was determined. The copper-deficient cuprous sulfide, denoted as "Cu₂S", was equilibrated with lead and lead sulfide; the decreased copper potential in the cuprous sulfide resulted in a somewhat lower residual copper concentration of 0.0358 w/o.

Lead sulfide as a source of sulfur for decopperizing was found not to be as efficient as pure sulfur. A residual copper concentration of 0.02 w/o was observed. This result agrees with those of other investigators (Willis and Blanks, 1959, p. 991), who have claimed that lead sulfide will not decopperize lead.

Analysis of Copper Dross

Several samples of the dross obtained by decopperizing pure lead-copper alloys with sulfur were sampled and qualitatively analyzed by x-ray diffraction techniques. It was determined that the major constituents of the dross were metallic lead and lead sulfide accompanied by lesser amounts of lead oxide (PbO), cupric sulfide, and cuprous sulfide.

INTERPRETATION OF RESULTS

Lead bullion normally contains about 1 w/o of copper as it is received from the blast furnace. The copper content of the lead is usually removed in two stages. First the bullion is allowed to cool to about 400°C; the dross thus formed is skimmed off. The residual copper concentration following this operation is approximately 0.05 w/o.

The second operation involves the stirring in of elemental sulfur in the amount of 1 to 2 lb/ton of alloy at a temperature close to the melting point of the alloy. The dross formed during this operation is skimmed off. Residual copper concentrations of 0.001 to 0.004 w/o are frequently obtained. This second stage of copper removal is accomplished in 10 to 20 minutes on as much as 100 tons of lead bullion.

Table 3 is presented to illustrate the copper concentrations obtainable by commercial decopperizing methods. The data for this table were taken from Willis and Blanks

(1959 p. 993 Table I).

Table 3. Operating results for decopperizing lead bullion.

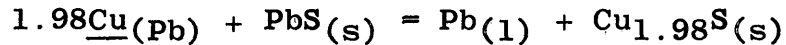
Operation	Temp. (°C)	Approximate weight %				Reference
		Cu	As	Sb	Ag	
From blast furnace		1.20	0.28	0.003	0.16	Gallagher, 1951, p. 31
After drossing	385	0.03	0.12	0.003	0.16	
After S treatment	315-20	0.004	0.12	0.003	0.16	Green, 1950, p. 281
From blast furnace		0.44	0.1	0.003		Dice, 1936, p. 127
After drossing	427	0.15	0.05	0.003		
After S treatment	330	0.01	0.05	0.006		
From blast furnace						
After drossing	370	0.06	0.01			
After S treatment	327	0.02		0.008	0.31	Buchanan, 1953, p. 229
Before S treatment		0.25		0.004	0.2	Tafel, 1953, p. 141
After S treatment		0.005		0.004		

Equilibrium Between Pb, "Cu₂S", and PbS

The calculation has been made by Pin and Wagner (1963, p. 1275) to determine the concentration of copper remaining in liquid lead coexisting with lead sulfide and non-stoichiometric cuprous sulfide. The complete calculation

is presented in Appendix III.

The reaction of interest is:



The equilibrium copper concentration in the lead is calculated to be 0.0488 w/o and corresponds to the point m on the phase diagram for the system Pb-Cu-S shown schematically in Figure 13. The value obtained in the present study was found to be somewhat lower, (0.0358 w/o Cu), probably because the system did not have sufficient time to reach equilibrium.

The additional points n and x on the phase diagram of Figure 13 were also determined in this work. At point x, lead in equilibrium with metallic copper was found to contain 0.0616 w/o Cu, which is in good agreement with the results of Kleppa and Weil (1951 p. 4848) who reported 0.0652 w/o Cu. At point n, lead in equilibrium with metallic copper and stoichiometric Cu_2S was found to contain 0.0480 w/o Cu.

It was expected that the copper concentration of the lead at point n would be between those concentrations of points m and x due to the fact that the activity of copper in Cu_2S is less than that of pure copper but somewhat higher than that of copper in the copper-deficient cuprous sulfide.

Point	Davey (1963, p. 553)	This work
x	0.0645% Cu	0.0616% Cu
n	0.0645% Cu	0.0480% Cu
m	0.050% Cu	0.0358% Cu
y	0.0004% S	--

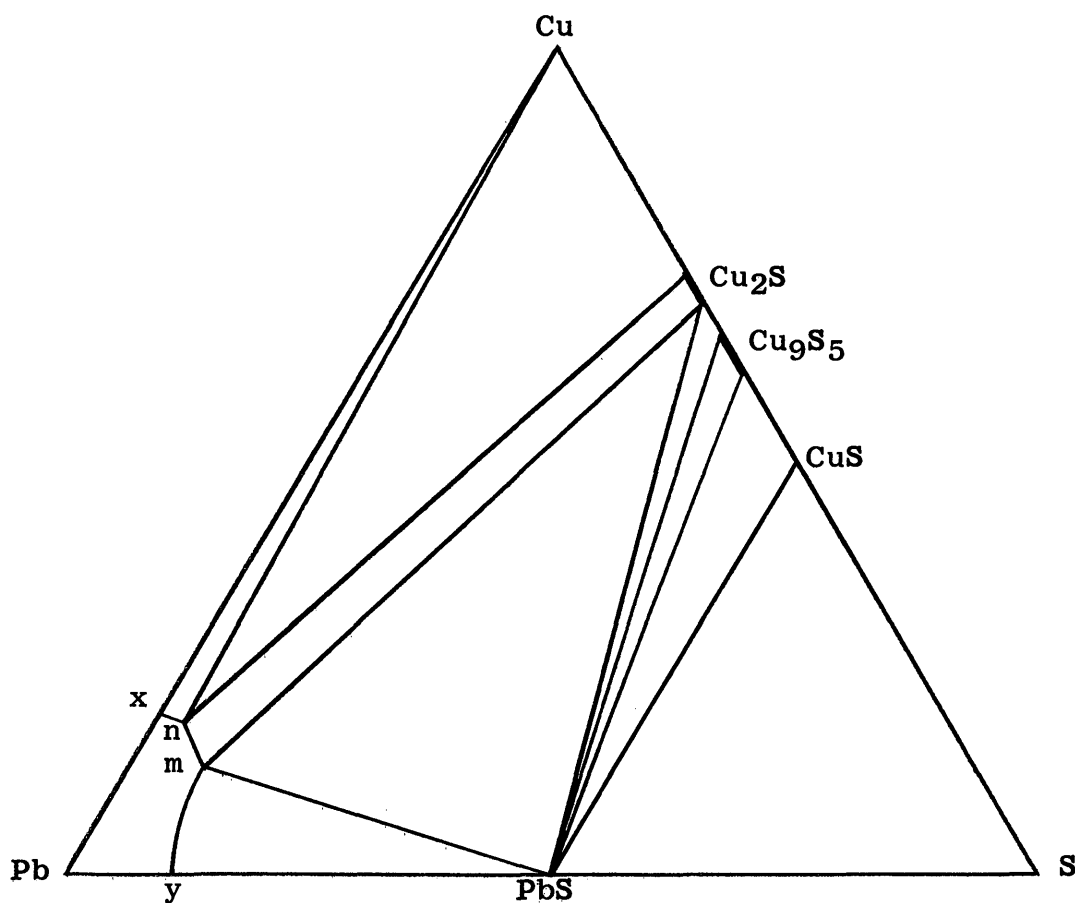


Figure 13. Schematic Phase Diagram for the Pb-Cu-S System at 330°C.

Mechanism of Decopperizing

Several theories have been proposed to account for the decopperizing of lead.

The mechanism suggested by Willis and Blanks (1959, p. 991) involves the formation of a copper-deficient cuprous sulfide. This formation of Cu_{2-x}S is possible at localized regions where high sulfur potentials exist.

The range of copper concentrations possible in cuprous sulfide has been studied by Wagner (1957, p. 1602), at 400°C. The copper content varies from $\text{Cu}_{1.9996 \pm 0.0002}\text{S}$ to $\text{Cu}_{1.93}\text{S}$. The activity of copper in cuprous sulfide has been shown by Wagner to vary greatly with copper content and temperature, e.g., at 300°C for $\text{Cu}_{1.98}\text{S}$, $a_{\text{Cu}} = 0.017$; at 400°C for $\text{Cu}_{1.98}\text{S}$, $a_{\text{Cu}} = 0.04$; at 400°C for $\text{Cu}_{1.995}\text{S}$, $a_{\text{Cu}} = 0.1$. Figure 14 illustrates the variation of copper activity in cuprous sulfide as a function of copper concentration (standard state, pure stoichiometric Cu_2S) as determined by Wagner (1957, p. 1602). Also shown are the results of Willis and Blanks (1959, p. 991) based on pure metallic copper as the standard state.

The activity of copper in copper-deficient cuprous sulfide thus decreases rapidly as the copper deficit increases by small amounts. This reduced activity is not sufficient, however, to account for the results of lead decopperizing. The calculation outlined in the preceding

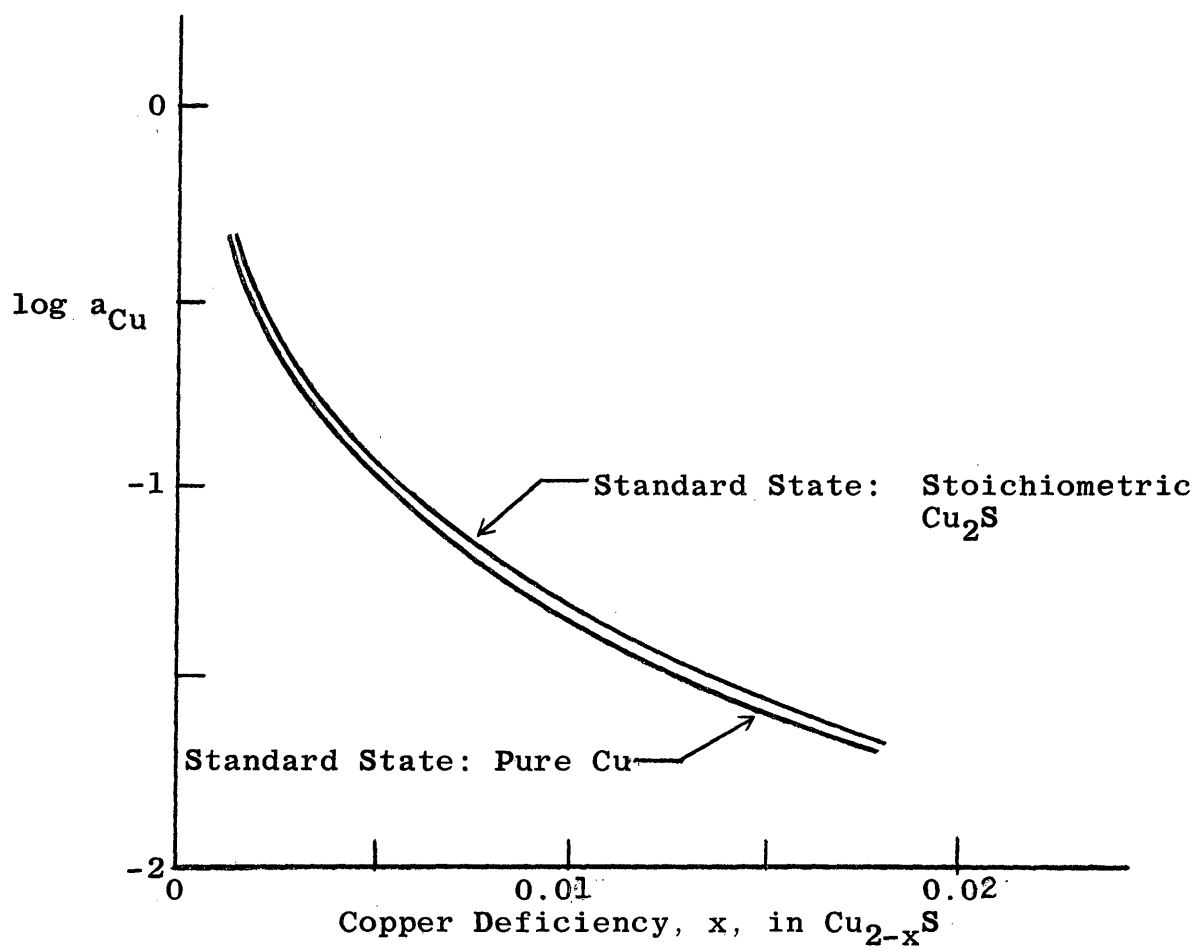
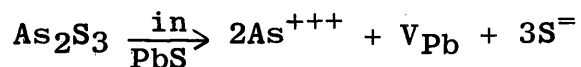


Figure 14. Logarithm of the activity of copper in cuprous sulfide as a function of copper deficiency.

section illustrates that copper in lead in equilibrium with $\text{Cu}_{1.98}\text{S}$ and PbS will contain 0.0488 w/o Cu. This concentration exceeds actual results by a factor of 10 or more. Therefore, the mechanism proposed by Willis and Blanks does not account for the real results obtained in lead decopperizing.

A second mechanism for the removal of copper from blast-furnace lead bullion has been proposed by Pin and Wagner (1963, p. 1275). The suggested mechanism involves the diffusion of copper atoms into cation vacancies within the crystal structure of lead sulfide crystals. The formation of these cation vacancies has been ascribed to the dissolution of solutes which have a higher valence than does lead. Thus, two trivalent solute atoms, such as As^{+++} in As_2S_3 , will enter the lead sulfide crystal lattice with the resultant formation of one point defect. This process can take place only when the sulfur potential coexisting with the solid solution is maintained to keep equal concentrations of electrons and holes. The dissolution reaction for As_2S_3 , as an example, may be formulated as follows:



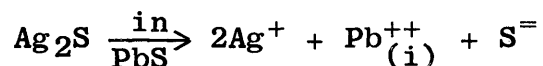
where V_{Pb} represents a cation vacancy in the lead sulfide. The copper is thought to then diffuse into the lead sulfide and reside in the pre-existing vacancy.

Bloem and Kroger (1957, p. 281) claim that copper will diffuse into PbS rapidly at low temperatures (100° to 400°C). It would thus be expected that copper would diffuse more rapidly into lead sulfide doped with trivalent solute species.

The experiments performed by Pin and Wagner showed that copper removal was increased over that obtained with undoped lead sulfide when lead sulfide was used that had been doped with small amounts of Bi₂S₃ and Sb₂S₃.

When lead sulfide was doped with a divalent solute species such as Sn⁺⁺, no appreciable difference was noted in the degree to which copper was removed from the lead.

Monovalent solute species were expected to decrease the diffusion of copper into lead sulfide due to the formation of interstitial lead ions. The formation of the interstitial lead ions, with Ag₂S as an example, may be formulated as follows:



where Pb_(i)⁺⁺ represents the interstitial lead ion. Experiments made with Ag-doped lead sulfide did show a slight decrease in the extent of copper removal.

It is important to note that the experiments made on lead decopperizing with solute-doped lead sulfide were made under equilibrium conditions. The lead-copper alloy was

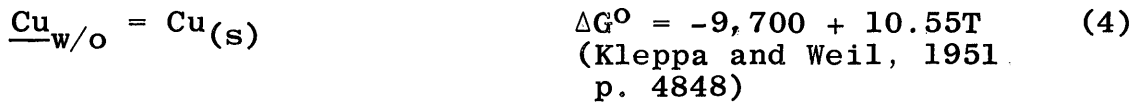
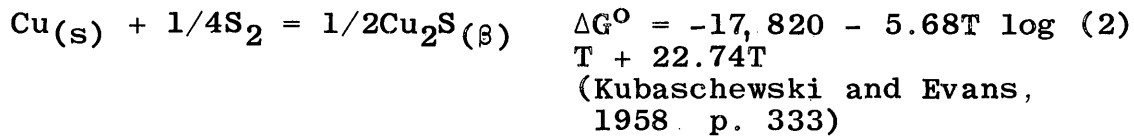
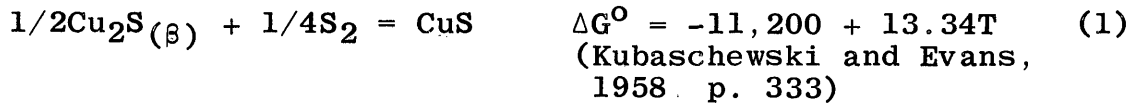
sealed under vacuum with the lead sulfide and allowed to react for one week. It must be accepted that solute-doped lead sulfide can be the cause of copper concentrations on the order of 0.002 w/o. On this basis alone, however, it is not possible to state that this is the mechanism responsible for commercial decopperizing where the times involved are much less than one hour.

Neither of the two suggested mechanisms described above satisfactorily account for the results of lead decopperizing. A third suggested mechanism, however, can be offered, based on the results of the present study.

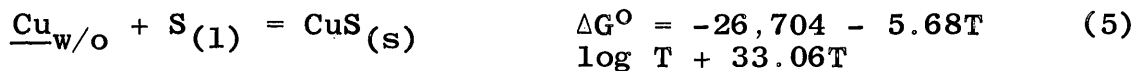
X-ray diffraction analysis of samples of the dross formed during the decopperizing of pure lead-copper alloys revealed that both cupric and cuprous sulfide were present in approximately the same relative amounts. The formation of cupric sulfide is possible at localized regions of very high sulfur potential. Decopperizing provides such regions in the form of the liquid-sulfur-metal interface.

If it is assumed that the rate of formation of CuS is rapid enough, it can be reasoned that the copper dissolved in the lead will tend to approach equilibrium with the liquid sulfur. This equilibrium between dissolved copper and liquid sulfur can be represented thermodynamically by a summation of the following equilibria and their corresponding

free energy expressions. References to the sources of the free energy expressions are included with each.



By summation of equations (1), (2), (3), and (4), and their free energies,



From the Van't Hoff reaction isotherm,

$$\Delta G_{T,P} = \Delta G^\circ + RT \ln a_{\text{CuS}}/a_{\text{S}_{(l)}} \cdot a_{\underline{\text{Cu}}_{w/o}}$$

at equilibrium,

$$\Delta G_{T,P} = 0$$

$$\Delta G^\circ = -RT \ln a_{\text{CuS}}/a_{\text{S}_{(l)}} \cdot a_{\underline{\text{Cu}}_{w/o}}$$

$$= -26,704 - 5.68T \log T + 33.06T$$

As a first approximation, a_{CuS} and $a_{\text{S}_{(l)}}$ will be assumed to be unity.

$$RT \ln a_{\underline{\text{Cu}}_{w/o}} = -26,704 - 5.68T \log T + 33.06T$$

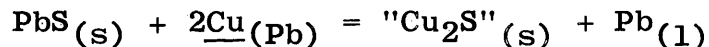
By calculation for $a_{\underline{\text{Cu}}_{\text{w/o}}}$ at 330°C,

$$a_{\underline{\text{Cu}}_{\text{w/o}}} = 1.26 \times 10^{-6}$$

If the kinetics of the reactions involved are such that the copper dissolved in lead could achieve near equilibrium with the liquid sulfur, copper contents as low as 10^{-6} w/o might be expected.

The results obtained in this investigation were found to be as low as 2×10^{-4} w/o Cu, well within the limit imposed by the above calculation.

The stable equilibrium condition for the system Pb-Cu-S at the concentrations involved in normal decopperizing is represented by the reaction (see Alkemade triangle PbS-Pb-"Cu₂S" in Figure 13):



It would be expected, therefore, that the system would recover from the lower concentration to the higher value calculated in the preceding section (0.0488 w/o Cu). In order for this recovery to take place, the lead-copper alloy must be allowed to remain in contact with the dross for a sufficiently long time. This recovery is presented in Figure 15 as a plot of copper concentration against time. The results of several isolated experiments have

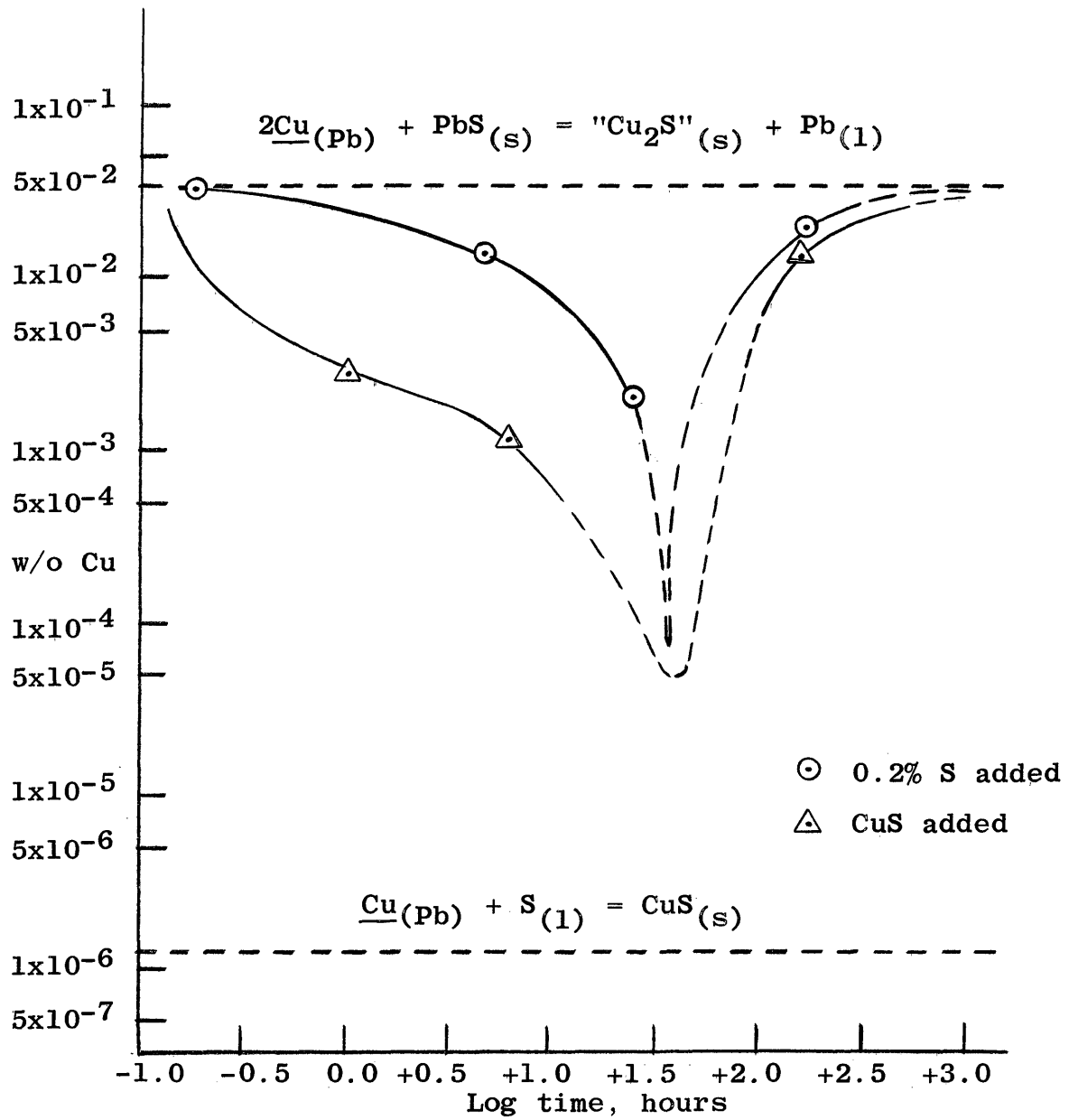
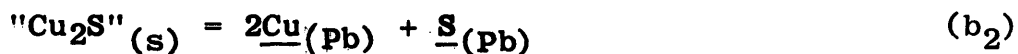
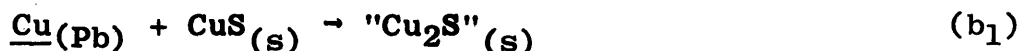
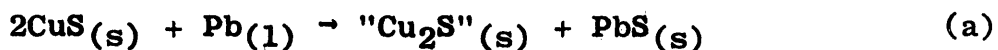


Figure 15. Residual copper concentration in lead versus logarithm of time during decopperizing.

been plotted on the curve to define its shape more clearly. Constant-composition lines have been drawn on Figure 15 to illustrate the equilibrium copper concentrations in lead for the stable equilibrium (as determined in this work) between $\text{PbS}_{(s)}$, $\underline{\text{Cu}}_{(\text{Pb})}$, " Cu_2S " $_{(s)}$, and $\text{Pb}_{(l)}$, and the unstable equilibrium (calculated) between $\underline{\text{Cu}}_{(\text{Pb})}$, $\underline{\text{S}}_{(l)}$, and $\text{CuS}_{(s)}$.

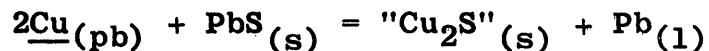
It is apparent from Figure 15 that the copper concentration in liquid lead continues to decrease after the sulfur has been completely reacted. This phenomenon may be explained by considering the following hypothetical reactions:



If reaction (a) proceeds at a faster rate than reaction (b₁), the copper concentration in the lead would begin to increase as soon as the sulfur had been completely reacted. However, if reaction (b₁) proceeds at a sufficient rate, it would be expected that the copper content of the lead would continue to decrease as shown in Figure 15.

Reaction (b₁) does play a significant role in long-time decopperizing experiments as evidenced by the facts that CuS will decopperize lead and CuS does exist in the dross from liquid-sulfur decopperizing. Experiments performed in this work have shown that the addition of CuS to a lead-copper alloy (0.035 w/o Cu) results in copper contents as low as 0.0019 w/o (see Figure 15). The rate of copper removal in the case of decopperizing with CuS is substantially more rapid than that observed in the decopperizing with sulfur.

When reaction (b₁) nears completion, it is presumed that solution of "Cu₂S" continues to take place slowly accompanied by the formation of additional PbS, according to reactions (b₂) and (b₃) respectively, and the system assumes the stable equilibrium:



Commercial decopperizing is successful because the rate of recovery of the system is quite slow. If the dross is removed from the surface of the lead after a short time, solution of copper from the dross will be prevented, and the system will not be capable of recovering.

Effect of Impurity Elements

It is not possible to state the manner in which impurity elements affect the decopperizing of lead. This investigation has, however, established that certain impurities do have a pronounced effect on the rate of decopperizing. A detailed analysis of the nature of these effects might be possible if existing thermodynamic data regarding solute interaction were more complete at the temperatures of interest. A rigorous treatment of the data would also necessitate a knowledge of the activities of all the species over a range of concentrations. At present, these data have not been determined.

Decopperizing with Sulfur. The experimental data presented in Figures 3 to 10 illustrate the extent to which certain impurities affect the decopperizing of lead.

As discussed above, Wagner has suggested that the function of the impurities is to migrate into the lead sulfide crystal lattice and form cationic vacancies or interstitial lead ions, depending on the valence of the solute species. Decopperizing would thus be enhanced if the impurity resulted in the formation of vacancies.

Using an equilibrium approach, Wagner was able to show that copper removal was increased when the lead sulfide was doped with the trivalent species Bi^{+++} and Sb^{+++} . The

results for the trivalent impurities As^{+++} , Sb^{+++} , and Bi^{+++} obtained in the present investigation reveal that copper removal is not increased but decreased. Similarly, the present results obtained for mono- and divalent-solute species were directly opposite to the predictions made by Wagner.

In view of the present results, it is difficult to accept Wagner's explanation of the effect of impurities on the decopperizing of lead. Since his experiments were performed under equilibrium conditions, it might be possible that such solid-state phenomena would govern the equilibrium copper concentration of an alloy containing various impurities.

Willis and Blanks (1959, p. 991) have shown that silver decreases the rate of reaction between sulfur and lead. It would thus be expected that a greater percentage of the added sulfur is available for reaction with the copper, hence a lower copper concentration in the lead. Visual examination of the drosses formed during the decopperizing of lead-copper alloys containing silver or tin as the third element showed an unusually small amount of sulfides present. This observation supports the findings of Willis and Blanks for silver and indicates that tin might also decrease the rate of reaction between sulfur and lead. It might be suggested, therefore, that the effect of the impurity

elements is to either increase or decrease the rate of formation of lead sulfide. Copper removal would thus be increased if the rate of formation of lead sulfide was decreased by a particular impurity. At present, work to substantiate this explanation has not been done.

The experimental results presented in Figure 10 show that decopperizing is increasingly efficient as the concentration of tin is increased from 0.05 w/o to 0.50 w/o. At a much higher concentration, 5.00 w/o, the copper content of the lead after decopperizing is observed to be somewhat higher. The quaternary alloy composition may be far removed from the area of primary crystallization of the lead solid solution and thus will not be in equilibrium with the low copper-lead alloys present in Figure 13. An accurate quaternary phase diagram of the system Pb-Cu-Sn-S would be necessary to prove this supposition.

Figure 11 illustrates the necessity of decopperizing at low temperatures. The beneficial effect of tin observed at 330°C is wholly absent at 430°C. Davey (1963, p. 553) has shown that the increase in the solubility of both copper and sulfur in liquid lead at this elevated temperature accounts for most of this decrease in copper removal.

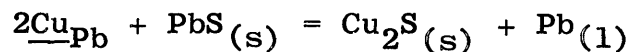
Decopperizing with H₂S. The experimental results obtained when a lead-copper alloy was decopperized with H₂S are presented graphically in Figure 12. It is observed that neither silver nor tin had any appreciable influence on the degree to which copper could be removed. Whatever the mechanism involved with this system, it is apparently not the same as that involved in the Pb-Cu-S system.

SUMMARY AND CONCLUSIONS

The influence of additive elements on the decopperizing of lead at 330°C has been determined. The effect of the individual elements Sn, Ag, and As is to increase both the rate and the degree to which copper can be removed from lead by sulfur treatment with a reaction time of 10 minutes. Antimony was found to have no effect on the decopperizing experiments. The individual elements Bi, Au, and Zn were observed to decrease the efficiency of copper removal. Due to a lack of thermodynamic data regarding the solution behaviour of the additive elements studied, no suggestion can be made as to the exact nature of their effects. It was determined, however, that impurities need not be present in the bullion in order to achieve successful decopperizing. Pure lead-copper alloys could be successfully decopperized to 0.002 w/o Cu if reaction times up to 24 hours were allowed.

The solid-state mechanism concerning the effect of additive elements on decopperizing, as suggested by Wagner, was not substantiated by the results of this study. There is a need for more research to be done in this area before a complete understanding of the decopperizing process can be realized.

The equilibrium copper concentration in lead following decopperizing has often been reported as determined by the reaction:



As determined by both calculation and experiment, the resulting equilibrium concentration is on the order of 0.05 w/o Cu. Commercially, and experimentally, obtained results range between 10^{-3} and 10^{-4} w/o, respectively.

It has been proposed by Willis and Blanks that the formation of a copper-deficient cuprous sulfide might account for much lower concentrations than those resulting from the formation of pure Cu_2S . The results of the present study agree with calculated values which show that a deviation from stoichiometry corresponding to $\text{Cu}_{1.98}\text{S}$ results in no appreciable decrease in the equilibrium copper concentration. The activity of copper in $\text{Cu}_{1.98}\text{S}$ is much lower than that in Cu_2S , however.

It has been established by the present study that cupric sulfide (CuS) forms in appreciable amounts during the first few minutes of decopperizing. If it is assumed that the rate of formation of CuS is sufficiently rapid, the unstable equilibrium between dissolved copper, liquid sulfur, and solid cupric sulfide can be taken as a limiting value for the residual copper concentration in the lead. The calculation has been made for this unstable equilibrium at 330°C with the result that,

$$a_{\text{Cu}}(\text{w/o in Pb}) = 1.26 \times 10^{-6}$$

The assumptions made in arriving at this concentration appear to be valid and, thus, the results of both commercial and experimental decopperizing are well within the calculated limiting value.

APPENDICES

Appendix I. Spectrographic analysis of the metals lead, copper, antimony, bismuth, silver, gold.
(American Smelting and Refining Company Specifications.)

<u>Impurity</u>	<u>Lead</u>	<u>Copper</u>	<u>Antimony</u>	<u>Bismuth</u>	<u>Silver</u>	<u>Gold</u>
Sb	N.D.*	<1 ppm	99.99+%	--	N.D.	N.D.
Tl	N.D.	--	--	--	N.D.	N.D.
Mg	<0.5 ppm	--	--	--	2 ppm	--
Mn	N.D.	--	--	--	--	--
Pb	99.999+%	<1 ppm	<1 ppm	1 ppm	2 ppm	<1 ppm
Sn	N.D.	<1 ppm	--	--	N.D.	--
Si	<0.5 ppm	<1 ppm	--	--	2 ppm	--
Cr	N.D.	<0.5 ppm	--	--	N.D.	--
Fe	<1.0 ppm	<0.7 ppm	<1 ppm	1 ppm	2 ppm	<1 ppm
Ni	N.D.	<1 ppm	--	--	N.D.	--
Bi	N.D.	<0.1 ppm	<1 ppm	99.999+%	N.D.	--
Al	N.D.	--	--	--	N.D.	--
Ca	N.D.	--	--	--	N.D.	--
Cu	<1.0 ppm	99.999+%	<1 ppm	2 ppm	3 ppm	<1 ppm
In	N.D.	--	--	--	N.D.	--
Cd	N.D.	--	--	--	N.D.	--
Zn	N.D.	--	--	--	N.D.	--
Au	N.D.	--	--	--	N.D.	99.999+%
Ag	N.D.	0.3 ppm	--	2 ppm	99.999+%	1 ppm
As	--	<2 ppm	<2 ppm	--	--	--
S	--	<1 ppm	--	--	--	--

*N.D. denotes, none detected, by standard spectrographic methods.

Appendix II. Analytical procedure for copper analysis
in lead.

DETERMINATION OF COPPER IN LEAD BY THE CUPRIC BROMIDE METHOD

A.S.T.M. Designation: E 87-58

Principle of Method:

Cupric copper in solution in HBr forms a red-violet-colored complex. Photometric measurement is made at 600 millimicrons.

Concentration Range:

The recommended concentration range is from 0.05 to 0.80 mg of copper per 25 ml of solution, using a cell depth of 2 cm.

Interfering Elements:

Gold, the platinum group metals, ferric iron, and, to a lesser extent, antimony interfere. The method provides for the removal of the interference due to iron and antimony.

Reagents:

Hydrobromic acid-bromine mixture	Add 20 ml of bromine to 180 ml of hydrobromic acid.
Standard copper solution	Dissolve 0.1000 gm of copper in 3 ml of HNO_3 by gentle heat in a 125-ml conical flask. Add 10 ml of HClO_4 and heat to copious

Appendix II (contd.)

	white fumes of HClO_4 to expel HNO_3 . Cool, add 10 ml of water, transfer to a 1-liter volumetric flask and dilute to the mark.
Nitric acid	Add 100 ml of HNO_3 to 300 ml of water.
Perchloric acid	Concentrated
Phosphoric acid	Concentrated
Hydrobromic acid	Concentrated
Test lead	Finely granulated test lead containing under 0.0001 percent of copper and under 0.001 percent of iron or nickel.

Preparation of Calibration Curve:

(a) Calibration Solutions-

- (1) Transfer 0.5, 1.0, 2.0, 3.0, 4.0, 6.0, and 8.0 ml of copper solution (1 ml = 0.1 mg Cu) to 125-ml conical flasks. Add 2 ml of HClO_4 and dilute to 40 ml with water.
- (2) Add 1 gm of test lead to each flask, cover, and boil at a moderate rate for 15 min to displace all the copper. Cool somewhat, remove the solution by decantation, and wash once with water -- decanting

Appendix II (contd.)

thoroughly. Heat the flask gently to remove moisture. Add 10 ml of HBr-Br₂ mixture to the flask, cover, and heat gently to dissolve the metal. Boil to expel excess bromine. Cool to room temperature. Transfer 10 ml of H₃PO₄ plus 1 drop (0.05 ml) of the HBr-Br₂ mixture to a dry, 25-ml volumetric flask. Transfer the metal solution to the volumetric flask, washing with a few milliliters of HBr. Dilute to the mark with HBr and mix. Proceed in accordance with Paragraph (c).

(b) Reference Solution-

Transfer 40 ml of water plus 2 ml of HClO₄ to a 125-ml conical flask and continue in accordance with Paragraphs (a) (2) and (c).

(c) Photometry-

Transfer a suitable portion of the reference solution to an adsorption cell and adjust the photometer to the initial setting, using a light band centered at 600 millimicrons. While maintaining this photometer adjustment, take the photometric readings of the calibration solutions.

(d) Calibration Curve-

Plot the photometric readings of the calibration

Appendix II (contd.)

solutions against milligrams of copper per 25 ml of solution. (The data for the calibration curve used in this study are given in Table 4 and are presented graphically in Figure 16 following the discussion of the analytical method.)

Procedure for Pig Lead:**(a) Sample Solutions-**

(1) Depending on the copper content, transfer up to 2.00 gm of the sample to a 125-ml conical flask. Add 10 ml of HNO_3 (1:3), cover, and heat gently until the sample is dissolved. Add 5 ml of HClO_4 , and boil to a volume of 2 ml.

(2) Add 40 ml of water and continue in accordance with Paragraph (a) (2) under Calibration Solutions.

(b) Reference Solution-

Carry a reagent blank through the entire procedure, using the same amounts of all reagents, for use as a reference solution.

(c) Photometry-

Take the photometric reading of the sample solution as described in Paragraph (c) under Calibration Solutions.

Appendix II (contd.)

(d) Calculation-

Convert the photometric reading of the sample solution to milligrams of copper by means of the calibration curve. Calculate the percentage of copper as follows:

$$\text{copper, percent} = \frac{A}{B \times 10}$$

where:

A = milligrams of copper found, and

B = grams of sample used.

Table 4. Calibration curve data for analysis of copper in lead.

<u>mg Cu</u> <u>25 ml solution</u>	<u>Transference</u> <u>(%)</u>	<u>log</u> <u>(%T)</u>
0.00	100.0	2.0000
0.05	91.9	1.9633
0.10	84.9	1.9289
0.20	71.5	1.8543
0.30	61.3	1.7875
0.40	51.9	1.7152
0.60	37.9	1.5786
0.80	27.4	1.4378

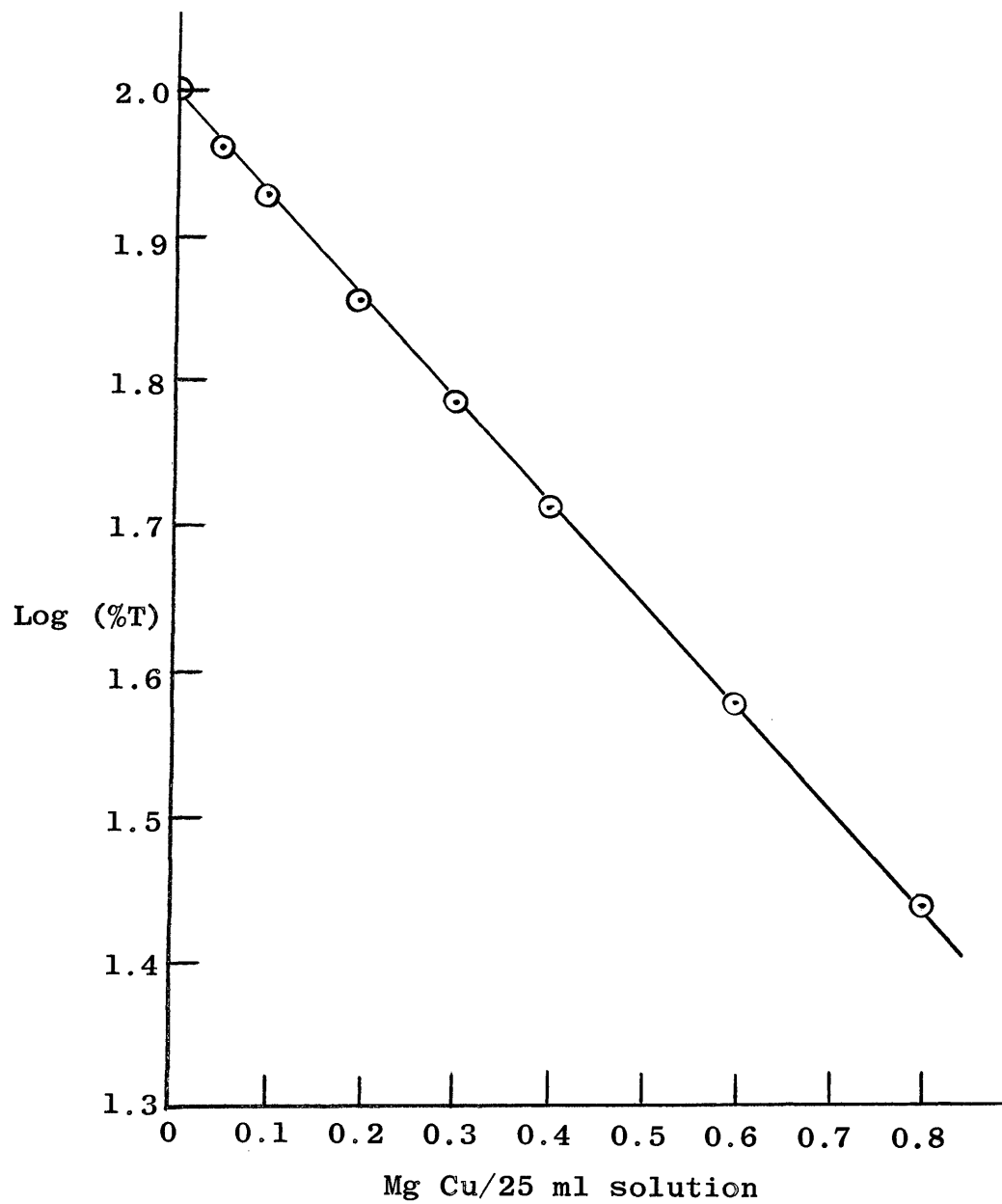
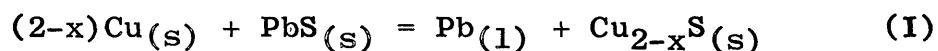


Figure 16. Calibration curve for Bausch and Lomb Spectronic 20 Colorimeter.

Appendix III. Calculation of the copper concentration in lead coexisting with PbS and "Cu₂S", at 330°C.

The reaction of interest is:



where x denotes a deviation from stoichiometry.

The free energy change for reaction (I) has been determined by Wagner (1957, p. 509). The emf of a cell using pure Pb and Cu as electrodes was determined as a function of temperature:

$$E_{(\text{v})} = (6.5 \pm 1) \times 10^{-3} + 0.3 \times 10^{-3} (t - 300) \quad (1)$$

where t is in degrees centigrade.

Solving equation (1) for E_(v) at 330°C,

$$E_{(\text{v})} = (15.5 \pm 1) \times 10^{-3} \text{ volts}$$

Using the relationship between reversible emf and Gibb's free energy:

$$\Delta G = -zFE \quad (2)$$

$$\Delta G = -715 \text{ cal}$$

The standard free energy change for reaction (I) may be calculated by applying a correction factor to the free energy change calculated above. Wagner (1957, p. 509) has shown that the standard free energy change for reaction (I) is related to the free energy change by the following expression:

$$\Delta G^{\circ} = \Delta G + xRT \quad (3)$$

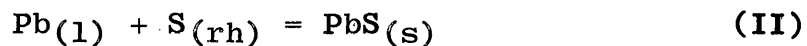
Appendix III (contd.)

where x is the copper deficit in Cu_{2-x}S .

By assuming an arbitrary value of $x = 0.02$,

$$\Delta G^{\circ} = -691 \text{ cal}$$

Considering the reaction,



the standard free energy of formation of PbS can be expressed by:

$$\Delta G^{\circ}_{\text{PbS}} = G^{\circ}_{\text{PbS}} - G^{\circ}_{\text{Pb}} - G^{\circ}_{\text{S}} \quad (4)$$

and,

$$G^{\circ}_{\text{PbS}} = \bar{G}_{\text{Pb}} + \bar{G}_{\text{S}} \quad (5)$$

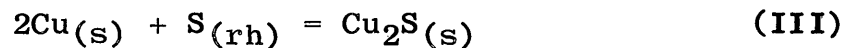
Under conditions where PbS coexists with metallic lead.

By combining equations (4) and (5), and assuming

$a_{\text{Pb}} = 1$,

$$\Delta G^{\circ}_{\text{PbS}} = \left[\bar{G}_{\text{Pb}} - G^{\circ}_{\text{Pb}} \right] + \left[\bar{G}_{\text{S}} - G^{\circ}_{\text{S}} \right] = \left[\bar{G}_{\text{S}} - G^{\circ}_{\text{S}} \right] \quad (6)$$

A similar treatment can be applied to the formation of Cu_2S by the following reaction:



The standard free energy of formation by reaction (III) can be expressed by:

$$\Delta G^{\circ}_{\text{Cu}_2\text{S}} = G^{\circ}_{\text{Cu}_2\text{S}} - 2G^{\circ}_{\text{Cu}} - G^{\circ}_{\text{S}} \quad (7)$$

When Cu_2S is formed from sulfur and copper in liquid lead,

$$G^{\circ}_{\text{Cu}_2\text{S}} = 2\bar{G}_{\text{Cu}} + \bar{G}_{\text{S}} \quad (8)$$

Appendix III (contd.)

Addition of equations (7) and (8) yields,

$$\Delta G^{\circ}_{\text{Cu}_2\text{S}} = 2\bar{G}_{\text{Cu}} + \bar{G}_{\text{S}} - 2G^{\circ}_{\text{Cu}} - G^{\circ}_{\text{S}} \quad (9)$$

or,

$$\left[\bar{G}_{\text{Cu}} - G^{\circ}_{\text{Cu}} \right] = 1/2 \left[G^{\circ}_{\text{Cu}_2\text{S}} - (\bar{G}_{\text{S}} - G^{\circ}_{\text{S}}) \right] \quad (10)$$

The left-hand side of equation (10) is the partial molar free energy of mixing of copper in lead ($\Delta \bar{G}^{\text{M}}_{\text{Cu}}$) and values for the right-hand side may be substituted from equations (6) and (2).

$$\begin{aligned} \Delta \bar{G}^{\text{M}}_{\text{Cu}} &= \left[\bar{G}_{\text{Cu}} - G^{\circ}_{\text{Cu}} \right] = 1/2 \left[\Delta G^{\circ}_{\text{Cu}_2\text{S}} - \Delta G^{\circ}_{\text{PbS}} \right] \quad (11) \\ &= -346 \text{ cal} \end{aligned}$$

Since,

$$\Delta \bar{G}^{\text{M}}_{\text{Cu}} = RT \ln a_{\text{Cu}} = RT \ln \left[X_{\text{Cu}} / X_{\text{Cu sat.}} \right] \quad (12)$$

$$X_{\text{Cu}} = 0.1588 \times 10^{-2} = 0.0488 \text{ w/o}$$

The term X_{Cu} in equation (12) is the mole fraction of copper in the alloy in equilibrium with $\text{Cu}_{1.98}\text{S}$ and PbS , and the term $X_{\text{Cu sat.}}$ is the mole fraction of copper in a saturated pure lead-copper alloy (in the absence of sulfur). The value of $X_{\text{Cu sat.}}$ was obtained from the data of Kleppa and Weil (1951, p. 4848). It must be remembered that equation (12) is valid only for dilute solutions (<1 w/o).

Appendix IV. X-ray diffraction patterns of PbS, CuS, Cu₂S
as compiled from the A.S.T.M. card file.

1. PbS (Galena)

<u>d spacing</u> (A.U.)	<u>Relative</u> <u>Intensity</u>	<u>2θ</u> (degrees)
3.43	84	25.96
2.97	100	30.07
2.10	57	43.06
1.79	35	50.97
1.71	16	53.41
1.48	10	62.54
1.36	10	68.88
1.33	17	70.96
1.21	10	78.92

Appendix IV (contd.)

2. CuS (Covellite)

<u>d spacing</u> <u>(A.U.)</u>	<u>Relative</u> <u>Intensity</u>	<u>2θ</u> <u>(degrees)</u>
8.18	7	10.81
3.29	14	27.12
3.22	28	27.68
3.05	67	29.28
2.81	100	31.78
2.72	56	32.84
2.32	10	38.84
2.10	6	43.10
2.04	7	44.30
1.90	25	47.78
1.90	75	47.94
1.74	34	52.72
1.63	3	56.25
1.61	8	57.20
1.57	15	58.68
1.56	37	59.34
1.46	6	63.54
1.39	6	67.30
1.35	7	69.34
1.34	5	70.00
1.28	9	74.00
1.23	5	77.77

Appendix IV (contd.)

3. Cu_2S (Chalcocite)

<u>d spacing</u> <u>(A.U.)</u>	<u>Relative</u> <u>Intensity</u>	<u>2θ</u> <u>(degrees)</u>
3.93	5	22.60
3.77	10	23.58
3.60	10	24.71
3.39	30	26.27
3.31	10	26.91
3.21	20	27.77
3.05	20	29.26
2.97	5	30.06
2.88	20	31.02
2.84	5	31.47
2.73	10	32.78
2.67	10	33.53
2.58	5	34.74
2.54	10	35.31
2.47	20	36.34
2.40	70	37.44
2.34	5	38.44
2.22	20	40.60
2.14	10	42.19
2.06	10	43.91

Appendix IV (contd.)

3. Cu_2S (Chalcocite) (contd.)

<u>d spacing</u> <u>(A.U.)</u>	<u>Relative</u> <u>Intensity</u>	<u>2θ</u> <u>(degrees)</u>
1.97	80	46.06
1.94	5	46.86
1.87	100	48.65
1.79	5	51.07
1.70	40	54.06
1.65	20	55.84
1.59	5	58.03
1.51	20	59.96
1.47	5	63.15
1.35	10	69.52
1.28	30	74.13
1.12	10	87.00

LITERATURE CITED

- American Society for Testing Materials Standards, 1965:
Copper in Lead: Chemical Analysis of Metals, Sampling
and Analysis of Metal Bearing Ores, Part 32, p. 498.
- Blanderer, J., 1959, Theory of Lead Refinement: Metall.,
v. 11, p. 662.
- Bloem, J., and Kroger, F. A., 1957, Interstitial Diffusion
of Copper in PbS Single Crystals: Philips Research
Reports, v. 12, p. 281.
- Darken, L. S., and Gurry, R. W., 1953, Physical Chemistry
of Metals: McGraw Hill, p. 211.
- Davey, T. R. A., 1963, Phase Systems concerned with the
Copper Drossing of Lead: Trans. of the Inst. of Min.
and Met., v. 72, part 8, p. 553.
- Dennis, W. H., 1954, Metallurgy of the Non-Ferrous Metals:
Pitman, p. 244.
- Dice, C. M., Oldright, G. L., and Brighton, T. B., 1936,
Drosses in Lead Smelters: Transactions of the
Metallurgical Society of A.I.M.E., February, p. 127.
- Gahkaishi, 1964, Effects of Added Elements on the Removal
of Copper from Liquid Lead by Addition of Sulfur:
Nippon Kinzoku Gahkaishi, v. 24, p. 601.
- Gallagher, D., 1951, The Recovery of Copper from Lead
Blast Furnace Bullion: Proceedings Australasian
Institute of Mining and Metallurgy, No. 162-163,
p. 31.

- Green, F. A., 1950, The Refining of Non-Ferrous Metals, Institute of Mining and Metallurgy, p. 281.
- Haig, R. V., 1950, The Refining of Non-Ferrous Metals, Institute of Mining and Metallurgy, p. 316.
- Haney, L. B., 1950, The Refining of Non-Ferrous Metals, Institute of Mining and Metallurgy, p. 321.
- JANAF Thermochemical Tables: The Dow Chemical Company, Midland, Michigan, December 31, 1960.
- Kleppa, O. J., and Weil, J. A., 1951, The Solubility of Copper in Liquid Lead below 950°C: Journal of the American Chemical Society, v. 73, p. 4848.
- Kubaschewski, O., and Evans, E., 1958, Metallurgical Thermochemistry: Pergamon Press, p. 333.
- Kunchev, and Nikolov, 1964, Effects of Arsenic, Antimony, and Tin on Removal of Copper from Lead: Rudodobiv. Met., No. 7, p. 19.
- Pin, C., and Wagner, J. B., 1963, The Removal of Copper from Liquid Lead by Lead Sulfide Containing Controlled Atomic Defects: Transactions of the Metallurgical Society of A.I.M.E., December, p. 1275.
- Wagner, J. B., and Wagner, C., 1957, Investigations of Cuprous Sulfide: Journal of Physical Chemistry, v. 26, p. 1602.
-
- 1957, Determination of the Standard Free Energy of Formation of Cuprous Sulfide at 300°C: J. Electrochem. Soc., v. 104, p. 509.
- Willis, G. M., and Blanks, R. F., 1959, Equilibria between Lead, Lead Sulfide, and Cuprous Sulfide and the Decopperizing of Lead with Sulfur: Physical Chemistry of Process Metallurgy, Part 2, p. 991-1025.

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