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THE ELECTROREFINING OF COPPER FROM
A CUPROUS ION COMPLEXING ELECTROLYTE:
II. EXPERIMENTAL COMPARISON OF
POSSIBLE ALTERNATIVE ELECTROLYTES AND
PRELIMINARY COST ENGINEERING ANALYSIS

by

A. P. Brown, R. O. Loutfy,
and G. M. Cook

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS
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April 1980

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ABSTRACT

The energy saving potential and refining capability of three copper(I)/electrolyte systems for the electrorefining of copper were compared experimentally. The alternative electrolyte systems studied were copper(I)/acid chloride, copper(I)/acetonitrile and sulfuric acid, and copper(I)/ammonia solutions. These were compared to the conventional copper(II)/sulfuric acid electrolyte. All of the alternative electrolyte systems demonstrated at least some potential for saving energy when run at an equal deposition rate to the conventional process; the chloride electrolyte showed the greatest energy saving potential, about 70%, and the ammonia electrolyte showed the least, about 25%. All of the alternative electrolyte systems, however, exhibited performance problems, primarily with regard to inadequate separation of impurities. A preliminary capital cost estimate was made for the copper(I)/chloride system. This estimate showed that, for the alternative electrolyte system to be cost competitive (that is, a reduction of capital cost of about 15-20%) with the conventional electrorefining process, the refining cells would have to be operated at a current density of about 25-30 mA-cm⁻². At this current density, the estimated energy saving potential for the copper(I)/chloride system was still about 50%.

I. INTRODUCTION

In a previous report,¹ we projected that electrorefining of copper using a cuprous ion intermediate to transfer the copper from the anode to the cathode had a significant potential for energy savings over the present copper electrorefining operation. Current practice is to use an aqueous copper(II)/sulfuric acid electrolyte where two electrons are required per deposited copper atom. The need to transfer only one electron when using a copper(I) intermediate is the basis for the energy saving potential.

From a literature survey, we identified three possible alternative aqueous electrolyte systems which are capable of stabilizing univalent copper: sodium chloride/hydrochloric acid, acetonitrile/sulfuric acid, and ammonium chloride/ammonia solutions. The literature on these alternative electrolytes contains insufficient information to enable us to draw definitive conclusions concerning their technical feasibility for industry or the potential for energy saving. Consequently, an experimental program was undertaken in which laboratory-scale electrorefining cells were tested with the above three electrolytes; for these tests, measurements were made of refining cell voltages (with a breakdown into

polarization and ohmic loss components), current efficiencies, refining capabilities, and the surface morphology of the cathode deposits. These experiments showed the copper(I)/chloride electrolyte system to have the greatest potential for improving energy consumption in copper electrorefining. In the second section of the report, we present the results of a preliminary cost engineering analysis carried out for the copper(I)/chloride electrolyte system.

II. EXPERIMENTAL PROGRAM

A. Experimental Procedure

The laboratory cells consisted of a glass case--7-cm wide, 12-cm long, and 20-cm deep--which had a capacity of about one liter with the electrodes in place. The electrodes consisted of one anode-cathode pair consisting of a 316 stainless steel cathode blank and a copper anode. The stainless steel cathode had its rear face masked with Teflon, leaving an exposed geometric surface area of about 100 cm². As a pretreatment, the cathode was degreased with a liquid detergent followed by a thorough washing with distilled water. Two types of copper were used for the anodes. Initially, the anode was made from oxygen-free, high-purity copper (OHFC) (A. D. Mackay, Inc., Darien, Conn.). For later experiments, however, in which the impurity flow characteristics of the cell were investigated, the anodes were made from industrial-grade blister copper. In both cases, the anodes had a slightly larger facial area than that of the cathodes and were kept a fixed distance of 2 cm from the cathodes by the use of polypropylene spacers.

In the glass cells, four different electrolyte solutions were tested whose compositions were not varied. They were: 0.65M Cu(II), 2M H₂SO₄; 0.65M Cu(I), 2M H₂SO₄, 25 vol % (≈4.8M) CH₃CN; 0.65M Cu(I), 1M HCl, 3M NaCl; and 0.65M Cu(I), 2M NH₄Cl, 4M NH₄OH. All solutions were made up using A.C.S. reagent grade chemicals and doubly distilled water. Solutions of copper(I) were prepared by dissolving the required amount of copper(II) salt and then reducing it with copper shot. Absorption of oxygen into these copper(I) electrolyte solutions was inhibited by maintaining a layer of paraffin oil (≈1-mm thick) on the electrolyte surface. In every experiment, the electrolyte was flowed through the cell (in at the bottom and out at the top) at a constant rate of about 300 ml/min. The electrolytes were maintained at constant temperatures by placing the glass cell in a thermostated water bath. The copper(II)/sulfuric acid and copper(I)/chloride electrolytes were tested at 60°C; the other two copper(I) systems were tested at 35°C. The cells were operated at a constant current provided by a (20A, 25V) Sorensen SRL power supply. Cell voltages and individual electrode potentials were measured with respect to a mercury/mercurous sulfate reference electrode; for these measurements an electrometer buffer amplifier (Aardvark Instruments) was connected to a digital voltmeter and strip chart recorder.

Two sets of experiments were carried out with the above described cells. In the first set, steady-state measurements were made of the cell-voltage components of over-potential and electrolyte iR drop as a function of current density. Electrolysis times of up to 1 hr were allowed at each current density to allow the system to reach a steady-state. The iR drops in the cell were obtained using the current-interruption technique; switching of the current

was provided by a mercury wetted relay, and the potential *versus* time characteristics after interruption of the current were recorded on a storage oscilloscope.

The purposes of the second set of experiments were: (1) to determine the refining capability of each alternative electrolyte system, (2) to monitor the visual characteristics of the cathodic deposit, and (3) to assess the ability of the oil layer on top of the electrolyte to minimize the absorption of oxygen into the electrolyte. In these experiments, the impure copper anodes were used. The cells were run for a total of about three days to allow sufficient time for any accumulation of impurities in the electrolyte to reach a measurable value. The procedures for these extended-time electrolyses were essentially the same for all these alternative systems. Electrolysis was started with a copper(I) concentration of about 0.65M (41 g/l) and a nickel(II) concentration of about 0.17M (10 g/l). Such large concentrations of nickel are generally encountered in industrial electrolytes, but would take too long to accumulate in laboratory-scale experiments. Due to the low solubility of nickel(II) in the ammoniacal electrolyte, the 10 g/l nickel was not added to this electrolyte. The electrolyte was sampled at the start, after 48 hr, and after 72 hr of electrolysis. A sample of cathode copper was taken from the deposit obtained during the last 24 hr of the 72 hr electrolysis. The anode slimes (impurities in the anode which are not soluble in the electrolyte) were collected at the conclusion of the experiment (after 72 hr). These slimes adhered to the anode, causing the anodic over-voltage to increase by about 30 mV in every case, and were collected by spraying the anodes with distilled water. Emission spectroscopy was used to study the level of the impurities in the anode, the cathode, the dried anode slimes, and a residue obtained by boiling to dryness the final electrolyte sample for each system. The estimated accuracy of these analyses is a factor of two up to an order of magnitude. Atomic adsorption spectroscopy was used to monitor the copper and nickel concentrations in the electrolyte as a function of the electrolysis time. These analyses have an estimated accuracy of better than $\pm 5\%$ of the amount of metal ion measured. All the spectroscopic work was carried out by the Analytical Chemistry group at ANL.

B. Results

Plots of steady-state cell voltage *versus* current density for the copper/electrolyte systems examined are shown in Fig. 1. This figure shows that all of the systems behave in a regular manner with respect to their cell voltage characteristics. Also, Fig. 1 shows that, at any given current density, the cell voltage will follow the order $\text{Cu(I)/NH}_3 > \text{Cu(I)/MeCN} > \text{Cu(II)/H}_2\text{SO}_4 > \text{Cu(I)/Cl}^-$. The current density used with the $\text{Cu(II)/H}_2\text{SO}_4$ system is generally about 20 mA-cm^{-2} . It was assumed that a copper(I)/electrolyte system would be operated at an equal deposition rate to that of the copper(II) one; thus, the current density for the copper(I) system would be 10 mA-cm^{-2} . As can be seen in this figure, the $\text{Cu(II)/H}_2\text{SO}_4$ and the Cu(I)/MeCN systems have about the same cell voltage at current densities of 20 and 10 mA-cm^{-2} , respectively. Figure 2 shows the total ohmic potential drop between the anode and cathode as a function of current for the four systems. As expected, the iR drops in the four electrolytes were linearly related to the current density; the slopes of these plots divided by the electrode separation are equal to the conductivity of the electrolyte. At any given current density, the two

Fig. 1. Cell Voltage vs. Current Density

simple acid electrolyte systems showed the lowest iR drops. The addition of acetonitrile to sulfuric acid decreased the slope of the current *versus* iR drop curve, corresponding to a decrease in conductivity of about 30%. The Cu(I)/ammoniacal solution had the highest iR drop of the four systems; this high iR drop contributed a significant fraction of the high cell voltage of this system (see Fig. 1). Figure 3 presents the electrode overpotentials for the copper(I)/electrolyte systems as a function of the logarithm of the current density (Tafel plot). The overpotential data do not conform to any simple behavior. On the cathodic side (negative overpotentials), the data are essentially linear, whereas the anodic behavior seems to result in curved Tafel lines. These inconsistent data are probably caused by a non-uniform current and potential distribution over the electrode surfaces; the measurements were made by probing only a single position between the electrodes. No great import should, therefore, be attached to the data in Fig. 3; the data in Figs. 1 and 2, however, should be more representative since they were measured for the total cell.

Fig. 2. Current *vs.* iR Drop

For the second set of experiments, Table 1 shows the starting conditions, average cell voltage, electrolysis time, bulk material balance, and current efficiency for each of the alternative electrolyte systems. In general, after the cells had stabilized following switch-on, the cell voltages over 72 hours were relatively constant; the variations in the cell voltages noted in Table 1 can probably be attributed to changes in the cathodic surface area. For each of the cells reported in Table 1, the cell voltages are about 30 mV higher than those obtained at the same current density in the previous cells with pure copper anodes. The increased cell voltage was due to an increase in the anodic overpotential caused by the insoluble anode slimes adhering to the surface of the electrode. Since the bulk material balance and cathode current efficiencies measured for the cells with chloride and acetonitrile electrolytes showed almost 100% current efficiency, it was concluded that the protective oil layer on the surface of these two electrolytes was satisfactory in minimizing the absorption of atmospheric oxygen. The data for the ammoniacal electrolyte show a low cathode current efficiency (79%), with a concomitant increase in the amount of copper in the electrolyte. Such behavior is consistent with significant oxygen absorption into the electrolyte, *i.e.*, the oxygen oxidizes the copper(I) to copper(II) which

Fig. 3. Logarithmic Current Density vs. Anodic and Cathodic Overpotential

then oxidizes the copper of the cathode. Whether or not this effect accounted for the loss in current efficiency in the present case was not verified experimentally.

The emission spectroscopic analyses for selected elements are reported for the chloride system in Table 2, the acetonitrile system in Table 3, and the ammoniacal system in Table 4. The numbers in parentheses represent the mass balance for the bulk material flow given in Table 1. For comparison, the impurities in a modern copper refinery using a copper(II)/H₂SO₄ electrolyte¹ are given in Table 5. The atomic adsorption results for the concentrations of nickel and copper in the electrolyte as a function of the electrolysis time are shown in Table 6. These data were used to calculate the increase in the amount of copper in the electrolyte for the mass balance data given in Table 1.

Table 1. Results of Extended-Time (72 hr) Electrolyses

	Cu^+/Cl^-	Cu^+/MeCN	Cu^+/NH_3
Electrolyte Composition	1M HCl, 3M NaCl	2M H_2SO_4 4.8M CH_3CN ^a	2M NH_4Cl 4M NH_4OH
Temperature, °C	60	35	35
Cathode Current Density, ^b A-cm ⁻²	0.01	0.01	0.01
Average Cell Voltage, ^c V	0.105 ± 0.002	0.175 ± 0.01	0.225 ± 0.01
Total Electrolysis Time, hr	69.95	71.77	71.18
Cathode Current Efficiency, %	99	100	79
Weight Loss of Anode, g	154.6	162.1	166.9
Weight Gain of Cathode, g	150.9	157.2	122.4
Weight of Slimes Recovered, g	3.9	1.3	1.0
Increase of Copper in the Electrolyte, g	0.9	2.0	41.1
Copper Mass Balance, g	+1.1	-1.6	-2.4

^aElectrolyte also contained 30 ppm Cl^- .^bCathode electrode area is 92.2 cm².^cElectrode separation is 2 cm.

Table 2. Spectroscopic Analyses for the Chloride System^a

Element	Anode, ppm (g)	Cathode, ppm (g)	Dried Electrolyte Residue, ^b % (g)	Slime, % (g)
Ag	7000 (1.08)	2000 (0.302)	0.005 (0.017)	10 (0.39)
As	600 (0.093)	<10 (0.002)	<0.01 (0.033)	6 (0.234)
Bi	30 (0.005)	<0.2 (3×10^{-5})	0.003 (0.01)	0.006 (2×10^{-4})
Fe	FT ^c	FT ^c	0.02 (0.066)	0.004 (1.6×10^{-4})
Ni	4000 (0.618)	4 (6×10^{-4})	5 (16.7, 12.1 ^d)	0.01 (3.9×10^{-4})
Pb	300 (0.046)	VFT ^e	0.02 (0.067)	0.02 (7.8×10^{-4})
Sb	150 (0.023)	VFT ^e	0.001 (0.003)	0.2 (0.008)

^aNumbers in parentheses were calculated from the material flow given in Table 1.

^bResidue obtained from about 0.75 ml of electrolyte.

^cFaint trace (0.001-0.0001%).

^dFrom atomic adsorption analyses given in Table 6.

^eVery faint trace.

Table 3. Spectroscopic Analyses for the Acetonitrile System^a

Element	Anode, ppm (g)	Cathode, ppm (g)	Dried Electrolyte Residue, ^b % (g)	Slime, % (g)
Ag	7000 (1.13)	2 (0.0003)	NT ^c	VS ^d
As	600 (0.097)	<10 (0.0016)	<0.01 (0.016)	5 (0.065)
Bi	30 (0.005)	40 (0.0063)	0.002 (0.003)	0.1 (0.0013)
Fe	FT ^e	<10 (0.0016)	<0.001 (0.002)	0.006 (8 x 10 ⁻⁵)
Ni	4000 (0.65)	80 (0.013)	5 (7.85)	0.02 (0.0003)
Pb	300 (0.005)	<1 (0.0002)	FT ^e	2 (0.026)
Sb	150 (0.0024)	VFT ^f	0.005 (0.008)	0.07 (0.0009)

^aNumbers in parentheses were calculated from the material flow given in Table 1.

^bResidue obtained from about 0.75 ml of electrolyte.

^cNot detected.

^dVery strong (10-100%).

^eFaint trace.

^fVery faint trace.

Table 4. Spectroscopic Analyses for the Ammoniacal System^a

Element	Anode, ppm (g)	Cathode, ppm (g)	Dried Electrolyte Residue, ^b % (g)	Slime, % (g)
Ag	7000 (1.17)	25 (0.003)	FT ^c	VS ^d
As	600 (0.10)	20 (0.0024)	T ^{e,f}	0.3 (0.003)
Bi	30 (0.005)	0.2 (2.4 x 10 ⁻⁵)	<0.001 (0.0015)	0.3 (0.003)
Fe	FT ^c	FT ^c	T ^f	5 (0.05)
Ni	4000 (0.67)	<4 (0.0005)	0.06 (0.09)	0.04 (0.0004)
Pb	300 (0.05)	5 (0.0006)	FT ^c	1.5 (0.015)
Sb	150 (0.025)	50 (0.006)	W ^g	0.6 (0.006)

^aNumbers in parentheses were calculated from the material flow given in Table 1.

^bResidue obtained from about 0.75 ml of electrolyte.

^cFaint trace (0.001-0.0001%).

^dVery strong (10-100%).

^eSome material probably lost during evaporation and drying.

^fTrace (0.01-0.001%).

^gWeak (0.1-0.01%).

Table 5. Mass Balance Characteristics of Impurity Elements in Modern Copper Refinery^a

Element	Anode Composition Range, ppm	Proportion into Anode Residues, %	Proportion into Electrolyte, %	Cathode Composition Range, ppm
Ag	trace-1000	98	2	5-10
As	0-3000	25	75	trace-1
Bi	0-100	50	50	trace-1
Fe	20-300	--	100	2-6
Ni	0-5000	5	95	trace-7
Pb	0-1000	98	2	trace-5
Sb	0-3000	60	40	trace-2

^aData in this table are from Ref. 1.

Table 6. Atomic Absorption Spectroscopic Analysis of Copper and Nickel in the Electrolyte as a Function of Electrolysis Time

	Ni, g/l	Cu, g/l
Cu(I)/Cl ⁻		
start	8.85 ± 0.3	39.7 ± 1.2
after 46.25 hr	9.70 ± 0.3	39.9 ± 1.2
after 69.95 hr	9.70 ± 0.3	40.4 ± 1.2
Cu(I)/MeCN		
start	11.4 ± 0.3	44.7 ± 1.3
after 47.60 hr	10.6 ± 0.3	46.4 ± 1.9
after 71.77 hr	10.5 ± 0.3	46.3 ± 1.4
Cu(I)/NH ₃		
start	-	37.2 ± 1.3
after 47.67 hr	-	50.4 ± 1.7
after 71.18 hr	0.5 ± 0.2	70.1 ± 2.1

The reason that the mass balance data in Tables 2, 3, and 4 rarely balance for each element is the relatively poor accuracy obtainable with emission spectroscopy (see experimental section). For example, with the chloride electrolyte system, the amount of nickel found in the residue was 16.7 g in 1.25 l of electrolyte by emission spectroscopy (Table 2), but 12.1 g in 1.25 l of electrolyte by atomic absorption spectroscopy (Table 6). This discrepancy in the findings is large, but within experimental error. The data in Tables 2-4 were used, in general, more for qualitative rather than quantitative assessments.

The data in Tables 2-4 show that none of the proposed electrolyte systems have the overall level of refining required by industry (Table 5).

With the chloride electrolyte (Table 2), a very poor separation of silver from the copper was obtained. About 50% of the silver in the anode was transferred to the cathode, with almost all the rest depositing in the anode slimes, probably in the form of complexes such as silver selenides and tellurides. Although not listed in Table 2, 40 ppm of vanadium was also found in the cathode sample from the chloride electrolyte. Since vanadium only appeared in the anode at less than 1 ppm, it was inferred that the vanadium detected in the cathode originated from an outside source such as the stainless steel cathode blanks.

The cathode sample from the acetonitrile/sulfuric acid electrolyte showed higher than acceptable levels of nickel and bismuth (Table 3). The finding of a high nickel contamination of the cathode with this electrolyte is contrary to results reported by Parker *et al.*², although they did not use the 10 g/l nickel in their test electrolyte normally encountered in present-day industrial electrolytes.* Because of the high nickel concentration in most samples of blister copper, a relatively high concentration of nickel is expected to build up in any alternative electrolyte in which nickel salts are soluble. These high concentrations of nickel in the electrolyte also appear to have a deleterious effect on the quality of the cathode deposit (discussed later). Parker *et al.* encountered problems with arsenic and bismuth impurities entering the cathode, and showed that such contamination can be controlled by the monitored addition of chloride ions to the electrolyte.

With the ammoniacal electrolyte, the cathode sample analysis (Table 4) showed higher than acceptable levels of arsenic and antimony; this finding is in agreement with the results of Schimmel.³ The concentrations of silver in the cathode also appeared to be somewhat high. The limited precision of the analysis places this silver concentration within the maximum quantity found industrially (Table 5).

As can be seen in Table 6, atomic adsorption analysis indicated very little change in the quantity of copper in the electrolyte over the electrolysis period for the chloride and acetonitrile electrolytes, but nearly a doubling of the copper concentration within the 72-hr electrolysis for the ammoniacal system. In the latter case, the increase of copper in the electrolyte can be associated with significant oxygen absorption into the electrolyte and the resultant low cathodic current efficiency. The atomic absorption analysis also showed that the nickel concentration increased slightly in the chloride and ammoniacal electrolytes. This increase in nickel corresponds to its dissolution from the impure anode; the emission spectroscopic data in Tables 2-4 indicate that the

* See appendix for added note.

increase in concentration should be about 0.5 g/l. With the acetonitrile electrolyte, a small decrease in the nickel concentration was found. The nickel impurity detected in the cathode with this electrolyte (Table 3) probably accounts for this effect.

The visual characteristics of the cathode deposits after the 72-hr electrolysis are summarized in Table 7. Of the three copper(I) electrolytes and the copper(II) electrolyte, the best deposit was obtained with the ammoniacal electrolyte. This deposit was smooth and very fine grained, with no tendency for dendrite growth at the current density used (0.01 A-cm^{-2}). The cathode deposit for the acetonitrile/sulfuric acid electrolyte was generally very poor and showed severe dendritic growth; in one case, the electrodes (spaced 2 cm apart) short-circuited within a 24-hr electrolysis period.

Table 7. Visual Characteristics of Deposits

System	Visual Characteristics
Cu(II)/H ₂ SO ₄	Medium to fine grained. Coherent. Striated vertically. Tendency for dendritic growth.
Cu(I)/Cl ⁻	Coarse grained. Crystalline. Coherent. No dendritic growth.
Cu(I)/MeCN	Medium grained. Nodular. Severely dendritic in the presence of Ni ²⁺ .
Cu(I)/NH ₃	Very fine grained. Smooth. Coherent. No dendritic growth.

Subsequent experiments revealed that, as a result of the elimination of the excess nickel from the electrolyte, the dendrite growth was reduced to a nodular one. This behavior, as with the nickel contamination in the cathode described above, is contrary to the results reported by Parker *et al.*,² who obtained fine grained, smooth deposits* at current densities up to about 25 mA-cm^{-2} . The cathode deposit obtained from the chloride electrolyte was rather coarse grained. Such a deposit is generally not acceptable industrially because it is usually indicative of a high amount of electrolyte inclusion, that is, entrapment of electrolyte between the grains of the cathode deposit. In the present case, however, the grains of the deposit appeared crystalline and different in structure from the grains of the deposit obtained from the copper(II)/sulfuric acid electrolyte. Additionally, the elemental analysis of the cathode did not indicate any significant electrolyte inclusion. These results are in total agreement with the nature of the deposit and the cathode purity reported by Cathro⁴ for the electrowinning of copper from copper(I)/chloride solutions. Furthermore, at a cathode current density of 25 mA-cm^{-2} , Cathro found that the addition of 2 g/l gelatin greatly improved the quality of the deposit, changing it from coarse to fine

* See appendix for added note.

grained; the cathodic overpotential penalty for this improvement was about 40 mV. This quantity of leveling agent appears unusually large; however, improvements in the deposit quality can be made with the right choice of leveling agent at a moderate increase in cell voltage in the electrorefining of copper(I)/chloride solutions. The type of deposit obtained from the conventional copper(II)/sulfuric acid in a laboratory-size cell (Table 7) was inferior to that obtained in industrial-sized cells, probably because these laboratory-cell deposits were obtained without the benefit of any leveling agents.

C. Concluding Remarks

The cell voltage and specific energy usage for the three alternative copper(I) electrolyte systems as well as the conventional copper(II) system are shown in Table 8. For case A, the voltage and energy data are given for the normal current densities of 20 mA-cm^{-2} for the copper(II) system and 10 mA-cm^{-2} for the copper(I) system; this case allows one to compare the copper(I) and (II) systems for refining plants having the same throughput and size. Since it is likely that current densities of greater than 10 mA-cm^{-2} will be necessary for the alternative systems to be economically competitive with the present one,¹ case B presents voltage and energy data for a current density of 12.5 mA-cm^{-2} in the copper(I) system; this case allows one to compare the copper(I) and (II) systems in refining plants having the same throughput and cost. These cell voltages were obtained from Fig. 1, with the addition of the anodic overpotential to account for the use of an impure anode with the consequent adhering slimes. These cell voltages with the current efficiencies shown in Table 1 were used to calculate the specific energy usages; a current efficiency value of 100% was taken for the copper(II) system. As can be seen, the copper(I)/chloride electrolyte system shows an excellent energy saving potential, about 70% over the present system; the copper(I)/acetonitrile electrolyte is also attractive, with a predicted 50% energy saving. The ammonia based system shows the least promise of the three, with a predicted energy savings of less than 25%.

Table 8. Cell Voltage and Specific Energy Usage in Laboratory Cells

	Cu(II)/H ₂ SO ₄	Cu(I)/Cl ⁻	Cu(I)/MeCN	Cu(I)/NH ₃
CASE A (constant plant size)				
Current density, A-cm ⁻²	0.02	0.01	0.01	0.01
Cell voltage, V	0.190	0.105	0.175	0.225
Specific energy usage, kW-hr (% saving)	0.160 (0)	0.045 (71.9)	0.074 (53.5)	0.120 (24.8)
CASE B (constant plant cost)				
Current density, A-cm ⁻²	0.02	0.0125	0.0125	0.0125
Cell voltage, V	0.190	0.114	0.202	0.255
Specific energy usage, kW-hr (% saving)	0.160 (0)	0.049 (69.5)	0.085 (46.9)	0.136 (14.8)

Although Table 8 shows that all three alternative electrolyte systems have at least some potential for energy savings, none of the alternatives is sufficiently free of problems to justify immediate scale-up experimentation. The problems encountered with the various systems in this work are summarized in Table 9. The primary problem areas were defined as those for which we can see no immediate solution; thus, a significant research program would be needed before this problem could be eliminated. The secondary problem of a coarse grained deposit obtained with the chloride electrolyte can be solved by the addition of leveling agents. The relatively poor energy-saving potential predicted for the ammoniacal system was classified as a secondary problem because it is at least partially caused by the primary problem of a low current efficiency.

Table 9. Principal Technical Problems Associated with Alternative Electrolyte Systems

Electrolyte System	Primary Problem	Secondary Problem
Acid Chloride	Poor separation of the copper from silver impurities	Coarse grained deposit
Acetonitrile/ sulfuric acid*	Dendritic deposit Contamination of the cathode with nickel and bismuth	None
Ammoniacal Solution	Contamination of the cathode with arsenic and antimony Low current efficiency	Relatively poor energy saving potential

Since the chloride electrolyte system has a large energy saving potential and only one major problem, we briefly examined the problem of the poor separation of copper from silver impurity. The cause of the separation problem appears to be related to the relatively small difference between the CuCl_2/Cu and AgCl_2/Ag potentials (0.25 V). Table 10 shows these standard potentials for each of the alternative electrolytes as well as sulfuric acid. As the standard potential for the electrodisolution of silver to the various Ag(I) complexes listed in Table 10 approaches the standard potential for the electrodisolution of copper, there will be a corresponding increase in the amount of silver being oxidized into the electrolyte solution during the oxidation of the impure copper anodes. Since the silver is more noble than the copper in all the electrolytes, any silver ions in the electrolyte will always be deposited on the copper cathode. Thus, the silver impurity in copper cathodes obtained by refining copper in the electrolytes, where the metal complexes shown in Table 10 are formed, increases as the difference between the standard potentials for the copper and silver decreases. With the industrially used copper(II)/sulfuric acid electrolyte, small amounts of

* See appendix for added note.

Table 10. Comparison of Ag(I)/Ag and Cu(I)/Cu Electrode Potentials

Redox Couple	E_o , V vs. NHE ^a	$(E_{o,Ag} - E_{o,Cu})$, V
$Ag(MeCN)_2^+/Ag$	0.54	
$Cu(MeCN)_2^+/Cu$	-0.10	0.64
$Ag(NH_3)_2^+/Ag$	0.37	
$Cu(NH_3)_2^+/Cu$	-0.12	0.49
$Ag^+/Ag(H^+)$	0.80	
$Cu^{2+}/Cu(H^+)$	0.34	0.46
$AgCl_2^-/Ag$	0.17 ^b	
$CuCl_2^-/Cu$	-0.08 ^b	0.25

^aNormal hydrogen electrode.

^bMeasured equilibrium potentials in 1M HCl, 3M NaCl with $10^{-3}M$ Ag^+ or Cu^+ .

chloride ion are added to precipitate the Ag(I) before it can be deposited at the cathode. Through experimentation and examination of solubility product data in the literature, we attempted to find a selective precipitant for silver in copper containing chloride solutions. However, none could be found because of the extremely similar chemical properties of silver(I) and copper(I) and the need to reduce the silver concentration in solutions to about $10^{-6}M$ while maintaining a 0.5-1.0M concentration of copper.

III. PRELIMINARY COST ENGINEERING ANALYSIS*

To justify any further experimental work on the development of the copper(I) electrorefining process, it is necessary to show that, if developed, the new process would be economically competitive with the currently used electrorefining process. Because the copper(I)/chloride electrolyte system was projected to attain the highest energy saving potential of the proposed electrolyte systems, it was chosen as the representative example for cost comparison with the conventional process.

*Based upon work conducted by Resource Engineering Incorp., Lexington, MA.

For the purpose of this analysis, the cost of a conventional (sulfate) electrolyrefinery for the production of 100,000 tpy (tons/yr) copper, schematically represented in Fig. 4 and discussed more fully in Ref. 1, was estimated to be $\$60 \times 10^6$ (1979); a breakdown of this cost is shown in Table 11.

Fig. 4. Flowsheet for 100,000 ton/yr Conventional Electrorefinery

Table 11. Capital Cost for Conventional Refinery (100,000 tpy)

Area	Capital Cost, \$ (1979) $\times 10^6$
Commercial Section	27
Starter Sheet	9
Liberator	3
Material Handling, Anode and Rod Casting	15
Building & Offsites	6
Total	60

Figure 5 shows the flowsheet for chloride-based refining for the production of 100,000 tpy copper. The implementation of this cuprous electrorefining will probably require several changes in the conventional refinery. Since cuprous ion is readily oxidized by air (oxygen) with this alternative process, steps must be taken to prevent contact of the electrolyte with air. This includes closed or blanketed storage tanks, solution-transfer launders, and sumps. The liquid surface of the electrolyte in the cells also should be protected from air. This may be achieved by covering and blanketing the cells (which interferes with anode and cathode handling) or, as utilized in our experiments, by floating a material (kerosene, paraffin, or hollow spheres) on the surface.

Fig. 5. Flowsheet for 100,000 ton/yr Electrorefining of Copper with a Chloride Electrolyte

Materials of construction for equipment in contact with chloride electrolyte, in some cases, will be different from those used for the conventional sulfate electrolyte. The cells, either concrete or steel shells, would be lined with a PVC or other suitable plastic material. Piping and other tankage would be similarly constructed. Although most conventional refineries employ lead linings, the use of plastics is becoming accepted practice.

The largest single modification required for the chloride-based system is in the operation of the liberator cells. The direct electrolysis of the chloride electrolyte may result in evolution of chlorine (gas) at the anode.

This gas, unlike the oxygen evolved in a conventional liberator section, must be collected and either recycled or otherwise treated. One possible method of avoiding this problem would be through the use of a solvent extraction step to remove copper from the bleed streams. The extracted copper would be recovered in a sulfate electrolyte through electrowinning, as is done in a conventional refinery. The stripped bleed would then be treated, either to be recycled or discarded.

A rough capital cost estimate for a 100,000 tpy refinery based on a cuprous chloride electrolyte is shown in Table 12. The key commercial cell parameters for this process are shown in Table 13; the commercial section accounts for the largest portion of the total refinery cost. Since the number of commercial cells is the same as in the sulfate-based refinery, the capital cost is about the same for both processes. In comparison with the conventional electrorefining process, the commercial section for the alternative process has lower costs for rectifiers and bus bars due to reduced power requirement, which are, however, more than offset by higher costs for cells and other equipment in contact with the chloride electrolyte due to the need for eliminating air contact with the electrolyte, and by higher costs for the liberator section due to the added cost of a solvent extraction step.

Table 12. Capital Cost for Refinery Using Chloride Electrolyte

Section	Cost, \$ x 10 ⁶
Commercial Section	28
Starter Sheet	9
Liberator with Solvent Extraction	7
Material Handling, Anode Casting, etc.	15
Building & Offsites	6
	65

A rough operating cost estimate for a 100,000 tpy conventional refinery is shown in Table 14. It can be seen that the operating costs associated with a copper refinery are dominated by capital-related costs (such as depreciation and taxes), and by labor and maintenance costs. The major advantage of a chloride electrolyte system would be a reduction in electric power in the commercial cells. However, for an energy saving of 50%, the operating cost saving would only be about 0.25¢/kg copper (*i.e.*, about 0.1 kW-hr/kg copper at electrical energy cost of 2.5¢/kW-hr), which is quite small compared to the total operating cost of about 20¢/kg (see Ref. 1).

Table 13. Operating Characteristics for Commercial Section of Electrorefinery (conventional and chloride based)

	Conventional	Chloride
Current Required, A-hr/kg	843.3	421.6
Current Density, A-m ⁻² (ASF)	215 (20)	108 (10)
Current Efficiency, %	95	95
Cell Voltage, ^a V	0.22	0.22
Anode Weight, kg (lb)	286 (630)	286 (630)
Anode Cycle, days	28	28
Cathode Weight, kg (lb)	120 (265)	120 (265)
Cathode Cycle, days	14	14
Cathode-Anode Separation, cm (in.)		
1st Cycle	3.3 (1.3)	3.3 (1.3)
2nd Cycle	4.1 (1.6)	4.1 (1.6)
Power Required, kW-hr/kg (kW-hr/lb)	0.196 (0.089)	0.097 (0.044)

^aA first approximation is to assume equal cell voltages.

Table 14. Approximate Operating Costs for Conventional Copper Refining

Section	Cost, \$/kg
Capital Dependent	0.10
Labor/Maintenance, etc.	0.095
Electrolytic Energy	<u>0.005</u>
	0.20

^aData derived from Ref. 7.

The copper(I)/chloride electrolyte at the same production rate as that of the conventional process is clearly not cost competitive. To have an economical advantage, the alternative technology must have a significant cost saving (15-20%) over the existing process. Since the number of cells required for a given production rate is inversely proportional to the current density, the number of cells, and therefore the cost, can be decreased by increasing the current density for the copper(I) system. (Similarly, the cost per annual ton of produced copper for a given refining plant can be reduced by operating the same number of cells at a higher current density, thereby increasing the annual capacity of the refinery). Figure 6 shows the effect of current density on the total refinery capital cost for a chloride-based process relative

Fig. 6. Relative (with respect to conventional process) Capital Cost and Estimated Energy Saving vs. Current Density for Copper(I) Electrorefining Process

to the conventional electrorefining process. Also shown in Figure 6 are estimated percentage energy savings as a function of the current density, based on an extrapolation of our experimental results for the chloride and acetonitrile electrolytes. As can be seen, the current density would have to be about 12-13 mA-cm⁻² for the cost of the alternative chloride-electrolyte system to be reduced to that of a conventional refinery. In order to save 15-20% of the capital cost, it would be necessary to operate at about 25 mA-cm⁻². For the chloride electrolyte, energy savings of about 50% are still possible at this high current density; with the acetonitrile electrolyte, however, the energy saving is likely to become less than about 15%. In both cases, it is assumed that the cells will produce a satisfactory product at 25-30 mA-cm⁻².

At present, there seems to be little incentive for the copper industry to increase its total production capacity by the construction of new smelters and refineries--the electrorefineries are currently running well below capacity because relatively cheap imported copper is readily available. The reason for this lack of incentive can be inferred from Table 15, which was derived from a recent National Research Council report.⁶ The estimated capital investment cost to produce copper metal from the ore is \$6,000/annual ton (1977), and the estimated primary metal price that would support new production capacity based on existing technology is \$1.27/lb. In December of 1977, the market price of copper was only \$0.61/lb--grossly insufficient to support capacity expansion in the copper industry based on existing technology. With

Table 15. Estimated Price (1977 dollars) to Support
New Productive Capacity in the Copper
Industry Using Existing Technology^a

Investment Costs, \$/annual ton	6,000
Operating Cost, ^b \$/lb	0.53
Calculated Cost, ^c \$/lb	1.27
Market Prices, \$/lb	
July 1976	0.74
December 1977	0.61

^aBased upon information in Ref. 6.

^bExcluding depreciation.

^cIncluding return on investment.

a current market price (November 1979) for copper of \$0.91/lb, the economic situation cannot have improved to any significant extent. Furthermore, since the capital cost of the electrorefining of copper only constitutes a relatively small part of the overall investment costs (7%), the introduction of new electrorefining technology for plant expansion would not significantly affect the required copper price of \$1.27/lb. Thus, at present, new electrorefining technology for plant expansion is not likely to be justifiable.

The alternative to plant expansion is to increase the annual capacity by retrofitting improvements to speed up the current operation. In the electrorefining process, there are already several improvements that might be used to increase throughput; these include the use of periodic reverse current and air sparging, both of which would permit operation at higher current densities. Since these improvements would probably require less capital investment to implement than the copper(I) chloride system and are not currently being exploited, we can only conclude that the outlook for commercial use of the copper(I) technology is not very bright and will remain so until other measures are taken to make the domestic copper production more cost competitive with imported copper.

IV. CONCLUSION

Of the three alternative cuprous ion electrolytes that we examined for copper electrorefining, only the one based on cuprous chloride showed any promise of being both energy and cost competitive with the conventional electrorefining process. The decision to proceed with the development of the cuprous chloride system requires a careful evaluation of the possible energy and economic benefits balanced against the risks and cost of the R&D effort. The energy saving incentive for the chloride system is estimated to be about $2-3 \times 10^{12}$ Btu/yr (based on electrorefined copper production in 1977) or about 6×10^{12} Btu/yr in the year 2000 (assuming a linear 5% growth in the refined copper produced), and the economic incentive is a possible capital cost saving of about 15%. The development risks include finding a satisfactory method for separating the silver impurity from the copper and proving that consistently good deposits can be obtained at current densities of at

least 25 mA-cm⁻². We estimate the cost of the necessary R&D programs to be about \$5-10 million through the demonstration stage. Also to be assessed is the question of commercial acceptability. This includes whether the new process will have sufficient economic incentive and whether demand for a new development that will significantly increase the refining capacity of a modified plant will occur. Taking all of the above factors into consideration, we concluded that, at present, there appears to be little or no justification for the development of new copper electrorefining technology.

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APPENDIX

NOTE ON DENDRITIC DEPOSIT AND NICKEL
CONTAMINATION OF CATHODE

In a private communication, Drs. D. M. Muir and A. J. Parker, who have worked extensively on the copper(I)/acetonitrile/sulfuric acid system, have suggested that a high chloride ion concentration in this system could have been the cause for the dendritic deposit and nickel contamination of the cathode. They have found that it is necessary to maintain the chloride ion concentration at less than about 50ppm to avoid the formation of dendritic deposits--significant electrolytic inclusion, a source for the nickel impurity, is generally associated with such deposits. Although our electrolyte solutions are no longer available for analysis to check this hypothesis, it is possible to estimate the chloride ion concentration from known sources. All solutions were made up from doubly distilled water and should, therefore, be essentially free from major impurities. The copper and nickel sulfates used were both A.C.S. reagent grade chemicals with quoted chloride ion concentrations of less than 0.0003% and 0.001%, respectively. Assuming these values are correct, we calculated that the chloride ion concentration due to these sources should have been less than 1ppm. However, we cannot state with absolute certainty that the chloride ion concentration was below 50ppm.

Thus, although a high chloride ion concentration is certainly a possible reason for the problems we encountered with the acetonitrile/sulfuric acid electrolyte, it can only be verified by further experimentation.

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