

RI 8934

RI	8934
-----------	-------------

Bureau of Mines Report of Investigations/1985

Minimizing Lead Contamination in Copper Produced by Solvent Extraction-Electrowinning

By T. H. Jeffers and R. D. Groves



UNITED STATES DEPARTMENT OF THE INTERIOR



MAY 02 1985

Report of Investigations 8934

Open-Access - Research
LIBRARY

Minimizing Lead Contamination in Copper Produced by Solvent Extraction-Electrowinning

By T. H. Jeffers and R. D. Groves



UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

BUREAU OF MINES
Robert C. Horton, Director

Library of Congress Cataloging in Publication Data:

Jeffers, T. H. (Thomas H.)

Minimizing lead contamination in copper produced by solvent extraction-electrowinning.

(Report of investigations / United States Dept. of the Interior, Bureau of Mines ; 8934)

Bibliography: p. 10-11.

Supt. of Docs. no.: I 28.23:8934.

1. Copper—Electrometallurgy. 2. Copper—Lead content. 3. Electrolyte solutions. 4. Anodes—Corrosion, I. Groves, R. D. (Rees D.). II. Title. III. Series: Report of investigations (United States. Bureau of Mines) ; 8934.

TN23.U43 [TN780] 622s [669'.3] 84-23011

CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	2
Materials, equipment, and procedure.....	3
Experimental results.....	6
Effect of cobalt concentration.....	6
Effect of entrained organic extractant.....	6
Maximum current density.....	7
Diluent variations.....	7
Effect of current density, copper concentration, acid concentration, and temperature.....	8
Effect of electrolyte impurities.....	8
Effect of anode composition.....	9
Conclusions.....	9
References.....	10

ILLUSTRATIONS

1. Photograph of solvent extraction-electrowinning unit.....	4
2. Schematic diagram of solvent extraction-electrowinning unit.....	5

TABLES

1. Effect of electrolyte cobalt concentration on lead content of electrowon copper.....	6
2. Effect of entrained organic extractant on lead content of electrowon copper.....	7
3. Effect of current density, temperature, copper concentration, and electrolyte acid concentration on lead content of electrowon copper.....	8

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A/ft ²	ampere per square foot	h	hour
°C	degree Celsius	in	inch
ft ²	square foot	pct	percent
g	gram	ppm	part per million
g/L	gram per liter	vol pct	volume percent
gpm/ft ²	gallon per minute per square foot	V	volt

MINIMIZING LEAD CONTAMINATION IN COPPER PRODUCED BY SOLVENT EXTRACTION-ELECTROWINNING

By T. H. Jeffers¹ and R. D. Groves²

ABSTRACT

The Bureau of Mines conducted a laboratory investigation of copper electrowinning from electrolytes produced by solvent extraction. The purpose of the research was to gain a better understanding of the fundamental relationship between copper electrowinning conditions, anode corrosion, and cathode purity. Processing variables were evaluated in a cyclic semicontinuous system in which the depleted electrolyte was used to strip copper from loaded organic extractant. For the production of high quality copper cathodes, the electrolyte was dosed with cobalt and stripped of organic solvent extraction reagent. An optimum cobalt addition of 60 ppm, and removal of the entrained extractant with activated carbon provided the best conditions for electrowinning copper containing the least amount of lead and controlling anode corrosion. As little as 13 ppm of the entrained organic extractant, LIX 64-N, significantly accelerated anode corrosion. However, the addition of 1,000 ppm of organic diluent kerosine did not affect anode corrosion. After cobalt dosing and removing the entrained extractant, cathodes containing less than 2 ppm lead were consistently electrowon at widely varied current densities, electrolyte copper and acid concentrations, and temperatures. Dosing of the electrolyte with selected impurities including magnesium, aluminum, manganese, and iron did not affect the cathode purity. However, 0.05 g/L of chloride ions markedly increased anode corrosion and the subsequent transfer of lead to the cathode copper.

¹Chemical engineer.

²Supervisory metallurgist.

Salt Lake City Research Center, Bureau of Mines, Salt Lake City, UT.

INTRODUCTION

The electrical industry is the largest consumer of refined copper in the United States, and nearly 75 pct of the refined copper production is used to make wire. Electrorefined, rather than electrowon, copper is preferred for wire drawing because of its relatively high purity. Impurities adversely affect the wire drawing characteristics and product resistivity. Quantitative data, however, relating impurity levels and their effects are lacking. ASTM standards only specify a minimum purity of 99.9 pct Cu, silver being counted as copper (1-2).³ Tolerable levels of other impurities are not specified.

Electrowon copper is deposited on copper starting sheets (cathodes) from copper bearing solutions. Insoluble anodes, generally lead alloys, constitute the other required electrodes. Historically, copper electrolyte was obtained by leaching copper ore, and soluble impurities reporting in the electrolyte contaminated the deposited copper. Recent development of solvent extraction-electrowinning (SX-EW) technology not only provided for concentrating copper from dilute process streams, but provided a relatively pure copper electrolyte. However, because lead alloy anodes are used, lead contamination of the electrowon copper remains a problem. Although some companies produce electrowon copper of sufficient purity and quality to be used as electrorefined copper without further treatment, the relationship between electrowinning conditions and cathode purity has not been completely determined.

The Bureau of Mines tested a copper SX-EW process to gain a better understanding of the fundamental relationship among electrowinning conditions, anode corrosion, and lead contamination of the cathode copper. The effects of occasional current interruptions, cobalt dosing,

organic entrainment, electrolyte purity, and current density were investigated, and the use of antimony-lead and calcium-lead alloy anodes were compared.

This investigation evolved from a study of native copper processing by ammoniacal leaching, solvent extraction, and electrowinning. Although leaching and solvent extraction were incidental to this study, they were necessary to maintain the electrolyte copper content. Although some electrowinning data were previously presented, this report consolidates the results and presents new findings (3-4).

The source of lead in electrowon copper is the insoluble particulate corrosion products of lead alloy anodes (5). Lead oxide is formed on the anodes, sloughs off, and is physically entrapped by the depositing copper. Evidence of this was provided in an investigation (6) in which each anode was enclosed in a porous fabric bag. Cathodes containing only 1 ppm lead were produced because anode corrosion products were retained in the bags. Without bags, the cathode lead contents ranged from 10 to 43 ppm. Anode bagging, however, is expensive and requires periodic maintenance.

Although lead alloy anodes are major contributors to cathode impurity, they are used for copper electrowinning because of low cost, durability, ease of fabrication, low maintenance, and excellent conductivity. The lead alloys that have had widespread use include antimony-lead alloy (containing 3 to 8 pct antimony) and calcium-lead alloy (with 0.01 to 0.10 pct calcium). Several alternative anodes have been investigated, including lead alloyed with silver, tin, or arsenic (6-8). The corrosion resistance of some of these alloys was impressive, but they were not adopted because of their high cost. Titanium coated with a conducting layer of noble metal or metal oxide has been considered for electrowinning anodes. In laboratory tests lead dioxide on a titanium substrate was used and very

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

little corrosion was noted (7). However, after 40 days of continuous use, the lead dioxide separated from the substrate and the anodes became inactive.

The presence of small amounts of cobalt in the electrolyte decreased the lead anode corrosion rate (5, 9) and reduced the lead content of electrowon copper (5, 10). In addition, the physical form of the lead oxide corrosion products was altered. Without cobalt in the electrolyte, the anode scale sloughed off; with cobalt, the scale adhered to the anodes. Apparently, the reduced amount of particulate lead suspended in the electrolyte lowered lead contamination of the depositing copper. Most commercial SX-EW plants add cobalt to their electrolyte to take advantage of this beneficial effect.

In SX-EW plants, the electrolyte contains some entrained extractant from the solvent extraction operation. This entrained extractant consists of very small droplets of suspended LIX 64N-kerosine, as well as some soluble organic material. Studies on the effect of entrained extractant on deposited copper determined that the extractant was coalesced and concentrated by anode gassing and was subsequently adsorbed on the cathode surface (8). The resulting copper was dark colored, granular, and loosely adherent to the cathode. This phenomenon is frequently observed in industrial tankhouses and is commonly referred to as "organic burn." The burned deposits are less pure than smooth adherent copper deposits. In tankhouse practice, coalesced extractant is skimmed from the electrolyte cells to control the organic burn.

MATERIALS, EQUIPMENT, AND PROCEDURE

The electrowinning investigation was conducted in a semicontinuous circuit utilizing cyclic leaching and solvent extraction to provide copper-enriched electrolyte. A photograph of the equipment is shown in figure 1, and a schematic is shown in figure 2. Solvent, 5 pct LIX-64N⁴ dissolved in kerosine, was mixed with leach liquor in a packed column, and the phases were separated in a settler. The copper-bearing organic phase (denoted by "O" in figure 2) was then washed with water (the aqueous phase, "A") to remove entrained ammonia. Copper was stripped from the extractant with high-acid copper-depleted electrolyte and, in some tests, entrained extractant was removed from the enriched electrolyte using activated carbon.

The copper electrowinning cell contained six, 6-in² lead anodes 3/16 in thick, and five, 6-in² copper cathodes 0.005 in thick. Cathode spacing was 1 in. The electrodes were immersed to a depth of 3.5 in; effective electrode surface areas

for the anodes and cathodes were 1.9 ft² and 1.5 ft², respectively. Electrolyte flow was 0.1 gpm/ft² of cathode area.

Cast lead anodes containing 3.6 pct Sb were used in most of the tests, but Ca-Pb anodes were also used. The Ca-Pb anodes, which were machined from a commercial anode, contained 0.052 pct Ca and 0.01 pct Sb.

The test procedure consisted of electrowinning for 8-h periods, and 5 to 8 electrowinning periods were completed for each variable investigated. A cathode from one of the cell positions was removed for analysis and replaced with a new starting sheet at the beginning of each period. Before electrowinning, the starting sheets were lightly coated with a lanolin-base wax and deposited copper was peeled off to obtain a sample for chemical analysis. After each test series, the anodes were cleaned of oxide coating by abrasion with a wire brush to prevent the results being biased by anode history. In some tests, after several cathodes had been produced using a specific set of operating conditions, the

⁴Reference to specific products does not imply endorsement by the Bureau of Mines.

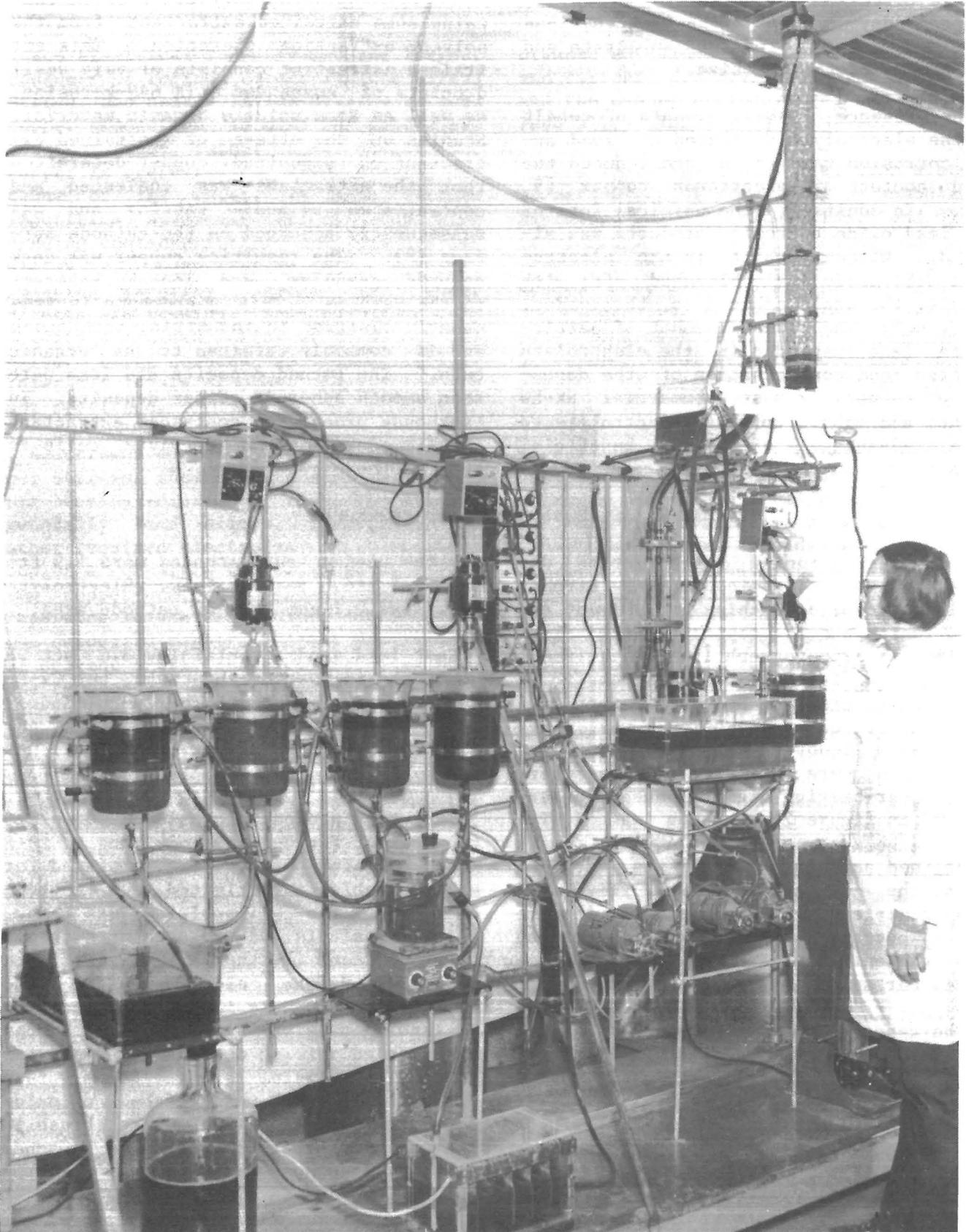


FIGURE 1. - Photograph of solvent extraction-electrowinning unit.

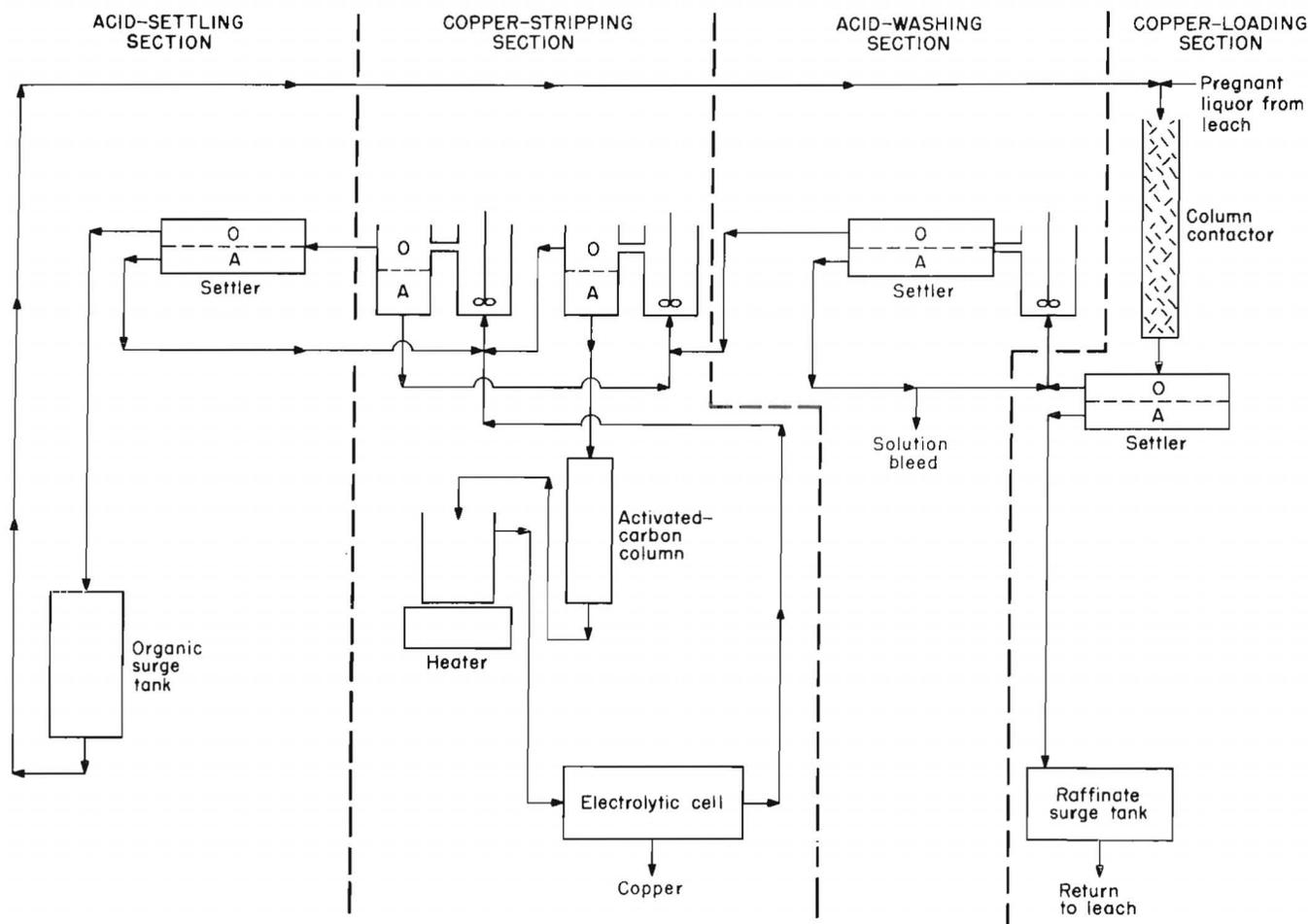


FIGURE 2. - Schematic diagram of solvent extraction-electrowinning unit.

anode corrosion products that had sloughed off were collected. Additionally, the conductive adherent anode corrosion layer was scraped off. These corrosion products and coatings were dried, weighed, and analyzed to determine the amounts and types of anode corrosion occurring with various processing conditions.

During the 16-h period when electrowinning was not in progress, cell voltage was reduced to 1.7 V from a normal plating voltage of 2.1 V to maintain the anodes in an anodic condition. Copper deposition was negligible at 1.7 V. Without an applied electrical potential, part of the anodic coating of lead oxide converted to lead sulfate. The loosely adhering lead sulfate would detach from the anodes and deposit with the copper when plating was resumed and cause an abnormally high

lead content. Applying the voltage during inactive cell time prevented lead sulfate formation and more closely simulated industrial practice.

Consistent results were obtained by dosing the electrolyte with cobalt and removing entrained extractant prior to electrowinning. Cobalt sulfate was added to the electrolyte to give a cobalt concentration of 60 to 100 ppm. Entrained extractant was removed by electrolyte filtration through 10- to 40-mesh activated carbon. Electrowon copper with less than 2 ppm lead was consistently produced at a current density of 16 A/ft² and a cell voltage of 2.1.

Research evaluation was strongly dependent upon the accuracy of the cathode

lead analyses. An atomic adsorption technique resulted in confidence limits

of ± 1 and ± 0.3 ppm at levels of 10 and 1 ppm Pb, respectively (11).

EXPERIMENTAL RESULTS

EFFECT OF COBALT CONCENTRATION

To determine the effects of cobalt concentration on anode corrosion, six series of tests were completed at a cathode current density of 16 A/ft², cell voltage of 2.1, and temperatures of 25° C using Sb-Pb anodes. The electrolyte contained 30 g/L Cu, 150 g/L H₂SO₄, and 0 to 1,000 ppm Co. Results in table 1 show the marked decrease in both anode spall and cathode lead content that resulted when cobalt was added to the cobalt-free electrolyte. No advantage was gained by increasing the cobalt concentration above 60 ppm.

TABLE 1. - Effect of electrolyte cobalt concentration on lead content of electrowon copper

Electrolyte Co, ppm	Average Pb content of electrowon Cu, ppm	Anode spall, g/40 h
0.....	38	1.6
20.....	4.1	.2
40.....	2.1	<.1
60.....	1	<.1
100.....	.9	<.1
500.....	1.2	<.1
1,000.....	1.3	<.1

The mechanism by which cobalt decreases anode corrosion is not completely understood. Although some researchers (7) have postulated that cobalt migrates into the anodic coating of lead oxide, no evidence of this was found in the present investigation. Spectrographic analysis of several antimonial lead anode coatings showed no detectable cobalt at an electrolyte concentration of 1,000 ppm Co. However, X-ray diffraction studies of anode coatings showed differences in the types of lead oxides formed when the electrolyte contained cobalt. For example, anode coatings formed in cobalt-free electrolyte contained 85 pct PbO₂ and 15 pct PbO, whereas coatings formed in

electrolyte containing 100 ppm Co contained 40 pct PbO₂ and 60 pct PbO. The PbO₂-rich coatings were flaky and thick, and adhered poorly compared with the PbO-rich coatings. Other researchers (12-13) showed that loose, porous corrosion layers enhance diffusion of SO₄⁼ and OH⁻ ions to the underlying metal.⁴ This diffusion favors the formation of poorly adherent PbO₂. The tight, dense coatings containing substantial amounts of PbO appear to resist ionic penetration and limit base metal attack. The ability of cobalt to promote the formation of PbO, rather than PbO₂, may explain its success in lowering anode corrosion and improving the quality of electrowon copper.

EFFECT OF ENTRAINED ORGANIC EXTRACTANT

The effects of entrained solvent extraction reagents on the cathode lead content and current density were studied in a series of tests using calcium-lead alloy anodes. Electrolyte containing 45 to 55 g/L Cu was circulated through the electrowinning cell at a rate of 0.03 gpm/ft² of effective cathode area. The current density was 16 A/ft² and the electrolyte temperature was 25° C. Various amounts of the LIX 64-N-kerosine mixture were added to the electrowinning cell and the effect on cathode lead content was studied.

Results presented in table 2 show that complete removal of entrained organic extractant ensured consistent low-lead cathode copper. Each of the 13 cathodes produced from electrolytes containing no more than 2 ppm extractant had Pb contents of less than 3.3 ppm. Cathodes obtained from electrolytes containing 13 ppm or more of extractant contained up to 18 ppm Pb and several contained more than 5 ppm Pb. The amounts of anode corrosion products collected from the electrowinning cell after 40 h of operation were less than 0.1 g when extractant in the

TABLE 2. - Effect of entrained organic extractant on lead content of electrowon copper

Extractant in electrolyte, ppm	Anode spill, g/40 h	Lead content of individual Cu cathodes, ppm							Average Pb content of Cu cathodes, ppm
		Cathode 1	Cathode 2	Cathode 3	Cathode 4	Cathode 5	Cathode 6	Cathode 7	
0.....	<0.1	0.9	1.8	0.5	3.3	0.3	0.3	1.2	1.2
2.....	<.1	1	1.3	2.1	1.5	.5	1.1	NA	1.3
13.....	.4	3.1	1.6	3.9	2	12	2.5	1.7	3.8
18.....	.5	2.7	3.1	3.8	4.9	5.3	4.3	NA	3.4
24.....	.3	1.1	.8	10.8	1.6	2.3	14.1	NA	5.1
44.....	.5	6.2	.9	18	3.4	1	2.7	NA	5.4

NA Not applicable.

electrolyte was 2 ppm or less, and between 0.3 and 0.5 g when the electrolyte contained 13, 18, 24, and 44 ppm extractant. The chemical nature of these corrosion products also changed when extractant was present in the electrolyte. With an electrolyte containing 18 ppm extractant, the anode coating contained 45 pct PbO, but when extractant was excluded, the coating contained 65 pct PbO. Again, it seems that conditions favoring the formation of anode coatings containing increased amounts of PbO also favored the production of low-lead cathode copper.

Maximum Current Density

Electrowinning tests were also conducted to determine the effect of entrained organic extractant on the maximum current density that would produce a smooth adherent cathode deposit. Using the same electrolyte, calcium-lead anodes and electrowinning conditions as in the previous tests studying the effects of entrained extractant, current densities were increased and the physical form of deposited copper was evaluated visually. In the first test, an extractant-free electrolyte was used and the maximum current density was 32 A/ft² of cathode area. The copper deposits were smooth, adhered to the starting sheets, and contained an average of 3.0 ppm Pb. In the next series of tests, the electrolyte contained 18 ppm entrained extractant. Cathode deposits electrowon at 32 A/ft²

were loose and spongy, and contained an average of 60 ppm Pb. The current density was then lowered to 30 A/ft² which produced adherent deposits. However, the deposits were coarse grained, somewhat nodular, and contained an average content of 18 ppm Pb. Thus, the removal of entrained extractant allowed a current density increase of about 7 pct and produced a deposit containing markedly less lead.

Diluent Variations

Tests were also conducted to evaluate the effects of four commercial solvent extraction diluents on the electrowinning process: kerosine, Exxon Aromatic 150, Escaid 200, and Kermac 470B. The latter three solvents are refined mixtures of aliphatic and aromatic compounds similar to kerosine. Each was used in a mixture containing 5 vol pct LIX-64N and 95 vol pct diluent, and was tested for 130 h. The data showed that the extent of entrainment of each organic mixture in the electrolyte and its detrimental effects on the electrowinning process were essentially the same. Furthermore, a test was conducted in which kerosine was added ahead of the electrowinning cell. With 1,000 ppm kerosine in the electrolyte, copper cathodes were produced containing less than 2 ppm Pb. Thus, the LIX reagent was responsible for increased anode corrosion, which resulted in the transfer of lead to the depositing copper.

EFFECT OF CURRENT DENSITY, COPPER
CONCENTRATION, ACID CONCENTRATION,
AND TEMPERATURE

To determine the effects of variations in operating parameters, several series of copper cathodes were electrowon under a wide range of conditions. Tests were made with variations in current density, electrolyte copper and acid concentration, and electrolyte temperature. Antimony-lead anodes were employed in an electrolyte containing 100 ppm Co that was filtered through carbon to remove the entrained organic. The variations in conditions and test results are presented in table 3.

The data show that low-lead cathode copper can be produced under a wide range of operating conditions. With current densities of 8 to 24 A/ft² copper concentrations of 20 to 50 g/L, acid concentrations of 50 to 150 g/L, and electrolyte temperatures of 25° to 45° C, 50 cathodes were produced of which only 5 contained more than 2 ppm Pb. However, when the electrolyte acid concentration was increased to 200 g/L, the cathode lead content increased to an average value of 8.1

ppm. Observations during the latter test indicated that more than normal amounts of anode spall were produced.

EFFECT OF ELECTROLYTE IMPURITIES

The impurities tested and amounts used, in grams per liter, were 4.5 Mg, 1.9 Al, 1.4 Mn, 2.8 Fe, and 0.05 Cl. Impurity selections and amounts used were based on analyses of electrolytes from commercial operations. In addition to the selected impurity, the electrolyte contained 30 g/L Cu, 150 g/L H₂SO₄, and 100 ppm Co. For each test, six to eight cathodes were produced with 8 h of electrowinning at 16 A/ft² of cathode surface. Calcium-lead alloy anodes were used, and the electrolyte temperature was 25° C.

The results showed that aluminum, magnesium, and manganese had no effect on the electrowinning process. Low-lead cathodes were produced when the electrolyte contained these impurities and <0.1 g of anode spall was collected after each test. However, the presence of 0.05 g/L Cl in the electrolyte significantly accelerated anode corrosion. The resulting cathodes contained 10 ppm Pb, and 0.26 g

TABLE 3. - Effect of current density, temperature, copper concentration, and electrolyte acid concentration on lead content of electrowon copper

Condition varied	Current density, A/ft ²	Cu content, g/L	Acid content, g/L	Electrolyte temp, °C	Lead content of electrowon Cu, ppm					Average Pb content of electrowon Cu, ppm
					Cathode 1	Cathode 2	Cathode 3	Cathode 4	Cathode 5	
Current density	8	30	150	25	1.2	1.0	2.0	1.0	1.2	1.3
	16	30	150	25	1.3	1	.6	.5	.9	.9
	20	30	150	25	6	2.6	1.2	1	1	2.3
	24	30	150	25	.7	.9	1	1.6	2.2	1.3
Temperature....	20	30	150	25	6	2.6	1.2	1	1	2.3
	20	30	150	35	1.7	1.5	1.8	1.5	1.9	1.7
	20	30	150	45	3.7	1.5	1.5	1.2	1.7	1.9
Copper content.	16	20	150	25	1.5	1.7	1	.5	1.1	1.2
	16	30	150	25	1.3	1	.6	.5	.9	.9
	16	50	150	25	.8	2.1	1.6	.9	1.1	1.3
Acid content...	16	30	50	25	.4	.7	1	.4	.6	.6
	16	30	100	25	1	.4	1.8	1.5	2	1.3
	16	30	150	25	1.3	1	.6	.5	.9	.9
	16	30	200	25	5.5	21	5.5	5.5	3.8	8.3

of anode spall was collected after 40 h of electrowinning. Iron in the electrolyte did not affect either anode corrosion or the transfer of lead to the cathode, but there was a 2.3-pct decrease in the current efficiency.

EFFECT OF ANODE COMPOSITION

Calcium-lead and antimony-lead anodes are currently employed in commercial tankhouses. Therefore, two series of tests were conducted to compare these anodes under various electrowinning conditions. In the first test series, the electrolyte contained 30 g/L Cu, 150 g/L H_2SO_4 , and 80 ppm Co. A current density of 16 A/ft² was used, and the electrowinning temperature was 25° C. Five cathodes containing 1.3, 1.0, 0.6, 0.5, and 0.9 ppm Pb were produced with the antimony-lead anodes, and five cathodes containing 0.5, 0.4, 0.3, 1.0, and 1.0 ppm Pb were electrowon with the calcium-lead anodes. These results show that cathodes with low levels of lead contamination were produced with both sets of anodes. The physical characteristics of all the cathodes were similar, and only insignificant amounts of anode corrosion products were found after each series of tests.

In the second test series, similar electrowinning conditions were employed

except the electrolyte contained 40 ppm of entrained organic extractant, which is similar to levels found in industrial electrolytes. Individual cathodes electrowon with the antimony-lead anodes contained 3.3, 1.7, 10.5, 1.4, and 21 ppm Pb for an average of 7.6 ppm Pb. Cathodes obtained with the calcium-lead anodes contained 14.0, 6.8, 10.0, 0.4, and 4.0 ppm Pb for an average of 7.1 ppm. Once again, similar cathodes were produced with each set of anodes. However, the amount of anode spall collected after testing with the antimony-lead anodes was 0.7 g, but only 0.3 g was obtained after electrowinning with the calcium-lead anodes. In this case, the cathode lead content was not directly related to the rate of anode corrosion. Microscopic analyses of the anode spall from the calcium-lead anode indicated a smaller average particle size when compared with spall obtained with the antimony-lead anodes. Apparently, the smaller particles remained suspended in the electrolyte for a longer period of time, and were more readily entrapped by the depositing copper. Thus, comparable levels of cathode contamination were obtained with both antimony-lead and calcium-lead anodes, but the anode corrosion rate was lower with the calcium-lead anodes and a longer service life would be expected.

CONCLUSIONS

The investigation showed that cobalt dosing of electrolyte from copper solvent extraction circuits materially retarded lead transfer to the copper cathodes and decreased the anode corrosion rate. The optimum cobalt level was 60 ppm. Cobalt addition altered the composition of the conductive coating formed on the anodes. With cobalt-dosed electrolyte, the anode coating contained 40 pct PbO_2 and 60 pct PbO. With cobalt-free electrolyte, the coating contained 85 pct PbO_2 and 15 pct PbO. The PbO was a dense adherent coating, whereas PbO_2 was a thick loose coating that readily flaked off.

The anode corrosion rate and lead impurity levels in the cathodes were

proportional to entrainment of the LIX 64N solvent extraction reagent. Entrained organic extractant also altered the composition of the lead oxide coating on the anode. With an electrolyte dosed with cobalt and containing 18 ppm of organic, the anode coating contained 55 pct PbO_2 and 45 pct PbO; whereas, with organic excluded, the coating contained 35 pct PbO_2 and 65 pct PbO. Thus, conditions that favor the formation of PbO on the anode also favor low-lead cathode copper and decreased anode corrosion.

With two exceptions, satisfactory copper cathodes were produced over a wide range of conditions, and impurity accumulations, after the electrolyte was freed

of organic and dosed with cobalt. Electrolyte acidity of 200 g/L and a chloride content of only 0.05 g/L increased anode corrosion and lead in the cathode.

Comparative tests with an electrolyte containing 40 and 80 ppm of organic extractant and cobalt, respectively, showed that anode corrosion was greater with antimony-lead anodes than with calcium-lead anodes. However, the lead contamination of the copper cathodes was essentially the same. In this case, the

lead transfer was not in proportion to the anode corrosion rate. Microscopic examination revealed that the spall from the calcium-lead anodes was smaller sized than the spall from the antimony-lead anodes. Apparently, the smaller particles remained suspended in the electrolyte and provided more opportunities for entrapment by depositing copper. Thus, the use of calcium-lead anodes does not decrease the cathode lead contamination, but a longer service life is expected.

REFERENCES

1. American Society for Testing and Materials. Standard Specifications for Electrolyte Copper Wire Bars, Cakes, Slabs, Billets, Ingots, and Ingot Bars. B 5-73 in 1974 Annual Book of ASTM Standards: Part 6, Copper and Copper Alloys (Including Electrical Conductors). Philadelphia, PA, 1974, pp. 22-26.
2. _____. Standard Specification for Electrolytic Cathode Copper. B 115-72 in 1974 Annual Book of ASTM Standards: Part 6, Copper and Copper Alloys (Including Electrical Conductors). Philadelphia, PA, 1974, pp. 22-26.
3. Jeffers, T. H., and R. D. Groves. Electrowinning Copper From Solvent Extraction Acid Strip Solution Using Pb-Sb Anodes. Metall. Trans. B, v. 8B, March 1977, pp. 115-119.
4. _____. Processing Conglomerate Native Copper Ore by Ammonia Leaching-Solvent Extraction-Electrowinning. Bu-Mines RI 8352, 1979, 17 pp.
5. Gendron, A. S., V. A. Ettel, and S. Abe. Effect of Cobalt Added to Electrolyte on the Corrosion Rate of Pb-Sb Anodes in Copper Electrowinning. Can. Metall. Quart., v. 14, No. 1, Jan.-Mar. 1975, pp. 59-61.
6. Eggett, G., and D. Naden. Developments in Anodes for Pure Copper Electrowinning From Solvent Extraction Produced Electrolytes. Hydrometall., v. 5, No. 1, 1975, pp. 123-137.
7. Anderson, T. N., D. L. Adamson, and K. J. Richards. The Corrosion of Lead Anodes in Copper Electrowinning. Metall. Trans., v. 5, No. 6, June 1974, pp. 1345-1349.
8. Hopkins, W. R., G. Eggett, and J. B. Scuffham. Electrowinning of Copper From Solvent Extraction Electrolytes--Problems and Possibilities. Paper in Second International Symposium on Hydrometallurgy (Chicago, IL, Feb. 25-Mar. 1, 1973). Min. Eng. AIME, New York, 1973, pp. 127-154.
9. Gendron, A. S., R. R. Mathews, and W. C. Wilson. Production of High-Quality, Electrorefined and Electrowon Copper at Inco's Copper Cliff Copper Refinery. CIM Bull., v. 70, No. 784, Aug. 1977, pp. 166-172.
10. Mining Journal. Anode Corrosion Overcome. V. 279, No. 7156, Oct. 20, 1972, p. 317.

11. Yamamoto, I. T., and T. Sukahara. Determination of Microamounts of Lead in Copper, Nickel, and Aluminum Alloys by Solvent Extraction and Atomic Absorption Spectrometry. *Anal. Chim. Acta*, v. 61, 1972, pp. 33-41.

12. Burbank, J. Anodization of Lead and Lead Alloys in Sulfuric Acid. *J. Electrochem. Soc.*, v. 104, No. 12, 1957, pp. 693-701.

13. Rey, M., P. Coheur, and H. Herbiet. The Behavior of Lead Anodes in a Sulfate Electrolyte With Particular Reference to the Influence of Cobalt Salts. Paper in *Trans. Electrochem. Soc.* (Electrochem. Soc. Annu. Meeting, Savannah GA, Apr. 27-30, 1938). *Electrochem. Soc.*, Columbia Univ., New York, 1938, pp. 315-325.