Functions of Chloride in Copper Refining Electrolyte.

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FUNCTIONS OF CHLORIDE IN COPPER-REFINING ELECTROLYTE

by

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ABSTRACT

New methods for determining small amounts of chloride in copper-refining electrolyte and determining traces of bismuth in copper were developed.

The antimony oxychloride hypothesis was studied critically.

The chloride concentration in copper-refining electrolyte is correlated with the grain size, the hardness and the bismuth content of the copper deposit and with the cathode polarization. Explanations are offered to explain these phenomena.

Part I

INTRODUCTION

In 1893 (5) Wesley Blair, a foreman of the Baltimore Electric * Refinery Company's plant, discovered that chloride in some form (NaCl or HCl), when added to the copper-refining electrolyte, changed the deposited copper from a dull dark red color to a bright crystalline deposit. Since then chloride has been added to the electrolyte at all copper refineries.

The importance of chloride can be seen from the following two quotations:

According to Ulke (41),

> "------ refineries in the United States find, in starting deposition from a normal acidified copper sulfate solution free from hydrochloric acid , that the starting sheets are generally brittle, and that good tough starting sheets may be secured by adding a small pitchful(about 300 c.c.) of hydrochloric acid to each tank. "

According to Addicks(1),

> "Regarding chlorides, I think it is the custom in all the refineries to add small quantities of salt or hydrochloric acid. -------- I have never tried omitting it, as the cost is negligible and its use almost a tradition. Early in my acquaintance with the refining of copper, I was told stories by tankhouse foremen of the terrible things that had happened when copper had been deprived of chlorine, and as nurses' tales have an influence in after life, I put salt in the electrolyte just as I do in my beefsteak."

As to the amount of chloride added, Walker(6) gives it as 24 to 72 mg./L, and Addicks(2) as 38 mg./L . Table I illustrates the average concentration of chloride in the electrolyte of several copper refineries. It is seen that the general range of the concentration of chloride is from 2 to 59 milligrams per liter.

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* This should have been " Electrolytic"

Table I

Concentration of Chloride in Copper-Refining Electrolyte

Refinery	Cl Concentration, mg./L	Reference
Mount Lyell Mining and Railway Company, Queenstown Plant	59	(27)
Nichols Copper Company, Laurel Hill Plant	4-7	(23)
Canadian Copper Refinery, Montreal East Plant	2	(25)
Anaconda Copper Mining Company, Perth Amboy Plant	30	(16)
Anaconda Copper Mining Company, Great Falls Plant	27-28	(9)

A high concentration of chloride is harmful. According to Wen and Kern (42),

"An excess of chlorine ions causes the deposits to become brittle and less pure; it is therefore of first importance that the amount of chloride added should be limited to a very small quantity, that is, to about 0.01 % of chlorine as chloride, preferably sodium chloride. A smaller amount is also beneficial."

According to Allmand and Ellingham(3),

" Too great a concentration of Cl' is to be avoided, as traces of Cu_2Cl_2 on the cathode surface may give rise to nodular growths."

The functions of chloride have been reported as follows: chemically it precipitates silver as silver chloride and bismuth and antimony as oxychlorides; electrochemically it acts as a cathode depolarizer(34); physically it refines the grain size of the copper deposit(8). It is well known that chloride reduces the loss of silver in the cathode. However, the other statements are not so well established. Many metallurgists in copper refineries do not believe that antimony or bismuth is precipitated as oxychloride in the copper-refining electrolyte. One large copper refinery has found in a large-scale experimental cell that there is a decided drop in the cathode potential when the electrolyte is practically dechloridized (31). According to Rouse and Aubel(35), the crystal size of deposits made in electrolyte containing 20 mg. per liter of chloride is much larger than the crystal size from one containing only 5 mg. per liter. Thus it is seen that there have been no adequate and consistent explanations for some of the effects of chloride in copper-refining electrolyte.

The purpose of the present work is to investigate the role of chloride in the copper-refining electrolyte. To simplify the study, the work is to be divided into two parts , one dealing with chloride in the electrolyte in the absence of addition agents and impurities and the other dealing with chloride in the absence of addition agents but in the presence of bismuth as an impurity.

Since the present methods of determining small amounts of chloride in the electrolyte and of determining traces of bismuth in copper are not satisfactory; quick, simple and reasonably accurate methods are to be developed to facilitate the investigation.

Since the antimony oxychloride hypothesis is given in several textbooks, this hypothesis is also to be studied critically.

Part II

DETERMINATION OF SMALL AMOUNTS OF CHLORIDE IN COPPER-REFINING ELECTROLYTE BY POTENTIOMETRIC TITRATION

Introduction

The ordinary method of determining small amounts of chloride in copper-refining electrolyte consists of precipitating chloride as insoluble silver chloride and weighing as such. The obvious disadvantages of this method are:

(1) It takes a couple of hours for small amounts of silver chloride to settle.

(2) The precipitate must be thoroughly washed to free it from all soluble substances. When the last trace of adsorbed silver is removed, the precipitate is apt to become colloidal.

Some laboratories take up the silver chloride so precipitated in lead, cupel it, and weigh the silver bead. Since there is significant loss of silver by volatilization, especially because of the presence of chloride, it is questionable whether the extra operation is justified.

The aim of this part of the investigation was to find a simple, rapid and accurate method of determining small amounts of chloride in copper-refining electrolyte.

Organic Reagents

The most promising reagents for determining minute amounts of chloride ion in most materials seem to be dithizone and diphenylcarbazide. Both involve indirect methods. In the former case excess silver nitrate is added to the unknown solution. Silver chloride is precipitated. The unused silver is then determined by an extractive titration with dithizone (20) .

The indicator is dithizone itself. It forms a yellow complex with silver in weak acid solution. In the latter case mercuric nitrate solution is added gradually to the unknown solution. So long as chloride is present, it will remove mercuric ion as practically unionized mercuric chloride . The excess mercuric ion is immediately shown by a violet color, which is the color of complex formed by diphenylcarbazide, added as indicator, with mercuric mercury(23). Both reagents are very sensitive if interfering elements are absent or removed, and if certain rigid requirements on the condition of the unknown solution are met.

Diphenylcarbazide

No experiments were made on dithizone. A series of experiments made by the author show that the results utilizing the diphenylcarbazide in determining chloride in copper-refining electrolyte is not satisfactory . The chief difficulties may be summarized as follows:

(1) It is necessary to isolate chloride from interfering elements such as Cu^{++}, Fe^{+++}, etc. in the electrolyte, because they develop the same color with diphenylcarbazide. Distillation of the electrolyte at 100 to 110°C. seems to be a good method of separation. The extraction of chloride in the distillate as hydrogen chloride is almost quantitative. However, distillation of 50 ml. of electrolyte takes about 1 1/2 hours and requires constant attention.

(2) When chloride is isolated in the distillate, the pH of the distillate must be adjusted to an optimum value before the titration with mercuric nitrate can be made. This is because diphenylcarbazide is an acid-base indicator. The color in acid solution is almost colorless and that in alkaline solution is orange. The end point is at pH 6. Evidently the pH of the unknown solution must be less than pH 6. Besides, the violet complex

formed by the diphenylcarbazide and the mercuric ion becomes colorless at pH less than 4. Even in this narrow pH range , namely , 4 to 6, the sensitivity of detecting the mercuric ion depends on the particular pH prevailing , as shown by the following table.

Table II

The Dependence of the End Point of Diphenylcarbazide On the pH of the Solution

Volume of solution: 50 ml.
Amount of chloride: equivalent to 5 ml. of 0.001 N NaCl solution
No interfering elements present

PH of the solution	Milliliters of 0.001 N mercuric nitrate solution required to develop a faint violet color
3	13.0
4	6.4
5.5	2.8
7	0.8

Thus the pH of the distillate must be adjusted to a value accurate to the first decimal place. Moreover, the intensity of the violet color depends also on the volume of the solution , the amount of indicator used, and the lapse of time. While it might be possible to duplicate conditions at each determination, the operations are too complex for a practical method.

Potentiometric Titration

Preliminary experiments in which chloride was titrated potentiometrically, using a silver electrode with a normal calomel reference electrode, have not proven satisfactory; it seems impossible to obtain a sharp value for the equivalence point even when differential titrations are carried out. The interference caused by oxidizing agents such as ferric ion in the electrolyte, presents an additional objection to the use of the silver electrode. After these preliminary experiments, investigation of the applicability of the silver-silver chloride electrode to the problem was undertaken.

Silver-Silver Chloride Electrode

The silver-silver chloride electrode is prepared , according to usual methods, by coating a small platinum wire with silver by electrolysis of argentocyanide solution with 3 milliamperes for 24 hours, this being easily done with a practcally exhausted ordinary dry cell. After washing with distlled water and then with concentrated ammonia and a final rinsing with distilled water, the surface is coated with silver chloride by electrolyzing a dilute chloride solution, using a silvered electrode as anode. It has been shown (37) that the washing with concentrated ammonia is necessary to remove the last trace of cyanide. A current of 5 to 7 milliamperes is passed for 20 minutes, preferably in a dark room. The silver-silver chloride electrode so prepared has a brown color and is sensitive in the cell for several months if kept in distilled water when not in use and not exposed to direct light.

The silver-silver chloride electrode is connected to the normal calomel electrode through a salt bridge, consisting of a saturated solution of potassium nitrate containing 5 % agar-agar.

The e. m. f. of the following cell at 25°C. :

$$\mathrm{Ag}\,|\,\mathrm{AgCl}\,(s)\,,\ \mathrm{H_2O}\ \text{saturated with AgCl}\ \|\ 1.0\ \mathrm{N\ KCl},\ \mathrm{Hg_2Cl_2}(s)\,|\,\mathrm{Hg} \qquad (1)$$

is $0.2224 + 0.0591 \log 1.33 \times 10^{-5} - 0.2841 = 0.226$ v., where 0.2224 and 0.2841 are standard potentials at 25°C. of silver-silver chloride electrode and normal calomel electrode respectively, and 1.33×10^{-5} is the solubility of silver chloride in mol/ L at 25°C.

In spite of the use of a salt bridge, it has not yet been found possible to eliminate the liquid junction potential. Owing to the high diffusion rate of hydrogen ion, there is a large liquid junction potential between the copper-refining electrolyte and the saturated potassium nitrate solution. We desire to know the e.m.f. of the following cell:

$Ag|AgCl(s)$, $CuSO_4$ and H_2SO_4 saturated with $AgCl|1.0$ N KCl, $Hg_2Cl_2(s)|Hg$ (2)

E. Müller(26) gives 0.24 v. as the inflection potential measured against the normal calomel electrode. However, the inflection potential depends on the acidity , the value decreasing at the higher hydrogen-ion concentrations. We shall expect the inflection potential in the copper-refining electrolyte to be considerably lower than 0.24 v.

Experiments were made by the author to determine the liquid junction potential arising from such an arrangement. The temperature was regulated at 25.0°C. thermostatically. The data are collected in Table III.

Table III

The e. m. f. of the Cell: N Calomel Electrode A | Solution X | Saturated KNO_3 Solution | N Calomel Electrode B at 25.0°C.

Experiment	" Solution X "	e. m. f.	
1	Distilled water	- 0.0153 v.	
2	Cu 20g./L , H_2SO_4 98 g./L	+ 0.0045	average + 0.0048 v.
3	Cu 30 H_2SO_4 98	+ 0.0042	
4	Cu 40 H_2SO_4 98	+ 0.0052	
5	Cu 50 H_2SO_4 98	+ 0.0051	
6	Cu 20 H_2SO_4 196	+ 0.0015	average + 0.0014 v.
7	Cu 30 H_2SO_4 196	+ 0.0014	
8	Cu 40 H_2SO_4 196	+ 0.0013	
9	Cu 50 H_2SO_4 196	+ 0.0013	

Since no chemical reaction takes place in this cell, the total e.m.f.

is merely the sum of liquid junction potentials. It is seen that the substitution of distilled water by acid copper electrolytes produces a difference of e.m.f. , which varies between

$$- 0.0153 - 0.0048 = - 0.0201 \text{ v.}$$

and $- 0.0153 - 0.0014 = - 0.0167$ v.

As an approximation we shall expect the e.m.f. of the cell(2) to vary between

$$0.226 - 0.0201 = 0.206 \text{ v.}$$

and $0.226 - 0.0167 = 0.209$ v.

From many titrations it was found that the potential of silver-silver chloride electrode, in a chloride-containing electrolyte of ordinary composition titrated to the equivalence point , is 0.214 v. at room temperature against a normal calomel electrode.

From this result it immediately suggests that the equivalence point can be estimated by titrating to a definite potential instead of by finding the maximum rate of change of potential with respect to the volume of titrant added as in the classic method. It was mentioned before that the classic method is not practical for the very diluted titrant used in the present case. By the titration to a definite potential method the progress of a titration is clearly shown by the potential recorded, so that there is little chance of missing the equivalence point. This is best illustrated by the data collected in Table IV. By interpolation the equivalence point is reached when 37.54 ml. of titrant has been added, as this volume corresponds to a potential of 0.214 v.

Table IV

Potentiometric Titration (Titration to a Definite Potential) of Chloride in Copper-Refining Electrolyte Using $AgNO_3$ Solution

Volume of Titrant Added	Potential
20.00 ml.	0.1418 v.
30.00	0.1710
35.00	0.1945
36.00	0.2015
37.00	0.2092
37.35	0.2124
37.46	0.2135
37.70	0.2151

Table V shows the experimental results. These titrations were purposely carried out at room temperature (24 to 28°C.) without any temperature adjustment. In each case a blank was run first. The blank was found by interpolating the number of milliliters of titrant required to bring the potential against the normal calomel electrode of a particular solution to 0.214 v. Then the measured amount of chloride was added. Silver nitrate solution was added gradually. The potentials and the volumes were recorded. By interpolation the number of milliliters of silver nitrate solution required to bring the potential to 0.214 v. again was found. The difference gave the net amount of silver nitrate solution used. It seems that the amount of silver nitrate solution consumed in the blank is a rough measure of chloride present in the reagents used. In the analysis of an unknown solution, no blank test is needed.

Table V , Part a, shows the calibration of the strength of an approximately 0.001 N silver nitrate solution. It is seen clearly that there is a linear relation between the amount of chloride added and the volume of silver nitrate consumed. For the particular silver nitrate solution used, 1 ml. of the solution is equivalent to 0.0363 mg. AgCl. The mean deviation is 1 %.

Table V

Potentiometric Titration with Silver Nitrate (Titration to a Definite Potential) of Chloride in Copper-Refining Electrolyte

Volume of sample: 25 ml. Room temperature (24 to 28° C.)

Part a

Calibration of strength of silver nitrate. 40 g./L Cu, 184 g./L H_2SO_4

Chloride added		Gross	Blank	Net	mg. Cl/ml.	Deviation
0.106 mg. or	4.24 mg./L	3.81 ml.	0.80 ml.	3.01 ml.	0.0352	- 3.0 %
0.266	10.6	8.09	0.80	7.29	0.0365	+ 0.5
0.532	21.3	15.22	0.80	14.42	0.0369	+ 1.7
0.798	32.0	22.85	0.80	22.05	0.0362	- 0.3
1.06	42.4	30.10	0.80	29.30	0.0362	- 0.3
1.33	53.2	37.54	0.80	36.74	0.0362	- 0.3
1.60	64.0	44.57	0.80	43.77	0.0366	+ 0.8
				Average	0.0363	1.0

Part b

Effect of various impurities in the copper electrolyte

40 g./L Cu, 184 g./L H_2SO_4; Chloride added, 0.532 mg. or 21.3 mg./L

Impurity	wt.	Form	Gross	Blank	Net	Cl found	Error
Ni^{++}	1.5 %	sulfate	17.15 ml.	2.30 ml.	14.85 ml.	0.539 mg.	+ 1.3 %
Fe^{+++}	0.1	sulfate	14.90	0.40	14.50	0.526	- 1.1
Fe^{++}	0.1	sulfate	15.75	0.88	14.87	0.540	+ 1.5
Sb^{+++}	0.02	trioxide	15.54	0.98	14.56	0.529	- 0.6
Sb^{+++}	0.1	tartrate	15.73	0.78	14.95	0.543	+ 2.1
Sb^{+++++}	0.02	antimonic acid	16.30	1.63	14.67	0.533	+ 0.2
Bi^{+++}	0.1	nitrate	15.10	0.70	14.40	0.523	- 1.7
As^{+++++}	0.02	arsenic acid	15.98	1.10	14.88	0.540	+ 1.5
As^{+++}	0.02	trioxide	15.95	1.60	14.35	0.521	- 2.1
Glue	0.0001	gelatin	16.73	1.64	15.09	0.548	+ 3.0
Glue	0.0005	gelatin	16.32	1.47	14.85	0.539	+ 1.3
Glue	0.001	gelatin	16.30	1.41	14.89	0.541	+ 1.7
Glue	0.005	gelatin	16.53	1.37	15.16	0.550	+ 3.4

Part c

Effect of various concentrations of copper and sulfuric acid in the electrolyte

Chloride added, 0.532 mg. or 21.3 mg./L

Cu	H_2SO_4	Gross	Blank	Net	Cl found	Error
20 g./L	98 g./L	15.00 ml.	0.42 ml.	14.58 ml.	0.529 mg.	- 0.6 %
30	98	14.59	0.58	14.01	0.509	- 4.3
40	98	14.76	0.80	13.96	0.507	- 4.7
50	98	15.00	0.95	14.05	0.510	- 4.2
20	122.5	14.81	0.38	14.43	0.524	- 1.5
30	122.5	15.50	0.60	14.90	0.541	+ 1.7
40	122.5	15.93	0.75	15.18	0.551	+ 3.6
50	122.5	15.41	0.98	14.43	0.524	- 1.5
20	147	15.25	0.60	14.65	0.532	0
30	147	15.85	0.62	15.23	0.553	+ 4.0
40	147	15.50	0.90	14.60	0.530	- 0.4
50	147	15.63	1.00	14.63	0.531	- 0.2
20	171.5	15.78	0.65	15.13	0.549	+ 3.2
30	171.5	15.65	0.70	14.95	0.543	+ 2.1
40	171.5	15.25	0.90	14.35	0.521	- 2.1
50	171.5	15.39	1.10	14.29	0.519	- 2.5
20	196	15.15	0.73	14.42	0.524	- 1.5
30	196	15.95	0.75	15.20	0.552	+ 3.8
40	196	16.14	1.00	15.14	0.550	+ 3.4
50	196	16.32	1.20	15.12	0.549	+ 3.2

Part b shows the effects of various impurities ordinarily present in the electrolyte. It is seen clearly that none of the impurities interferes with the titration. The maximum error is 3.4 % .

Part c shows the effects of the change of the concentration of copper and sulfuric acid. It is seen clearly that within the range of concentrations tested, the liquid junction potential does not vary enough to affect appreciably the accuracy of the results. The maximum error is 4.7 %.

In these experiments no special precautions were taken with regard to the effects of change of temperature, change of solubility of silver chloride with increasing ionic strength, adsorption of chloride by silver chloride and the change in liquid junction potential. This results in a comparatively large error of about 5 %. However, we gain time and simplicity. Moreover, in each determination in Parts b and c of Table V only 0.532 mg. of chloride is present. This degree of accuracy is quite satisfactory for routine control purposes.

Summary

The small amount of chloride in copper-refining electrolyte can be determined by titrating the electrolyte directly with silver nitrate at room temperature. The equivalence point is found by interpolating the volume of titrant required to bring the potential of silver-silver chloride electrode against the normal calomel electrode to 0.214 v.

1. The method is accurate to 5 % when 25 ml. of electrolyte containing 0.532 mg. of chloride is taken as a sample.

2. The method is rapid. Only ten minutes is required for a titration.

3. The method is fairly simple. All that is required is a normal calomel electrode, a silver-silver chloride electrode and a potentiometer.

Part III

DETERMINATION OF TRACES OF BISMUTH IN COPPER BY DITHIZONE METHOD

Introduction

Several methods have been proposed for the determination of traces of bismuth in copper. In brief, bismuth is first separated from large quanties of copper by a collecting agent, such as ferric hydroxide(38) or hydrated manganese dioxide (24,29), or an extractive agent such as dithizone(19); it is then determined spectrographically(29) or colorimetrically (38,24,19). An entirely different method(18) consists of the formation of a bismuth mirror when copper millings are heated at 1050 to 1060°C. in a stream of hydrogen.

The bismuth mirror method and the spectrographic method require elaborate apparatus not usually available in copper refineries. The extraction of bismuth directly from copper solution in alkaline cyanide medium is objectionable in that large quantities of cyanide have to be added to keep the copper ion in complex form, which results in the liberation of much toxic hydrogen cyanide and cyanogen. The colorimetric method(iodobismuthite method) is interfered with by many ions which liberate iodine or form insoluble iodides. The isolation of bismuth presents marked difficulties in view of the small quantity present. If bismuth is not isolated, the method is not accurate. Thus a simple and accurate method of determining traces of bismuth in copper is needed for control purposes.

A dithizone method incorporating the following principles is found useful.

(1) Hydrated manganese dioxide is used as a collector of bismuth(29). This effects a rough separation of bismuth from copper, without loss of bismuth.

(2) The manganese dioxide precipitate is dissolved and bismuth is extracted from ammoniacal cyanide solution with dithizone solution in carbon tetrachloride. According to Fischer(21), Bi^{+++}, Pb^{++}, Sn^{++}, and Tl^{+} are the possible ions so extracted. Thallium is not likely to be present in ordinary copper. Tin is oxidized during the dissolution of copper. Therefore lead is the only other element coextracted with bismuth in appreciable amounts.

(3) The dithizonates of lead and bismuth are thrown back from the carbon tetrachloride phase into the water phase by shaking them with dilute acid. Bismuth is the only element titrated out by dithizone solution at pH=2 (43).

Procedure

Dissolve a suitable weight of copper, containing about 10 to 60γ of bismuth, in 50 percent nitric acid. Boil off the nitrous acid fumes. Cool. Neutralize the excess acid with 50 percent ammonium hydroxide until the solution is just alkaline to methyl orange indicator. Add sufficient nitric acid to give an acid concentration of about 0.02 N . Heat the solution to boiling. Add 5 ml. of 20 percent potassium bromide solution and 3 ml. of 3 percent potassium permanganate solution. Keep boiling until the violet solution changes into a brown suspension. Filter out the manganese dioxide precipitate through a Gooch crucible. Wash with a little water. Add the same volume of potassium bromide and potassium permanganate solution to the filtrate as before to obtain a second crop of manganese dioxide precipitate . Combine the precipitates and dissolve in a mixture of 10 percent sulfuric acid and 10 percent sodium sulfite solution. Add 4 ml. of 50 percent citric acid. Add 10 percent ammonium hydroxide drop by drop until the odor of ammonia is barely perceptible. Add also 4 ml. of 50 percent potassium cyanide solution. Transfer the solution to a separatory funnel. Add an excess of dithizone solution in carbon tetrachloride in 5-ml. portions from a buret. The concentration of dithizone solution is about 5 mg. per 100 ml. and the dithizone has been purified by the ordinary method(32) . Shake vigorously after each addition. Draw off the carbon tetrachloride phase before the next addition. The excess of dithizone is evidenced by the fact that the green color of the carbon tetrachloride phase remains unchanged for 1 minute. Collect the red dithizonates in a small beaker . Transfer them to the separatory funnel. Wash them with a little water . Add a little 5 percent nitric acid. After vigorous shaking, draw off the carbon tetrachloride phase to a second separatory funnel. Repeat the shaking with dilute nitric acid. Combine the acid extracts. Add 2 drops of 0.04 percent meta-cresol purple indicator. Neutralize with 10 percent ammonium hydroxide until the solution is almost colored orange. Extract with fresh carbon tetrachloride in 5-ml. portions to remove the yellow oxidation products of dithizone. Add about 0.2 g. hydroxylamine hydrochloride. Readjust the pH of the solution by adding dilute ammonium hydroxide or nitric acid until the solution is colored orange (pH = 2). Add dithizone solution in small volumes. Shake vigorously. Draw off the orange bismuth dithizonate before the next addition. The end point is reached when the green dithizone solution remains unchanged in color. The dithizone solution is previously calibrated against the standard bismuth solution. The standard bismuth solution is prepared by dissolving 0.1 g. of pure bismuth in nitric acid and then diluting to 1 liter. Take care to have sufficient nitric acid present so that no basic salt of bismuth is precipitated during the dilution. One milliliter of the solution contains 100γ of bismuth.

Analytical Results

To test this procedure, various amounts of bismuth were added to 25 ml. of acid copper sulfate solution (Cu, 40 g./L ; H_2SO_4 , 184 g./L). The results are collected in Table VI.

Table VI

Determination of Bismuth in Acid Copper Solution

One milliliter of dithizone solution equivalent to 13 γ of bismuth.

Bi added, γ	Gross ml.	Net ml.	Bi found, γ	Error, γ
0		0.15	2	
10	0.8	0.65	9	- 1
20	1.5	1.35	18	- 2
30	2.5	2.35	31	+ 1
40	3.1	2.95	38	- 2
60	4.5	4.35	57	- 3
80	6.1	5.95	77	- 3
100	7.5	7.35	96	- 4

Analyses were also run on different forms of copper. The results are collected in Table VII. These different forms do not come from the same source, so the results are not comparable.

Table VII

Determination of Bismuth in Refined Copper

Form	Bismuth content, percent
Copper sheet	0.0002
Copper shots	0.0007
Copper wire	0.00008
Copper powder	0.0018

Summary

The proposed method gives reproducible and reasonably accurate results. It does not require any special apparatus. It takes 2 to 3 hours to run a single analysis. It is suitable for a control method in a copper refinery.

Part IV

FUNCTIONS OF CHLORIDE IN COPPER-REFINING ELECTROLYTE IN THE ABSENCE OF ADDITION AGENTS AND IMPURITIES

Experimental

A rectangular glass jar holding about 10 liters of electrolyte was used as an experimental cell. This was placed in a large water bath, the temperature of which was maintained thermostatically so that the temperature of the electrolyte was held at 37°C. (99°F.). There were separate motor stirrers in the cell and in the water bath. The speed of the stirrer was about 2000 r.p.m.

The electrolyte used was a synthetic one, made from C.P. chemicals . The composition was: Cu, 40 g./L ; H_2SO_4 , 184 g./L . The electrolyte was frequently analyzed for copper and acid by the usual methods and minor adjustments were made to maintain this composition. The evaporation loss was compensated by the constant addition of distilled water.

Current was supplied by a small motor-generator set capable of delivering 15 amperes at 30 volts. Proper resistance was connected in the circuit to maintain the cathode current density at 15 amperes per square foot (1.6 amp./ sq. dm.) .

There were two anodes and one cathode. The anodes were cast electrolytic copper and the cathode was cast commercial lead . Lead was selected as the cathode to facilitate the stripping of the copper deposit without using oil. The immersed area of the cathode was 52 sq. in. (340 sq. cm.).

Attention had been paid to the possibility of the orientation of the base metal being copied by the deposit. At the beginning of the electrolysis, the current was interrupted three or four times. The cathode was taken out of the cell and washed with normal sulfuric acid and distilled water. Then the electrolysis was resumed. This had been shown(17) to have the effect of minimizing the continuity. The time of electrolysis in each run was 12 hours. It was improbable that the influence of the base metal extended very deep. As a final check, a portion of the deposit perpendicular to the depositing surface was examined microscopically. In each case the deposit was oriented freely.

In each run the operating conditions were maintained constant, as specified above. The only variable was the chloride concentration of the electrolyte. Chloride was determined potentiometrically (Part II). Starting from C. P. hydrated copper sulfate, which was practically chloride-free, and C.P. sulfuric acid, which was chloride-free, the original solution was found to contain 2.74 mg./L of chloride (experiment No. 1, Table VIII). This chloride concentration was reduced to 0.75 mg./L by agitating the solution with copper powder for 8 hours and filtering (experiment No. 2). The chloride concentration was further reduced to a negligible amount by adding an equivalent amount of silver nitrate to the solution (experiment No. 3). Later the chloride concentration was gradually increased by adding sodium chloride to the solution until a concentration of 84.8 mg./L was reached.

After the electrolysis the copper deposit was stripped from the lead cathode. Small specimens were mounted in bakelite and polished. One sample was used to determine the hardness and another was used for the estimation of the grain size.

A Haring cell(22) was used to determine the cathode polarization. The operating conditions such as composition of the electrolyte, current density and temperature were the same as those in the large experimental cell except that in the Haring cell the distance from the anode face to the cathode face was exactly 15 cm. (5.9 in.) and the electrolysis was carried out for several minutes without stirring . The other conditions were maintained constant; only the halide concentration was varied. The halides used were sodium fluoride, sodium chloride, potassium bromide and potassium iodide.

Results

The data correlating the chloride concentration of the electrolyte and the hardness and the grain size of the deposit are collected in Table VIII.

Table VIII

Hardness and Grain Size of the Copper Deposit

Exp.	Chloride concentration, mg./L				Average	Average	Micrograph
No.	Before the electrolysis	After the electrolysis	Av. conc. of the bulk	Av. conc. of the cathode film	Vickers hardness number	grain size, sq. in. $\times 10^{-6}$	No. (Fig. III)
3	0	0.20	0.10	0.23	72.1	1.13	a
2	0.75	0.79	0.77	0.95	66.9	1.23	b
1	2.74	2.63	2.69	2.80	72.6	0.64	c
4	5.72	5.52	5.62	5.84	75.4	0.43	d
5	18.5	16.5	17.5	21.9	73.3	0.52	e
6	32.2	30.2	31.2	30.6	72.4	0.60	f
7	49.5	43.9	46.7	44.3	71.0	0.66	g
8	63.3	42.5	52.9	46.4	68.5	0.60	h
9	84.8	40.0	62.4	54.7	66.4	0.72	i

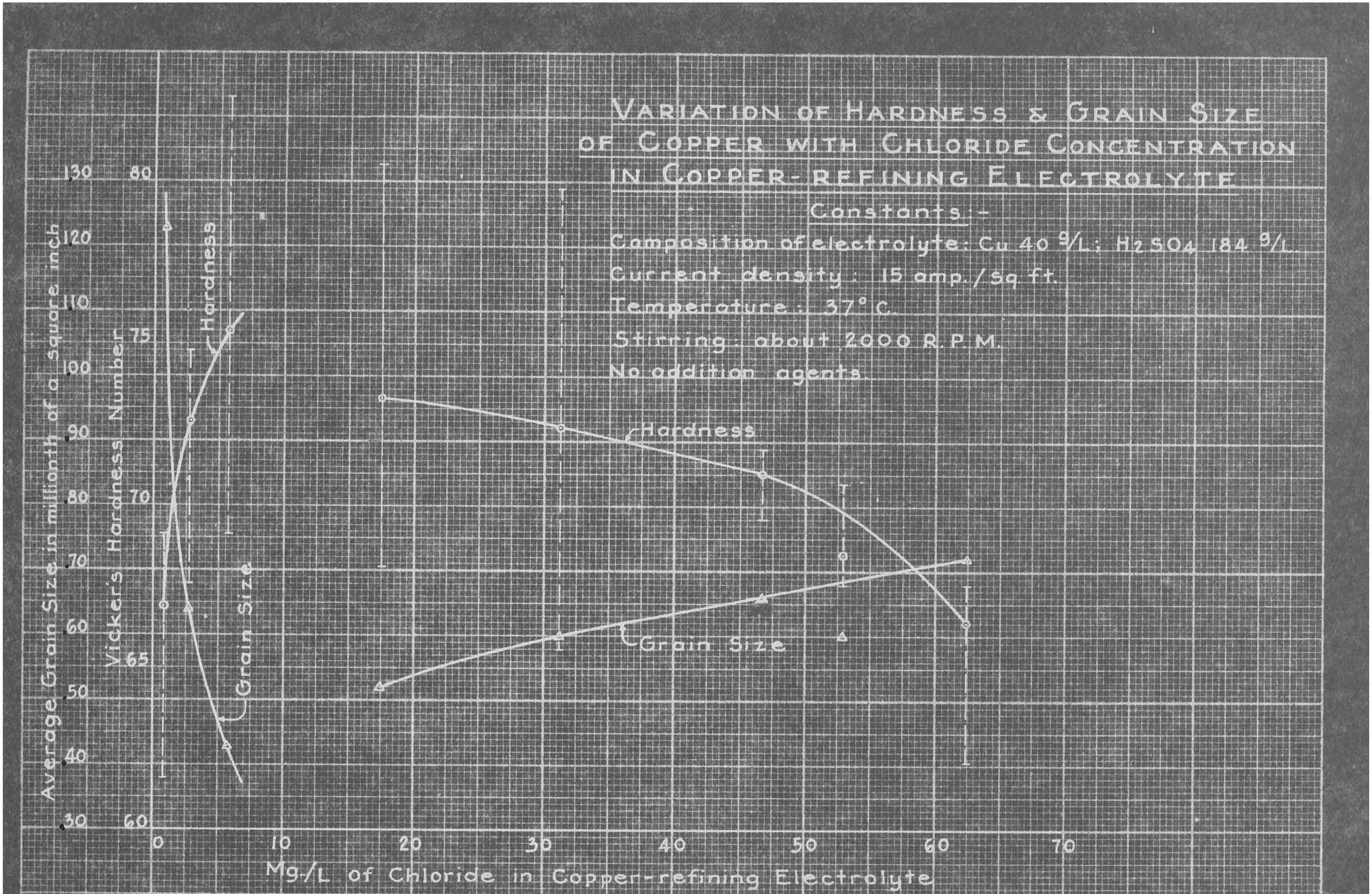
The fourth column records the average of the chloride concentration before and after the electrolysis, which represents the average chloride concentration of the bulk of the electrolyte. The fifth column records the average of chloride concentration of the cathode film determined from the composite samples taken during the electrolysis by the so-called "drainage" method(15). The sixth column records the Vickers hardness number, obtained by an average of five or six readings. The seventh column records the average grain size in millionths of a square inch. This was determined by cutting 100 grains from micrographs taken at a magnification of 100X, weighing them and comparing them with the weight of 1 sq. in. of the same photographic paper. Freshly prepared ammoniacal hydrogen peroxide solution was used as the etchant.

The hardness and the grain-size data are plotted in Figure I. The data from experiment No. 3(zero initial chloride concentration) are omitted because of their apparent anomaly. There is an increase of chloride concentration of 0.20 mg./L after the electrolysis. Probably some silver added as silver nitrate and precipitated as silver chloride was codeposited with copper and an equivalent amount of chloride was liberated. The hardness curve is drawn through the points of the average hardness while the bands show the range of values recorded.

The polarization data are plotted in Figure II. The ordinates are the excess cathode polarization over that of the original electrolyte without any addition of halide. The original electrolyte contains no fluoride, bromide and iodide, but contains 1.36 mg./L of chloride. Polarization is afunction of the smoothness of the electrode. It is very difficult to duplicate the smoothness of the electrode. By this method of plotting, all curves are shifted vertically to coincide at the polarization at zero halide concentration(in case of chloride, the excess cathode polarization is referred to a chloride concentration of 1.36 mg./L and the abscissaa are shifted 1.36 mg./L to the left also), and therefore the comparison is facilitated.

Discussion of Results

The solubilities of cuprous halides are collected in Table IX.



VARIATION OF HARDNESS & GRAIN SIZE OF COPPER WITH CHLORIDE CONCENTRATION IN COPPER-REFINING ELECTROLYTE

Constants:-

Composition of electrolyte: Cu 40 g/L; H_2SO_4 184 g/L

Current density: 15 amp./sq ft.

Temperature: 37° C.

Stirring: about 2000 R.P.M.

No addition agents

Fig. I

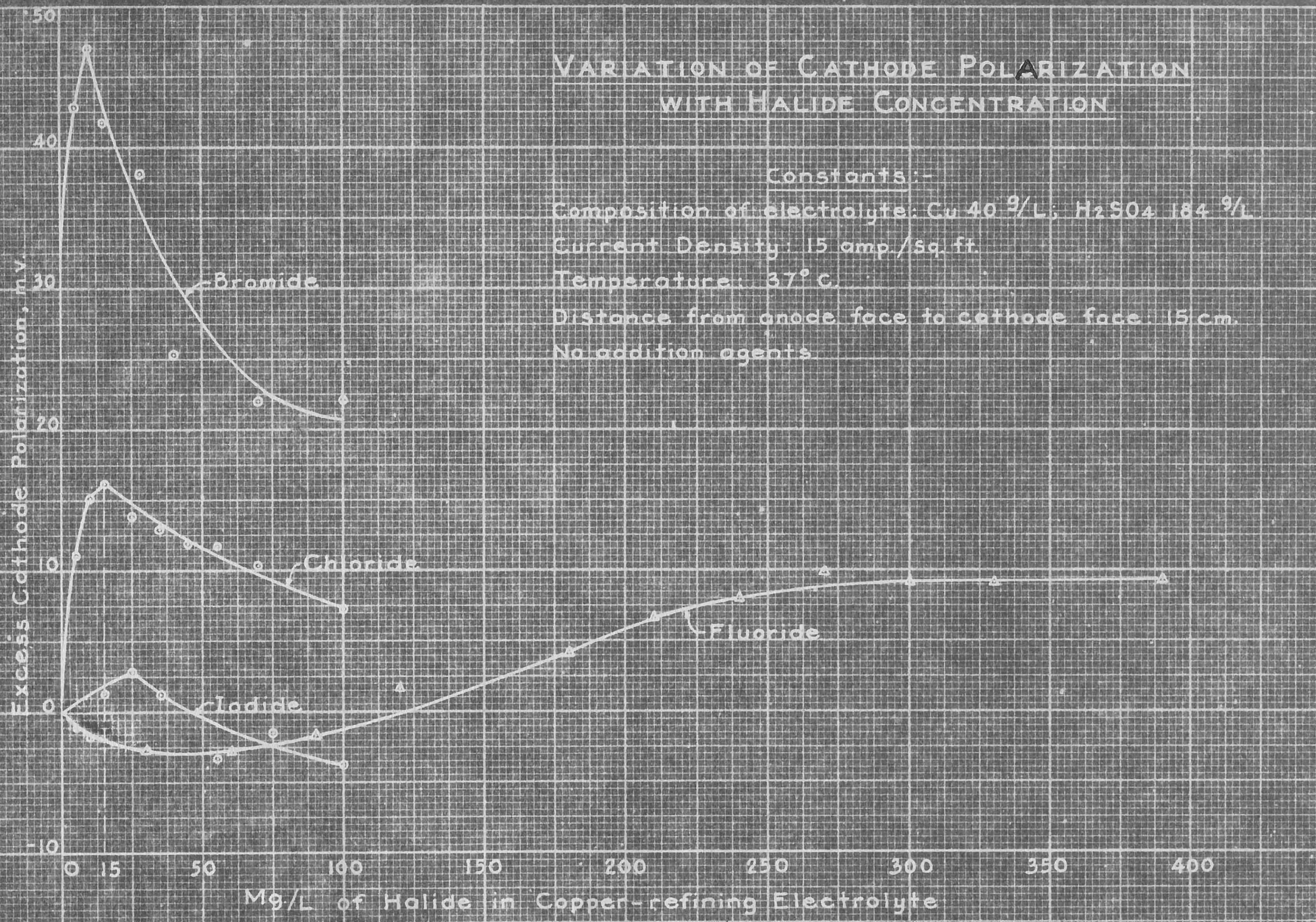

VARIATION OF CATHODE POLARIZATION
WITH HALIDE CONCENTRATION
Constants:-
Composition of electrolyte: Cu 40 g/L; H2SO4 184 g/L
Current Density: 15 amp./sq. ft.
Temperature: 37° C.
Distance from anode face to cathode face: 15 cm.
No addition agents
Bromide
Chloride
Iodide
Fluoride
Excess Cathode Polarization, m.v.
50
40
30
20
10
0
-10
0
15
50
100
150
200
250
300
350
400
Mg/L of Halide in Copper-refining Electrolyte

Fig. II

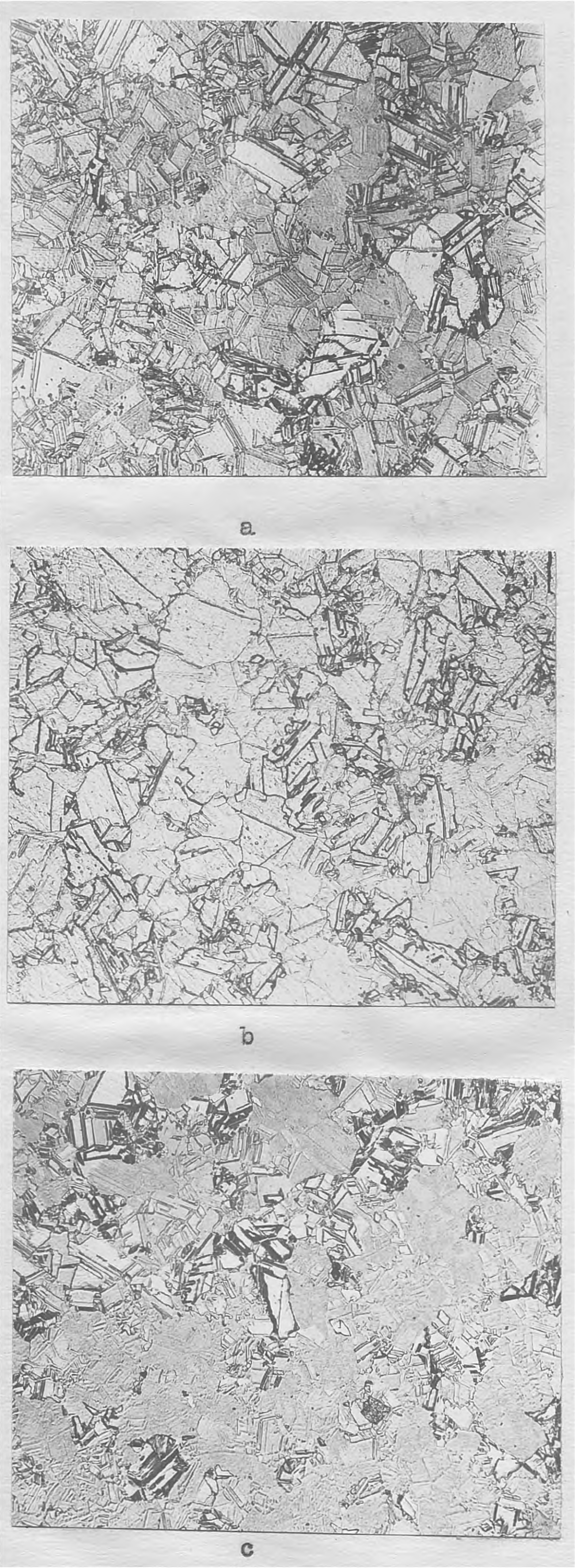


Figure III

Electrolytic copper, X 100, etched with ammoniacal hydrogen peroxide.

a Concentration of chloride,
0.10 mg./L

b Concentration of chloride,
0.77 mg./L

c Concentration of chloride,
2.69 mg./L

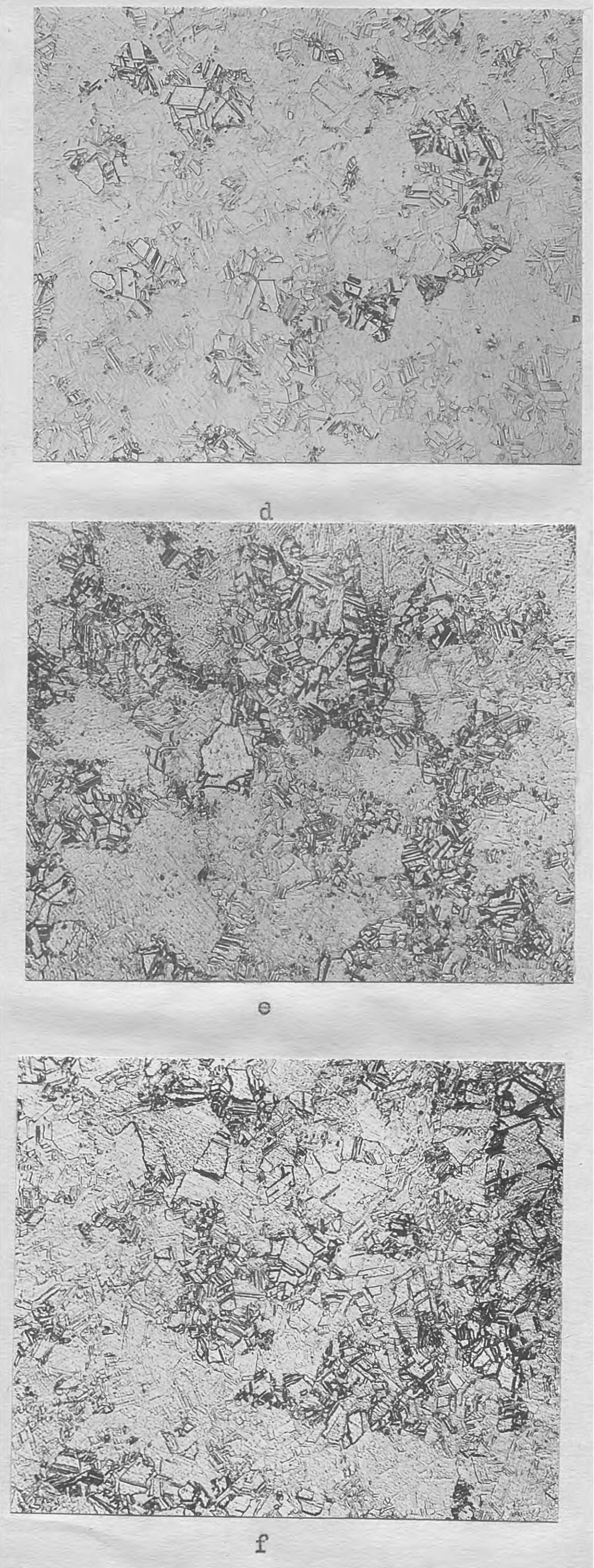


Figure III (continued)

Electrolytic copper, X 100, etched with ammoniacal hydrogen peroxide.

d Concentration of chloride, 5.62 mg./L

e Concentration of chloride, 17.5 mg./L

f Concentration of chloride, 31.2 mg./L

Figure III (continued)
Electrolytic copper, X 100 , etched with ammoniacal hydrogen peroxide.

g Concentration of chloride, 46.7 mg./L

h Concentration of chloride, 52.9 mg./L

i Concentration of chloride, 62.4 mg./L

Table IX

Solubilities of Cuprous Halides at about 20°C.

Compound	Solubility product in $(\text{mols/L})^2$	Solubility of halides in mg./L in copper-refining electrolyte	Reference
CuF	?		
CuCl	3.4×10^{-6}	24	(14)
CuBr	4.6×10^{-8}	0.7	(14)
CuI	5×10^{-12}	0.0001	(36)

The solubility product of the respective halide is calculated or taken from the reference marked in the last column of this table. In making the calculations for the third column, the following values, which are approximate only, are assumed:

$$\frac{(\text{Cu}^{+})^2}{(\text{Cu}^{++})} = 0.5 \times 10 \quad \text{and} \quad (\text{Cu}^{++}) = 0.5\ \text{M}$$

It is seen from the polarization curves that bromide is a more powerful polarizing agent than chloride. This is linked with the fact that CuBr is more insoluble than CuCl.

The maximum of the fluoride polarization curve occurs at a higher concentration of fluoride than that of bromide or chloride. Although no data on the solubility of CuF are available, it is reasonable to believe that CuF has a higher solubility than CuCl.

After certain maximum concentrations of bromide and chloride (for chloride, about 15 mg./L ; for bromide, about 10 mg./L), they act as depolarizers. This may be explained by the increase of solubility of halide due to the formation of a complex ion such as CuCl_2^- .

However, CuI is more insoluble than CuBr, yet the polarizing effect of the former is weak. Moreover, when small amounts of silver nitrate are added to an electrolyte containing 1.36 mg./L of chloride, the author found that at first there is a decided drop in cathode polarization. Silver chloride is more insoluble than the cuprous halides, except cuprous iodide. Thus we can not explain the polarization by merely connecting it with the precipitation of an insoluble compound.

The three electrochemical reactions occurring at the cathode of a copper-refining cell are:

$$Cu^{++} + 2e \rightarrow Cu \text{ ------------------------------------ } (1)$$

$$Cu^{++} + e \rightarrow Cu^{+} \text{ ------------------------------------ } (2)$$

$$Cu^{+} + e \rightarrow Cu \text{ ------------------------------------ } (3)$$

These must proceed in such a way that the relative amounts of Cu^{++} and Cu^{+} ions deposited satisfy the equilibrium constant K of the following reaction :

$$Cu^{++} + Cu \rightarrow 2\,Cu^{+} \text{ ------------------------------------ } (4)$$

if equilibrium is reached and persists (4).

If equilibrium is disturbed, that electrochemical reaction which tends to restore equilibrium will proceed to the larger extent. Although that reaction will be the predominant one, it will not necessarily proceed most quickly.

To explain the polarization phenomena, we assume that reaction (2) is a slow process. If Cu^{+} be removed, e.g. , as an insoluble halide, to an amount larger than that demanded by the Cu^{++} ion concentration and the constant K, reaction (2) will predominate. By the assumption this will involve higher polarization. Thus the lower the solubility of halide, the higher the polarization. This explains why fluoride, chloride, and bromide at lower concentrations act as polarizers.

The assumption that reaction (2) is a slow process is not new . Thompson(39) assumed that in the anodic solution of copper, $Cu \rightarrow Cu^{++} + 2e$

has a greater polarization than $Cu \rightarrow Cu^{+} + e$, too much Cu^{+} is dissolved and therefore the reaction $2Cu^{+} \rightarrow Cu^{++} + Cu$, with the precipitation of powdered copper, takes place. This is another way of saying that $Cu^{+} \rightarrow Cu^{++} + e$ is a slow process, as otherwise the excess Cu^{+} can be removed by this reaction.

The anomalous behaviour of iodide is due to the following two consecutive reactions:

$$\begin{array}{l} 2\,Cu^{++} + 2\,I^{-} \rightarrow 2\,Cu^{+} + I_2 \\ 2\,Cu^{+} + 2\,I^{-} \rightarrow 2\,CuI \\ \hline 2\,Cu^{++} + 4\,I^{-} \rightarrow 2\,CuI + I_2 \end{array}$$

This involves no removal of Cu^{+} ion. Reaction (2) will proceed to almost the same extent as if no iodide were present, and therefore the polarization effect is not great.

In contrast to what happens at the anode, the reaction $Cu^{++} + Cu \rightarrow 2\,Cu^{+}$ will not predominate at the cathode, since one of the reactants is a solid. Probably because of this, the cathode polarization is always higher than the anode one. As chloride or bromide concentration increases above a certain value, corresponding to the saturation concentration of the respective cuprous halide, we assume further that the following electrochemical reaction will partly replace reaction(2):

$$Cu^{++} + 2\,Cl^{-} + e \rightarrow CuCl_2^{-} \text{------------------------------------} (5)$$

It is conceivable that reaction (5) takes place more easily than reaction (2), as Cu^{+} has a natural tendency to form a complex ion. Consequently the following two consecutive reactions will shift from the right to the left.

$$Cu^{+} + Cl^{-} \rightleftarrows CuCl \text{--} (6)$$

$$CuCl + Cl^{-} \rightleftarrows CuCl_2^{-} \text{--} (7)$$

Thus less Cu^{+} is removed as compared with the removal of Cu^{+} by reaction (6) alone. That chloride(or bromide) acts as a depolarizer is accordingly explained.

Applying these considerations to the anode, in the absence of chloride, reaction (4) takes place in the reverse direction. with the deposition of powdered copper. As chloride concentration is increased, the reverse reaction of (5) will not predominate ; the forward reactions of (6) and (7) will compete with the reverse reaction of (4). As a result cuprous chloride will be precipitated with copper in the vicinity of the anode.

Blum and Hogaboom(13) have modified the statement of W. L. Bancroft that " increasing the potential difference at the cathode decreases the size of the crystals " into " increasing the cathode polarization usually decreses the crystal size". It is seen from Figures I and II that there is such a correlation between the grain size and the cathode polarization.

Indentation hardness increases with the increasing fineness of the grains in polycrystalline metals(7, 11) . It is seen from Figure I that there is such a correlation.

Referring to Table VIII, there is a decrease of chloride concentration after 12 hours' electrolysis. The decrease is not significant until the initial chloride concentration is at or above 18.5 mg./L . This is due to the precipitation of CuCl, which gradually settles out. As to the chloride concentration of the cathode film, it is interesting to note that the average chloride concentration of 17.5 mg./L also forms a demarkation point. At or below that concentration the cathode film has a higher concentration than the bulk of the electrolyte, but the reverse is true above that concentration. As was mentioned before, when the chloride concentration is above the saturation concentration of CuCl in the copper-refining electrolyte, the reactions (6) and (7) are shifted from the right to the left, and therefore cuprous chloride is precipitated near the cathode surface.

Conclusions

Up to about 15 mg./L , chloride acts as a cathode polarizer in the copper-refining electrolyte. It refines the crystal size and increases the hardness of the copper deposit. Above that concentration chloride acts as a cathode depolarizer, with simultaneous reversal in effects on grain size and hardness. This concentration probably represents the saturation concentration of CuCl in the copper-refining electrolyte.

It must be emphasized that the work in this part is carried out in a synthetic copper-refining electrolyte in the absence of impurities and addition agents. In the present case the chief effect of chloride is to refine the crystal size of the copper deposit. This effect is overshadowed by the presence of glue or other addition agent in the actual copper-refining electrolyte.

Part V

A STUDY OF THE POSSIBILITY OF PRECIPITATION OF ANTIMONY AS OXYCHLORIDE IN COPPER-REFINING ELECTROLYTE

It is well known that chloride in copper-refining electrolyte minimizes the tendency for codeposition of antimony with copper. It has often been assumed that antimony is precipitated, at least partly, as oxychloride. Although most metallurgists in the copper refineries do not accept this hypothesis, it appears in several text books. The aim of this part of the investigation was to critically examine this hypothesis.

It has been known that freshly precipitated hydrated antimony trioxide retains chloride very firmly. According to Bloom(12), three months' washing of freshly precipitated antimony trioxide with distilled water under constant agitation does not suffice to remove chloride completely. The amount of chloride so adsorbed is not definite. It varies with temperature and the chloride concentration of the solution when the precipitation of antimony trioxide takes place. While freshly precipitated antimony trioxide retains chloride strongly, there is little, if any, tendency to retain nitrate or sulfate. These phenomena are characteristic of adsorption, which varies with the specific nature of adsorbing and adsorbed material, temperature, and concentration of adsorbed material.

It has also been known that saturated sodium chloride solution prevents the hydrolysis of antimony if the amount of water added is not too great. In fact, the sodium chloride solution need not be saturated and solutions of other chlorides, if sufficiently concentrated, have the same protecting power. The author took 5-ml. portions of acid antimony trichloride solution, which was 0.506 M in antimony and 2.77 M in hydrochloric acid . Various solutions of salts having a concentration of about 3.0 N were added to them. The minimum volume of the solution required to produce turbidity in each case was recorded. Since the turbidity is due to the precipitation of antimony trioxide formed by hydrolysis, the volume so recorded represents the protecting power of the particular salt solution against the hydrolysis of antimony. The greater the volume, the better the protecting power. The data are collected in Table X.

Table X

Protecting Power of Various Salt Solutions against the Hydrolysis of Antimony Trioxide

Solution	Concentration	Minimum volume required to produce turbidity
H_2O		2.5 ml.
NaCl	6.1 N (saturated)	>50.0
NaCl	5.0 N	>50.0
NaCl	4.0 N	>50.0
NaCl	3.0 N	18.0
NaCl	2.0 N	4.0
NaCl	1.0 N	3.9
KCl	3.0 N	6.8
$BaCl_2$	2.9 N (saturated)	15.6
$CaCl_2$	3.0 N	>50.0
NH_4F	3.0 N	>50.0
KBr	3.0 N	>50.0
KI	3.0 N	>50.0
$NaNO_3$	3.0 N	4.0
Na_2SO_4	3.0 N	2.4
K_2SO_4	1.4 N (saturated)	2.8

It is thus seen clearly that the protecting power is tied up with the halide ion concentration. Halides of concentration of about 3 N have more or less protecting power while sulfates and nitrates of the same concentration have no protecting power.

The author next took two identical samples of antimony trichloride solution in hydrochloric acid. One was diluted with distilled water, while the other was diluted with the same volume of saturated sodium chloride solution. There was immediate precipitation of antimony trioxide in the first sample, but the second sample remained clear. Both samples were titrated with sodium hydroxide solution and the changes in pH were measured with a Beckman PH meter. The results are plotted in Figure IV. It is seen that, in spite of the initial differences in pH and differences in behaviour after the neutralization point , the shapes of the two curves are similar.

This suggests that the hydrolysis does take place when acid antimony chloride solution is diluted with saturated sodium chloride solution. Because of the large amount of chloride adsorbed, the antimony trioxide may be peptized and give rise to a colloidal solution.

This inference is supported by the fact that this colloidal solution can be made unstable by removing a large part of the adsorbed chloride by cold dialysis with parchment paper. The dialyzer is placed in a large vessel filled with distilled water and changed frequently. After eight hours so much chloride has diffused out through the parchment membrane that antimony oxychloride is precipitated. The precipitate is not due to the hydrolysis of antimony chloride during the dialysis, as the precipitate is heavy and settles readily, in contrast with ordinary antimony oxychloride, which is light and slow to settle.

To sum up, antimony oxychloride is nothing but antimony trioxide plus adsorbed chloride. It is precipitated whenever antimony trioxide is precipitated in presence of chloride. If the amount of chloride present is great, there is no apparent precipitation of either antimony trioxide or oxychloride.

From this consideration it is hard to understand why a small amount of chloride added to copper-refining electrolyte should initiate the precipitation of the dissolved antimony, if it has no tendency to precipitate out by itself.

Three further experiments made by the author show results which can

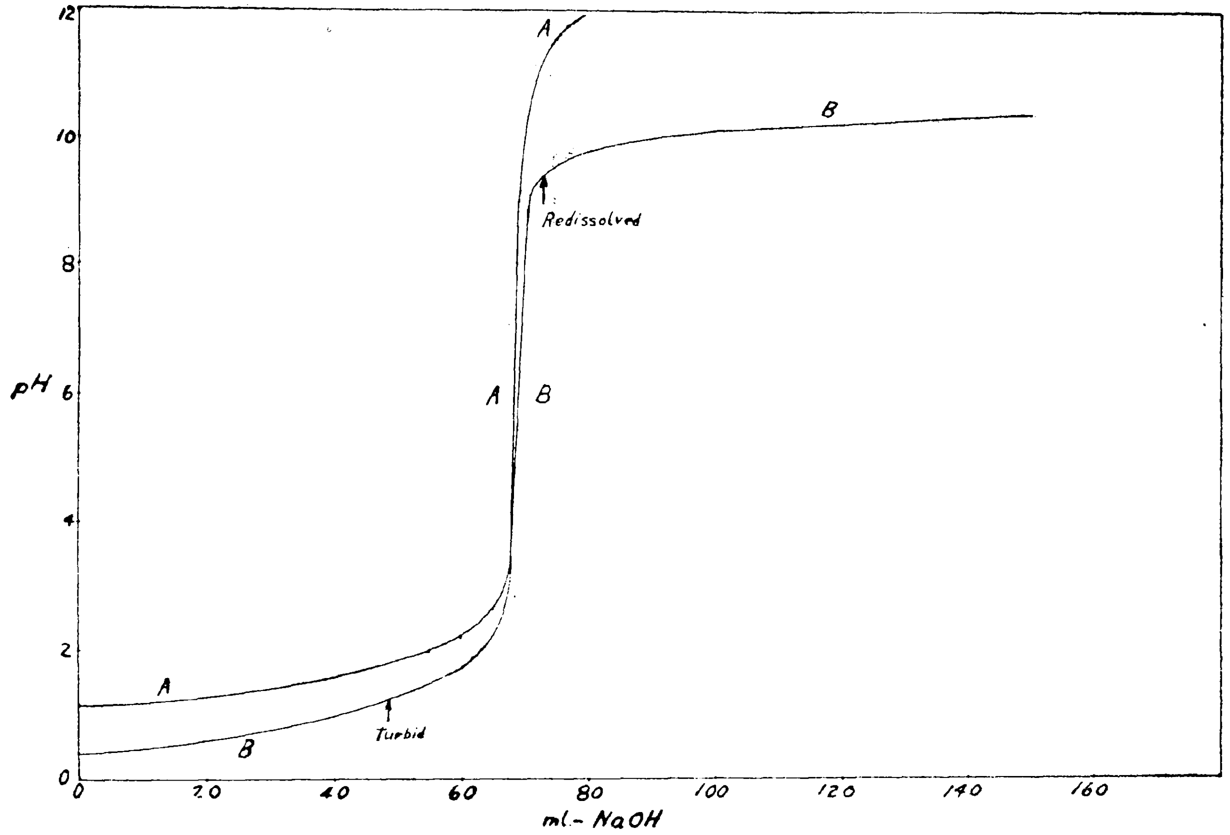


Fig. **IV** Titration curves of acid antimony chloride solution. A—1 ml. acid $SbCl_3$ solution (Sb, 0.304 *M*) + 49 ml. water. B—1 ml. acid $SbCl_3$ solution (Sb, 0.304 *M*) + 49 ml. saturated NaCl solution. Normality of NaOH 0.08184.

not be explained by the antimony oxychloride hypothesis.

The antimony trioxide used for the following experiments was prepared from C. P. antimony tartrate solution by adding excess ammonium hydroxide. The precipitate so formed was allowed to settle and then was filtered, washed and dried. The powder pattern by x-ray of the antimony trioxide so prepared registered every line of antimony trioxide but none of foreign substances.

A synthetic copper-refining electrolyte was made, containing Cu , 40 g./L ; H_2SO_4, 184 g./L. The electrolyte was saturated with antimony trioxide(sulfate) by constant stirring with a motor stirrer. The temperature was kept at 25°C. in a water bath. After 8 hours the solution was filtered. Various amounts of chloride were then added to different portions of the filtrate. After 24 hours, during which the solution was kept at 25°C. in a water bath, they were filtered again, washed with dilute sulfuric acid, and the filtrates were analyzed for chloride by a potentiometric method (Part II). The data are collected in Table XI.

Table XI

Amounts of Chloride Left in a Copper-Refining Electrolyte

Saturated with Antimony Sulfate

Chloride added		Chloride found in solution		Discrepancy
0.532 mg. or	21.3 mg./L	0.555mg. or	22.0 mg./L	+ 4.3 %
1.06	42.4	1.08	43.2	+ 1.9 %
1.60	64.0	1.59	63.6	- 0.6 %

The amount of antimony per liter in approximately 3 N H_2SO_4 saturated with antimony sulfate at 25°C. is about 220 mg. (see Table XIII). If the atomic ratio of antimony to chlorine in antimony oxychloride is assumed to be 1 : 1, 220 mg. of antimony will precipitate 76 mg. of chloride, provided complete reaction takes place. This would result in absence of chloride in the solution tested. Actually the same amount of chloride as added was found within the limits of error of the potentiometric method(± 5 %). This fact indicates that none of the chloride is precipitated as oxychloride.

In another experiment, approximately 3 N H_2SO_4 (copper was omitted in order to simplify the analysis for antimony) was agitated with antimony trioxide for 8 hours at 25°C. It was then filtered. A part of the filtrate was analyzed for antimony and chloride. Antimony was determined iodometrically and chloride potentiometrically. The rest of the filtrate was agitated with antimony oxychloride for another 8 hours at 25°C. It was filtered again and the new filtrate was analyzed for antimony and chloride. The difference in antimony content between these two filtrates should indicate the relative solubilities of antimony sulfate and oxychloride. The data are collected in Table XII.

Table XII

Relative Solubilities of Antimony Sulfate and Oxychloride in Sulfuric Acid at 25°C.

	Sb	Cl
2.6 N H_2SO_4 saturated with antimony sulfate	0.0012 M	0.00002 M
Same solution saturated afterwards with antimony oxychloride	0.0021 M	0.00561 M

It is seen that there is an increase in concentration of both antimony and chloride after the further saturation of antimony oxychloride. We can but conclude that antimony oxychloride is more soluble than antimony sulfate in the 2.6 N H_2SO_4 .

In the third experiment the solubilities of antimony sulfate in approximately 3 N H_2SO_4 without and with small amounts of chloride at 25°C. were determined. The solution was agitated for 24 hours in each case. The filtrates were then analyzed for acid and antimony. The data are collected in Table XIII.

Table XIII

Solubility of Antimony Sulfate in Sulfuric Acid at 25 °C.

Concentration of H_2SO_4, N	Concentration of Cl, mg./L	Concentration of Sb	
		M	g./L
3.079	0	0.0017	0.21
3.079	18.2	0.0018	0.22
3.079	30.4	0.0018	0.22
3.079	54.6	0.0018	0.22
3.079	60.8	0.0018	0.22
2.607	saturated	0.285	3.47

It is seen that there is no decrease of solubility of antimony sulfate in approximately 3 N H_2SO_4 when a minute amount of chloride is present, as would be required by the oxychloride hypothesis.

This is in good agreement with Skowronski's experiment (10) if his data are extrapolated for the amount of antimony in absence of arsenic. Since he used actual copper-refining electrolyte, the agreement indicates that copper probably has no appreciable influence on the solubility of antimony in sulfuric acid.

When sulfuric acid is saturated with sodium chloride, there is a great increase in solubility of antimony sulfate. This is probably due to a much larger solubility of antimony chloride as compared with antimony sulfate. It is interesting to note that antimony dissolves as basic sulfate.

Conclusion

From chemical considerations and direct experiments , no evidence can be found to support the statement that antimony in copper-refining electrolyte is precipitated as oxychloride by the small amount of chloride purposely added.

Part VI

FUNCTIONS OF CHLORIDE IN COPPER-REFINING ELECTROLYTE IN THE ABSENCE OF ADDITION AGENTS BUT IN THE PRESENCE OF BISMUTH

Introduction

In Part IV the author has correlated the cathode polarization, the grain size and the hardness of the copper deposit with the chloride concentration in a synthetic copper-refining electrolyte containing no addition agents and practically no impurities. It was shown that the chief effect of chloride is to refine the crystal size of copper. This effect is overshadowed by the presence of glue or other addition agent in actual copper-refining electrolyte, therefore it seems reasonable to conclude that the importance of chloride in actual copper-refining electrolyte lies in the control of impurities.

It is well known that chloride minimizes the loss of silver in copper. It is also well known that chloride minimizes the codeposition of antimony and bismuth with copper. These influences can be illustrated by Table XIV.

Table XIV

Effects of Chloride on the Enrichment of Impurities in Anode Slime

Element	Standard potential		Relative ratio of enrichment in anode slime
Au	Au/Au^{+},	1.5 volts	171
Ag	Ag/Ag^{+},	0.7975	420
Te	Te/Te^{++++},	0.549	154
As	As/As^{+++},	0.3	65
Sb	Sb/Sb^{+++},	0.2	112
Bi	Bi/Bi^{+++},	0.2	84
Pb	Pb/Pb^{++},	- 0.1264	75
Ni	Ni/Ni^{++},	- 0.231	5
Fe	Fe/Fe^{++},	- 0.4402	4
Se	Se/Se^{--},	- 0.77	29

The standard potentials are taken from Thompson's book (40). The relative ratio of enrichment in anode slime is simply calculated by dividing the content of an element in the anode slime by that of the same element in the anode, the data representing the practice at the Raritan Copper Works(28).

Theoretically these elements, in the increasing order of dissolution, can be arranged as follows:

Au, Ag, Te, As, $\substack{\text{Bi}\\\text{Sb}}$, Pb, Ni, Fe, Se

Actually the order is as follows:

Ag, Au, Te, Sb, Bi, Pb, As, Se, Ni, Fe

These two series are in the same order except for silver, antimony, bismuth, lead and selenium. Probably the standard potential of Se/Se^{++++}, which is unavailable, should be used instead of Se/Se^{--}. The enrichment of lead in the anode slime is due to the fact that lead sulfate is only slightly soluble, but it is chloride which throws proportionally more silver, antimony, and bismuth into the anode slime than is present in the anode.

The explanation of the enrichment of silver in the anode slime is simple. Chloride precipitates silver almost quantitatively as insoluble silver chloride, which then settles down in the anode slime.

No plausible explanation has been offered for the enrichment of the anode slime in antimony and bismuth. The aim of this part of the investigation is to study the behavior of bismuth in copper refining.

Preliminary Considerations

Several explanations can be offered to explain the enrichment of the anode slime in bismuth. Bismuth may be precipitated as oxychloride. It may be occluded by the precipitate of silver chloride or cuprous chloride. It may form a complex anion with chloride and migrate to the anode, where it is occluded into the anode slime.

As to the oxychloride hypothesis, it has been shown (Part V) that antimony is unlikely to be precipitated as oxychloride in the copper electrolyte. Since antimony and bismuth are chemically alike, arguments against the antimony oxychloride hypothesis can be used also as objections to the bismuth oxychloride hypothesis, especially because bismuth is more soluble than antimony in the copper electrolyte.

To test the complex-ion formation hypothesis, a transference experiment of bismuth in copper electrolyte was performed. An improved design of Hittorf's apparatus was used. The anode was a copper wire and the cathode was a copper sheet. The anode was placed at a lower level than the cathode. The results are collected in Table XV.

Table XV*

Transference Number of Bismuth in the Electrolysis of Copper

Composition of electrolyte: Cu, 42 g./L; H_2SO_4, 188 g./L
Bi, 3.06 g./L (saturated); Cl, 0.100 g./L
Current : 0.022 ampere
Time : 3 hours

	Anode	Middle	Cathode
Weight of solution	11.9729	11.1986	30.1175
Weight of bismuth	0.0283	0.0288	0.0785
Weight of water	11.9446 g.	11.1698 g.	30.0390 g.
Initial bismuth in above water	0.0306	0.0285	0.0765
Gain in weight of bismuth	-0.0023	0.0003	0.0020
Gain in equivalent of bismuth	-0.000033		0.000029
Transference number of bismuth	0.013		

It is seen that the transference number of bismuth in the copper

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* Bismuth is analyzed by the dithizone method (Part III). In Table XV, the ratio of bismuth to copper is comparatively high, so the first step of using hydrated manganese dioxide as the collector of bismuth is omitted. In Table XVI, the manganese dioxide is formed by the interaction between potassium permanganate and manganous sulfate instead of that between potassium permanganate and potassium bromide.

electrolyte containing less than 0.100 g./L of chloride is normal. This indicates that bismuth migrates toward the cathode.

To test the silver chloride occlusion hypothesis, a synthetic copper electrolyte (Cu, 42 g./L ; H_2SO_4 , 188 g./L) was saturated with silver sulfate. Sufficient bismuth was added to give a concentration of 0.0020 g./L . Then various amounts of chloride were added to 50-ml. portions of this electrolyte. These different portions were allowed to settle for 24 hours. Finally they were filtered, washed with two portions of 5-ml. water, and sucked dry. The filtrates were analyzed for bismuth. The results are collected in Table XVI.

Table XVI

Occlusion of Bismuth by Silver Chloride

Exper. No.	Cl concentration, mg./L	Bi concentration , g./L
1	0	0.0018
2	10	0.0020
3	20	0.0019
4	30	0.0018
5	50	0.0019

It is seen that bismuth is not occluded by silver chloride.

To test the cuprous chloride occlusion hypothesis, the same procedure was used except that the electrolyte was not saturated with silver sulfate but 2 g. of copper powder was added to each portion. The results are collected in Table XVII.

Table XVII

Occlusion of Bismuth by Cuprous Chloride

Exper. No.	Cl concentration, mg./L	Bi conentration, g./L
6	1.5 *	0.0019
7	10	0.0012
8	20	0.0005
9	30	0.0004
10	50	0.0005

* This amount was originally presnt in the electrolyte.

Another series of experiments with the same electrolyte saturated with bismuth trioxide were also performed. The results are collected in Table XVIII.

Table XVIII

Further Experiments on the Occlusion of Bismuth by Cuprous Chloride

Exp. No.	Cl conc., mg./L	Further additions	Experimental procedure	Bi conc., g./L
11	1.5*		agitated by a motor stirrer for 3 hrs., then followed by filtering, washing with 10 ml. of water and sucking	3.06
12	1.5*	1 g. Na_2SO_3		0.81
13	50	1 g. Na_2SO_3		0.73
14	1.5*	2 g. Cu pow.		2.56
15	50	2 g. Cu pow.		2.50

These results show that cuprous chloride, whether formed by the reducing action of copper or sulfurous acid, is able to carry down bismuth with it(exp. No. 13 and 15). Experiment No. 12 is misleading in that there was sufficient chloride in the sodium sulfite used to boost the chloride concentration to 3.5 mg./L. The result of experiment No. 14 is to be explained on the assumption that the following reaction can take place:

$$3\ Cu + Bi_2(SO_4)_3 \longrightarrow 3\ Cu\ SO_4 + 2\ Bi$$

This point will be treated more fully later on.

The author does not wish to use the results of these experiments as conclusive evidences to accept or to discard any hypothesis, but they are helpful in the choice of a working hypothesis. So far it indicates that the cuprous chloride occlusion hypothesis has a better chance of survical.

Experimental Procedure

To study the behavior of bismuth in copper refining, a rectangular glass jar holding about 10 liters of electrolyte was used as an experimental

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* This amount was originally present in the electrolyte.

cell. Every working condition ,except the chloride concentration in the electrolyte, was kept as constant as possible.

In each run the time of electrolysis was fixed for 12 hours. The temperature of the electrolyte was kept at 37.2 to 39.2° C. by a large water bath surrounding the cell, the temperature of the former being maintained thermostatically. The cathode current density was kept at 15 amp. per sq. ft. (1.6 amp./ sq. dm.). The electrolyte was stirred by a motor stirrer, whose speed was maintained at about 1200 r.p. m.

There were two anodes and one cathode. The anodes were cast from electrolytic copper, with the addition of some master copper-bismuth alloy containing about 10 % of bismuth. The assays of bismuth in the anodes, by taking composite samples from the drillings of four equal-spaced holes in each anode, were 0.79 and 0.54 % respectively. The cathode was cut from regular starting sheets furnished by a copper refinery. No stripping oil nor any addition agents were used.

The electrolyte used was a synthetic one, prepared from C. P. hydrated copper sulfate and sulfuric acid. This was first saturated with bismuth by agitating it with bismuth trioxide for 8 hours and then filtering. The composition of the electrolyte was Cu, 42 g./L; H_2SO_4 , 188 g./L; Bi, 3.06 g./L (Table XIX, exp. No. 21). After each run the chloride was redetermined(Part II). Sodium chloride of C. P. grade was then added to give a definite chloride concentration. The average concentration of chloride before and after the electrolysis represents the chloride concentration in that run(Table XIX, Column 4). In experiments No. 22 and 30, the zero chloride concentration was obtained by adding an equilivalent amount of silver sulfate and filtering out the silver chloride so formed. Experiment No. 22 was performed after experiment NO. 21 and experiment No. 30 after experiment No. 29. Frequent analyses of copper and acid were made by usual methods and minor adjustments were made to maintain their concentration. No attempts were made to adjust the bismuth concentration, but bismuth was determined after each run. The average concentration of bismuth before and after the electrolysis represents the bismuth concentration in that run (Table XIX, column 5). Except that there was a surge of bismuth concentration in experiments No. 21, 22, and 29, the bismuth concentration was essentially constant.

After each run the deposited copper was stripped from the smooth side of the starting sheet and analyzed for bismuth by the dithizone method (Part III).

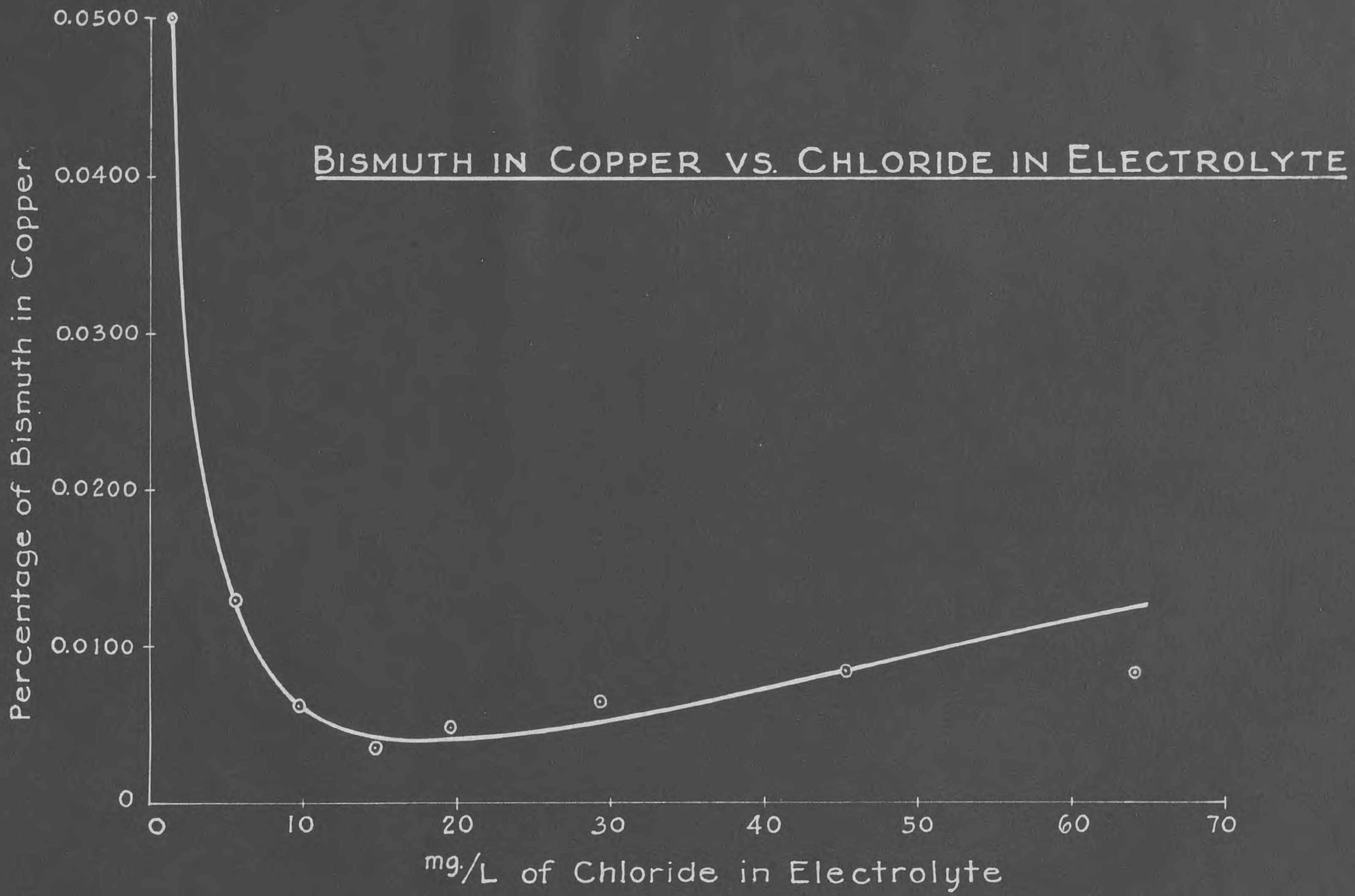
Experimental Results

The experimental results are collected in Table XIX. The relation between the bismuth content in copper deposit and the chloride concentration in electrolyte was plotted in Figure V. The results of experiments No. 22 and 30 are omitted because of their apparent anomalies.

It is seen from Table XIX and Figure V that there is a great drop of bismuth content as the chloride concentration is increased to about 5 mg./L . The curve tapers off afterwards and reaches the minimum at about 15 mg./L. Then the curve rises but does not reach the original height.

Discussion of Results

If we accept the cuprous chloride occlusion hypothesis, the shape of the curve in Figure V is readily explained. At the lowest point cuprous chloride reaches its minimum solubility. Its precipitation carries down bismuth from anodes with it. The minimum bismuth content in the copper deposit then represents the sum of mechanical inclusion of anode slime and electrolyte.



BISMUTH IN COPPER VS. CHLORIDE IN ELECTROLYTE

Figure V

Table XIX

Correlation between Bismuth Content in Copper and Chloride Concentration in Electrolyte

Exp. No.	Initial Cl conc., mg./L	Final Cl conc., mg./L	Average Cl conc., mg./L	Average Bi conc., g./L	Percent Bi in copper
22	0	0	0	2.59	0.0450
30	0	0	0	2.41	0.0420
21	1.50	1.02	1.26	2.93	0.0500
23	5.50	5.40	5.45	2.36	0.0130
24	10.0	9.44	9.72	2.47	0.0062
25	15.0	14.3	14.7	2.47	0.0035
26	20.0	19.4	19.7	2.41	0.0049
27	30.0	28.4	29.2	2.36	0.0064
28	50.0	40.4	45.2	2.35	0.0083
29	80.0	48.6	64.3	2.60	0.0082

As chloride concentration is increased, the solubility of cuprous chloride is increased due to the formation of a complex anion. Less cuprous chloride is precipitated. The capacity of carrying down bismuth from the anodes is decreased. Although the electrolyte is saturated with bismuth and the bismuth concentration will not be increased by contributions from anodes, part of the insoluble bismuth may drift away from the vicinity of anodes, giving the notorious "float" slime. The chances of the contamination of the copper deposit with bismuth are increased.

Whatever may be the mechanism, it is a fact that there is excess Cu^+ ion at the anode. The excess Cu^+ ion beyond the Cu^{++}-Cu^+ equilibrium can be disposed of in two ways, the precipitation of copper powder and the precipitation of cuprous chloride. When the chloride concentration falls below the saturation value, the precipitation of copper powder is the predominant reaction. Normally antimony or bismuth displaces copper from the copper solution. Perley(30) has shown that traces of copper in industrial water can be detected by an antimony electrode. However, if the solution is saturated with bismuth and if copper is in the powdered form, it is conceivable that the reverse reaction, namely, the displacement of bismuth by copper, may take place, especially if we recall that the standard potentials of bismuth and copper are not far away from each other. The metallic bismuth so precipitated may also drift away from the vicinity of anodes , if there is insufficient amount of cuprous chloride to carry it down into the anode slime. The presence of the metallic bismuth in "float" slime is evidently more harmful in contaminating the copper deposit. Thus that the two branches of the curve in Figure V are not symmetrical and that the branch at lower chloride concentrations is higher than that at higher chloride concentrations are explained.

Of course, actual copper-refining electrolyte is not saturated with bismuth, but the above principles still apply. Peculiar to each refinery, there is one mimimum bismuth content in the copper deposit, corresponding to the quantity of anode slime and the concentration of bismuth in electrolyte. Proper management of the chloride concentration will carry down most, if not all, of bismuth from anodes into anode slime and will not materially increase the concentration of bismuth in the electrolyte if the content of bismuth in the anodes is not too great.

Conclusion

Up to about 15 mg./L, chloride decreases the tendency for the codeposition of bismuth with copper. This beneficial effect is greatest at the critical chloride concentration. Above the critical concentration this beneficial effect still exists but is less effective. A working hypothesis is proposed to explain these phenomena.

Part VII

CONCLUSIONS

The small amounts of chloride purposely added in copper-refining electrolyte have the beneficial effects of minimizing the codeposition of bismuth with copper and refining the crystal size of the copper deposit. While the latter effect is overshadowed by the presence of glue or other addition agent in ordinary copper-refining electrolyte, the former effect is of paramount importance in copper-refining. From the shape of the curves of many properties against the chloride concentration in electrolyte, it is concluded that the precipitation of cuprous chloride is the key mechanism. Thus the precipitation of cuprous chloride, which will carry down bismuth with it, together with the well-known precipitation of silver chloride, are the chief functions of chloride in copper-refining electrolyte.

BIBLIOGRAPHY

(1) L. Addicks, Trans. Am. Electrochem. Soc. 23, 265 (1913)

(2) L. Addicks, Met. Chem. Eng. 16, 689 (1917)

(3) A. J. Allmand and H. J. T. Ellingham, The Principles of Applied Electrochemistry, p. 273, Edward Arnold and Company, London (1924)

(4) Ibid, p. 262

(5) Am. Inst. Mining Met. Engrs. , Choice of Methods in Mining and Metallurgy, p. 59, McGraw-Hill Book Company, New York (1932)

(6) Ibid, p.61

(7) H. T. Angas and P. F. Summers, J. Inst. Metals 33, 115 (1925)

(8) K. Arndt, Technische Elektrochemie , p. 297, Verlag von Ferdinand Enke, Stuttgart (1929)

(9) E. S. Bardwell and R. J. Lapee, Trans. Am. Inst. Mining Met.Engrs. 106, 421 (1933)

(10) Ibid, p.420

(11) W. H. Bassett and C. H. Davis, Trans. Am. Inst. Mining Met. Engrs. 60, 428 (1919)

(12) M. C. Bloom, Am. Mineral. 24, 285 (1939)

(13) W. Blum and G. B. Hogaboom, Principles of Electroplating and Electroforming, p. 98, McGraw-Hill Book Company, New York (1930)

(14) G. Bodländer and O. Storbeck, Z. anorg. Chem. 31, 22, 460 (1902)

(15) A. Brenner, Proc. Am. Electroplaters Soc. , p.28 (1941)

(16) W. T. Burns, Met. Chem. Eng. 11, 509 (1913)

(17) A. Butts and V. de Nora, Trans. Electrochem. Soc. 79, 171 (1941)

(18) E. W. Colbeck, S. W. Craven and W. Murray, Analyst 59, 395 (1934)

(19) Fiscal Policy Joint Committee, Analyst 60, 554 (1935)

(20) H. Fischer, G. Leopoldi and H. von Usler, Z. anal. Chem. 101, 1 (1935)

(21) H. Fischer, angew. Chem. 47, 685 (1934)

(22) H. E. Haring, Trans. Am. Electrochem. Soc. 49, 417 (1926)

(23) C. S. Harloff and H. F. Johnson, Trans. Am. Inst. Mining Met. Engrs. 106, 406 (1933)

(24) N. Kameyama and S. Makishima, J. Soc. Chem. Ind. Japan 36, 364 B (1933)

(25) H. S. McKnight, Trans. Am. Inst. Mining Met. Engrs. 106, 357 (1933)

(26) E. Müller, Elektrometrische Massanalyse, p. 88, Verlag von Theodor Steinkoppff, Dresden and Leipzig (1926)

(27) R. M. Murray, Trans. Am. Inst. Mining Met. Engrs. 106, 415 (1933)

(28) J. Newton and C. L. Wilson, Metallurgy of Copper, pp 279-280, John Wiley and Sons, New York (1942)

(29) B. Park, Ind. Eng. Chem., Anal. Ed. 6,189 (1934)

(30) G. A. Perley, Trans. Electrochem. Soc. 76, 85 (1939)

(31) Private communication

(32) W. Prodinger, Organic Reagents Used in Quantitative Inorganic Analysis, p. 120, Elsevier Publishing Company, New York (1940)

(33) I. Roberts, Ind. Eng. Chem., Anal. Ed. 8, 365 (1936)

(34) E. W. Rouse and P. K. Aubel, Trans. Am. Electrochem. Soc. 52,195(1927)

(35) Ibid, p.204

(36) O. Ruff, Z. anorg. Chem. 185, 387 (1929)

(37) T. Shedlovsky and D. A. MacInnes, J. Am. Chem. Soc. 58, 1970 (1936)

(38) A.J.G. Smout and J.L. Smith, Analyst 58, 475.(1933)

(39) M. de K. Thompson, Chem. Met. Eng. 33, 298 (1926)

(40) M. de K. Thompson, Theoretical and Applied Electrochemistry, pp 120-123, MacMillan Company, New York (1939)

(41) T. Ulke, Modern Copper Refining, p.24, John Wiley and Sons, New York(1903)

(42) C. Y. Wen and E. F. Kern, Trans. Am. Electrchem. Soc. 20, 174 (1911)

(43) C. E. Willoughby, E.S. Wilkins and E.O.Kraemer, Ind. Eng. Chem., Anal. Ed. 7, 285 (1935)

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