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Electrorefining Copper at High Current Densities

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UNITED STATES DEPARTMENT OF THE INTERIOR

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ELECTROREFINING COPPER AT HIGH CURRENT DENSITIES

by

G. R. Smith,[1] F. X. McCawley,[2] P. B. Needham, Jr.,[3] and P. E. Richardson[4]

ABSTRACT

This report describes research carried out by the Bureau of Mines to develop new technology for electrorefining metals at much higher current densities than those normally used in commercial practice. Preliminary studies using rotating-ring and cylinder electrodes to increase the mass transport of copper are discussed. Following this work, single- and multichannel cells were developed that utilized a high electrolyte flow in the channels formed by the anode-cathode pairs. Using these cells, copper was successfully refined at current densities in the range of 70 to 300 amp/ft^2. The effects of flow rate, electrolyte composition, and grain-refining and leveling agents on the morphology and purity of electrodeposited copper were determined.

INTRODUCTION

This report discusses research conducted by the Bureau of Mines to increase the rate, deposit purity, and overall efficiency in industrial processes used to electrodeposit and purify metals by increasing substantially the operating current density range and optimizing the deposition process. Traditionally, copper refineries operate electrolytic cells at a current density of $\simeq$20 amp/ft^2. At this current density, the refining process is relatively slow, requiring about 28 days to refine a crude anode weighing about 650 lb. The maximum current density (refining rate) is essentially limited by the rate at which copper ions are transported through the electrolyte from the anode to the cathode. The mass transfer rate, in turn, is strongly dependent on the electrolyte flow conditions between the electrodes, increasing with increasing electrolyte circulation or degree of agitation. For practical reasons related to the basic design of traditional cells and electrode placement and mounting techniques, copper refineries circulate the electrolyte at rates of only 0.01 to 0.03 ft/min. This slow circulation also has other advantages. The insoluble anode impurities readily settle as a

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sludge on the cell bottom minimizing the probability of sludge inclusion in the cathode as an undesirable impurity. In addition, the nearly quiescent electrolyte may minimize acid misting in tank houses, as opposed to the amount of misting that would be expected from a more turbulent electrolyte. It is recognized (8)[5] that increasing the current density used in copper refining could yield significant economic benefits. Although as a rule, the energy required for electrorefining increases with increasing current density due to increased power losses in the electrolyte and bus bars, and to increased overvoltage components for the anode dissolution and cathode deposition process, the increased energy consumption must be balanced against the advantages of faster production rates. These advantages include small cells and plants and reduction in metal inventories.

Several methods to increase the current densities in copper electrorefining have been reported elsewhere. Balberyszski, Andersen, and Eaman (2) attained a current density of 60 amp/ft^2 by injecting the electrolyte directly beneath the electrodes. By forcing air under the electrodes and allowing it to bubble past the surfaces, Harvey, Randlett, and Bangerskis (6) produced electrorefined copper at a current density of 84 amp/ft^2. Tuddenham, Lewis, Lebrizzi, and Wood (15), increased the flow rate from 0.03 to 0.09 ft/min in a cell with the normal geometry by making a small change in the electrolyte circulating system, thus permitting an increase in current density to 40 amp/ft^2. Other methods have included moving the electrolyte downward with sufficient velocity to carry anode slimes out of contact with the electrodes by Guiterman (5), and successively passing electrolyte across the anode and then the cathode by Andersen and Archipov (1). Wallden, Henriksson, Arbstedt, and Mioën (16) increased the current density to 46 amp/ft^2 using an electrolyte flow of 42 ft/min in the channel formed between parallel anodes and cathodes. Channel cells of this design are ideally suited for very high current density refining processes because of the high relative motion that can be obtained between the flowing electrolyte and the stationary electrodes. For this reason, the Bureau of Mines, as part of a larger program to advance metals and minerals processing technology in an environmentally acceptable manner, undertook the research on channel cells described in this report. The objectives were to determine the effect of the rapid flow and high current density on the quality of the electrorefined copper, and to determine some of the technological problems of refining at high current densities.

In this report, three phases of this work are discussed. The first phase consisted of studies using small rotating electrodes to obtain a high mass transport of copper to the electrode surfaces. The effects of rotation rate and current density, as well as the effects of the concentrations of copper ions, sulfate ions, and thiourea $[(NH_2)_2C{=}S]$ in the electrolyte, on the physical and chemical properties of the refined copper were determined. In the second phase, a single-channel refining cell was built and tested. The effects of flow rate, current density, and grain refining additives on copper refining in this cell were determined. In the final phase,

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

a larger channel cell with multiple electrodes (four anodes and three cathodes) was designed and operated.

APPARATUS AND EXPERIMENTAL TECHNIQUES

Rotating Electrode Cells

In the first phase of this work using rotating electrode cells, two different electrode geometries were utilized; one with the electrodes in a plane-parallel configuration, the other with the electrodes in a concentric-cylindrical configuration. In the plane-parallel configuration, the rotating electrode, when used as a cathode, was constructed from rods of titanium, and, when used as an anode, from rods of copper. Both electrorefined copper and unrefined crude anode copper obtained from a refinery were used in the studies. The active dissolution or deposition area of the rods was defined by notching a ring (ID = 0.47 in, OD = 0.94 in) at one end of the rod, filling in the recessed areas with a self-setting acrylic resin and insulating the cylindrical portion with a tight fitting Teflon[6] sleeve (fig. 1A). During experiments, this electrode was placed 1.75 inches above a 9.5-in-diam flat copper disk such that the surfaces of the electrodes were parallel and on a horizontal plane. The immersion depth of the ring was 0.25 in below the electrolyte. The ring electrode was satisfactory for obtaining overvoltage values at the cathode and anode and photomicrographic evaluation of electrodeposits at several current densities and rotation rates. For cathode deposition or anode dissolution over 5 mils, however, the edge effect became a significant problem. Because of this difficulty, later studies, where a longer electrolysis period was desirable, were conducted with an improved concentric-cylindrical electrode configuration. In the concentric-cylindrical configuration, the inner rotating electrode consisted of a solid titanium cylinder 1 in in diameter and a total height of 2 in (fig. 1B). This electrode was always used as the cathode, and studies involved the effects of additives and electrolyte concentration on the morphology of the deposited copper. The active deposition area was confined to the lower

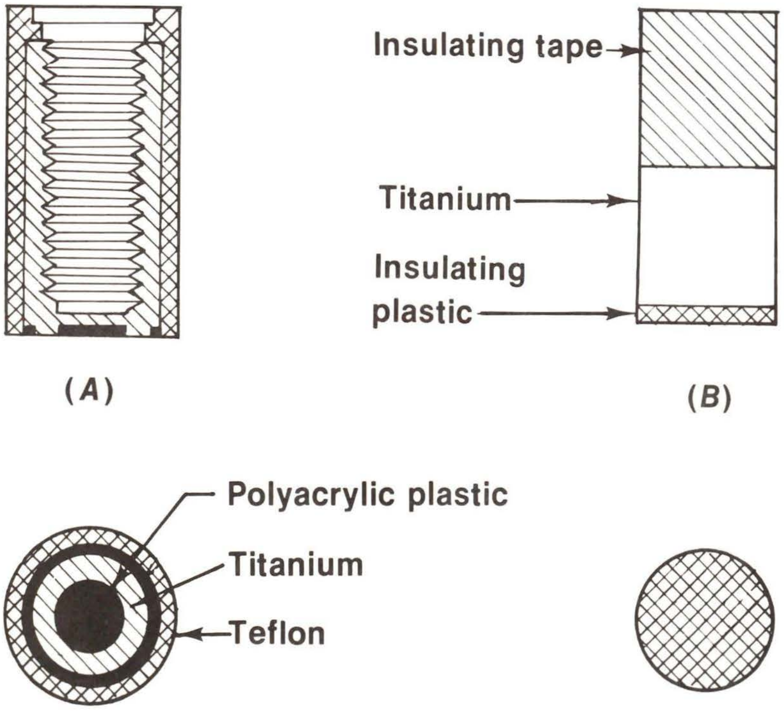

FIGURE 1. - Rotating ring (A) and rotating cylinder (B) electrodes.

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[6] References to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

1 in of the cylindrical surface. The lower and the upper portion of the cylinder were insulated with a self-setting acrylic resin and a standard electroplating tape. The outer electrode was a cylindrical tube of pure copper 4 in ID and 4 in high. During experiments, the inner rotating electrode was centered inside the outer cylinder, and immersed so that the top of the active deposition area was 0.75 in below the electrolyte. One advantage of the cylindrical configuration over the parallel configuration is that in the former, the relative motion between the cylindrical surface and the electrolyte is nearly constant over the entire active cathode surface. Using this cell, the deposits were uniform and the electrolysis periods were always selected to give a 32-mil-thick deposit.

Prior to electrolysis, the smaller rotating electrodes of both configurations were polished with 120-, 240-, and 320-grit alumina cloths, wet pumiced, rinsed with water and alcohol, and finally air dried.

Tests were generally conducted in 5.5 liters of electrolyte containing known concentrations of copper ion added as copper sulfate and free sulfuric acid. To study the effects of copper and sulfate ion concentrations on the electrodeposited copper, a series of experiments was conducted at copper ion concentrations of 10 to 50 g/l and at total sulfate ion concentrations of 100 to 250 g/l. Another set of tests was conducted using thiourea grain refining additive concentrations of 0.05 to 8.0 mg/l. In all experiments, the temperature was maintained at 55° ±2° C by immersing the polyethlene electrolysis cell in a constant temperature water bath. Figure 2 illustrates the electrolysis cell.

The effects of electrode rotation rate and current density on the overvoltage at the rotating electrodes were determined by measuring the voltage of the rotating electrode with a Luggin probe. The reference was a copper ion-saturated $CuSO_4$ half-cell that was coupled to the electrolysis cell by a salt bridge filled with the $CuSO_4$ electrolyte. To avoid the shielding effect of the 0.062-in-diam probe, voltage measurements were made with the probe at distances greater than 0.187 in from the rotating electrode. The probe was mounted on a manipulator that allowed accurate positioning within 0.016 in of the electrode. It could also be moved parallel to the rotating electrode surfaces to probe different areas.

The deposition or dissolution overvoltages were corrected for the voltage associated with the resistivity of the constant-low voltage mercury contact assembly (<u>17</u>), and the resistivity of the electrolyte between the probe tip and the rotating electrode surface. The mercury wetted a stainless steel shaft that connected to the rotating electrode. Resistance of the mercury contact was measured before and after each test and was less than 0.01 ohm. The total electrode voltage and the individual voltages related to resistivity were measured for each test. The contribution due to the resistivity of the electrolyte was determined by measuring the electrode voltage at several distances from the surface of the rotating electrode and extrapolating the values to the surface. After 5 mils of copper had been deposited, the overvoltage was calculated by subtracting the resistivity related voltages from the measured change in electrode voltage.

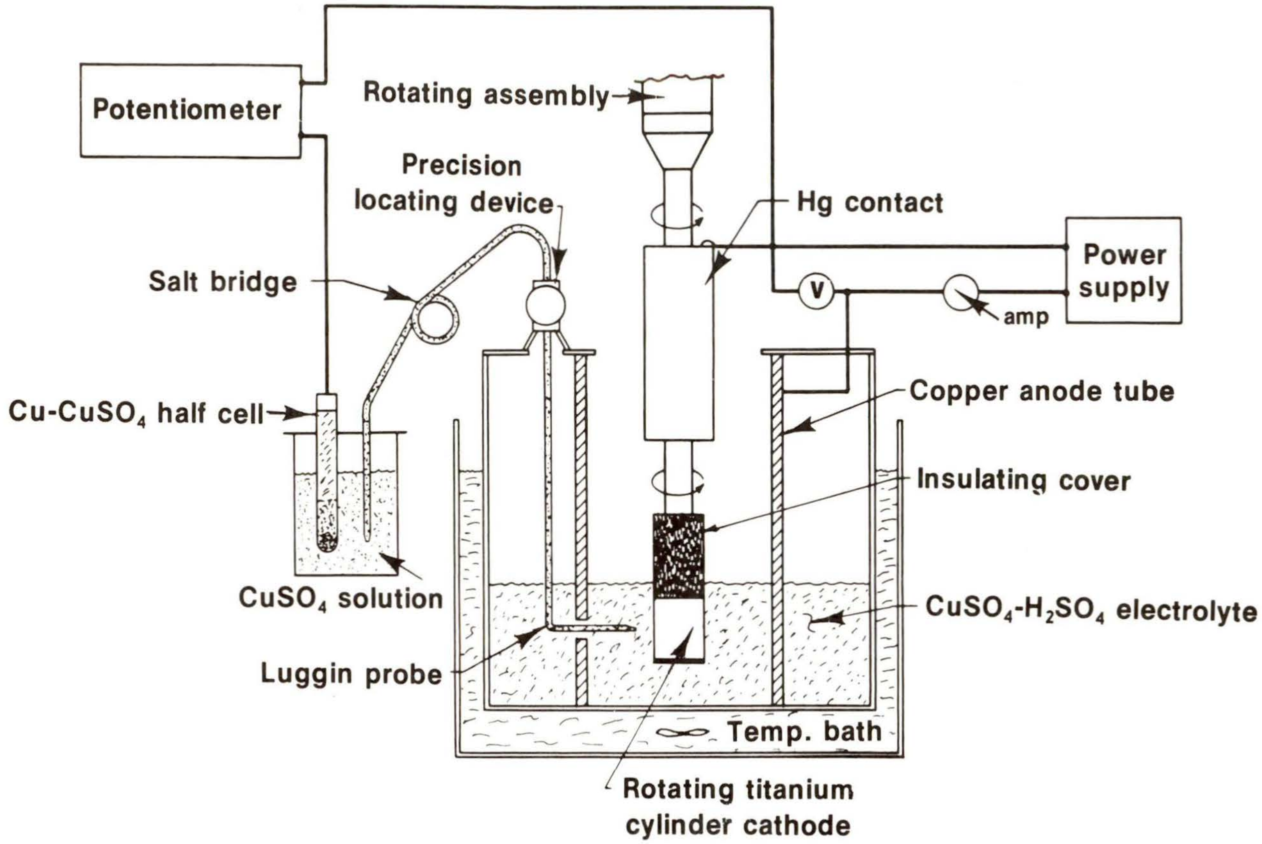

FIGURE 2. - Cell and circuitry used for electrodeposition and dissolution studies on rotating electrodes.

At the conclusion of a test, the deposits were thoroughly washed with water, rinsed in ethanol, and air dried. The surfaces were evaluated for smoothness and the growth of irregularities, such as nodules or dendrites. After stripping the deposits from the titanium cathode, they were weighed to determine the current efficiency. Cross sections of deposits were examined metallographically to determine the grain structure and the presence of voids. The grain size was determined by X-ray diffraction. Emission spectrographic analysis was used to determine the purity of the copper.

Single-Channel Cells

Several single-channel cells were designed and constructed for depositing copper at high current densities and high linear electrolyte flow rates (13). A typical single-channel cell is shown in figure 3. It was constructed of 1-in-thick polyacrylic plastic and was 8 ft long overall with an electrode section 4 in high by 2.25 in wide. The polyacrylic lid was connected to the cell body with stainless steel clamps and was sealed with a Neoprene gasket. The inlet section of each cell contained baffle plates to make the flow more uniform, followed by a tapering venturi entrance section, a rectangular venturi throat that served as the electrolysis chamber, and a tapering venturi exit section. The venturi entrance chamber was used to gradually accelerate and direct the electrolyte into the channel formed by the electrodes. The electrolysis chamber contained a 0.25-in-thick titanium cathode and a

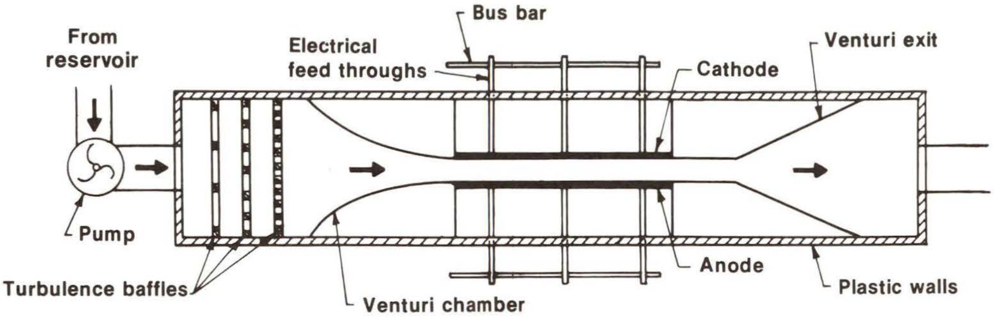

FIGURE 3. - Top view of single-channel electrolytic cell.

≃1.5-in-thick copper anode. The 0.5-in interelectrode spacing formed the channel. In the last section of the cell, the electrolyte was allowed to decelerate before returning to a holding tank.

In the first channel cell, the entrance of the venturi was permanently positioned but later cell designs allowed the venturi channel to be manually adjusted to compensate for the shift of the channel centerline as the anode underwent dissolution and the cathode deposit thickened.

The electrolysis chamber was 36 in long and 4 in high, and the electrodes ranged from this maximum dimension to 11 in long by 2 in high. When the smaller electrodes were used, the full channel dimension was maintained by using plastic filler. The anodes were machined from 1.5-in-thick crude copper anodes obtained from an industrial refinery. The anodes from this source were reported to have the typical composition shown in table 1. The electrodes were machined to a smooth surface. Immediately prior to each test, they were lightly sanded with 240-grit emery paper, washed in water, and air dried. Following each test, copper deposits were stripped from the titanium cathode, washed, dried, weighed, and evaluated according to surface morphology, grain type, grain size, and purity using the same methods as were used for evaluating the deposits produced on the rotating electrodes.

TABLE 1. - Typical composition of industrial electrorefining anode and electrolyte

Component	Anode, wt-pct	Electrolyte, g/1
Copper	99.67	40.5
Oxygen	.0018	0
Sulfur	.0024	0
Tin	.0004	.004
Lead	.0069	.005
Bismuth	.0010	.02
Nickel	.0440	10.4
Antimony	.0021	.7
Iron	.0021	1.3
Tellurium	.0074	0
Arsenic	.0280	1.1
Selenium	.0400	0
Gold	.0042	0
Silver	.0439	.001
Sulfate	0	298.4
Calcium	0	.4

The electrolyte circulation system consisted of a 125-gal-capacity polyethylene reservoir, a 1.5-hp corrosion-resistant pump, and 2-in-diam stainless steel or polyvinyl chloride (PVC) connecting pipe. The electrolyte flow rate was controlled by ball valves at each end of the cell and was measured with a float-type rotameter. An additional cell bypass system permitted the cell to be opened for electrode changes or inspection while still maintaining temperature and electrolyte circulation.

Quartz immersion heaters (up to 7.5 kw) were mounted within the reservoir to thermostatically control the electrolyte at a temperature of 55° C.

The electrolyte used in the channel cell was either a synthetic solution containing $\simeq$36 g/l of copper ion as $CuSO_4$ and $\simeq$200 g/l of free H_2SO_4 or actual industrial electrorefining electrolyte. Typical composition of an industrial electrolyte is shown in table 1. Thiourea was added to the industrial electrolyte at concentrations up to 2.0 mg/l in some experiments to determine the effects of this additive on the crystallographic structure of the deposits.

Direct current to the channel cell was supplied from a low-ripple, constant-current power supply. Electrical contact to the titanium cathode and copper anode was made through 0.25-by 2-in bus bars attached to 0.375-in-diam copper rods threaded into the back surface of the anode and the back or top of the cathode. These connecting rods were sealed in the cell side or top with a standard electroplating lacquer.

Multichannel Cell

The design of the system comprising this cell and related equipment was essentially a scaled-up version of the single-channel system with larger

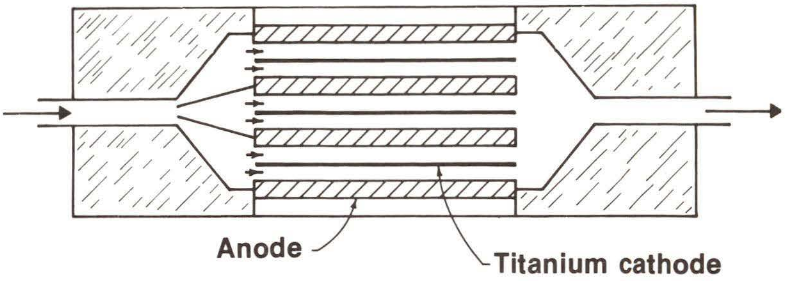

FIGURE 4. - Top view of multichannel cell.

holding tank, pump, valves, and piping. The cell was constructed of 2-in-thick polypropylene and was 9 ft long overall, with an electrode section 4 in deep by 10 in wide. The cell consisted of three sections, the acceleration, electrolysis, and deceleration chambers (figs. 4-5). One-quarter-inch-thick polyacrylic deflectors directed the electrolyte in the acceleration chamber into the channels of the electrolytic chamber. The lid also was made of 2-in-thick polypropylene and was used to support both the cathodes and anodes by copper rods sealed in the top and threaded into the electrodes. The lid, when fully assembled with three cathodes and four anodes, weighed ≃650 lb. The lid assembly, when positioned on the cell, formed an electrolysis chamber with six channels, each 0.5-in wide. Figure 5 shows the

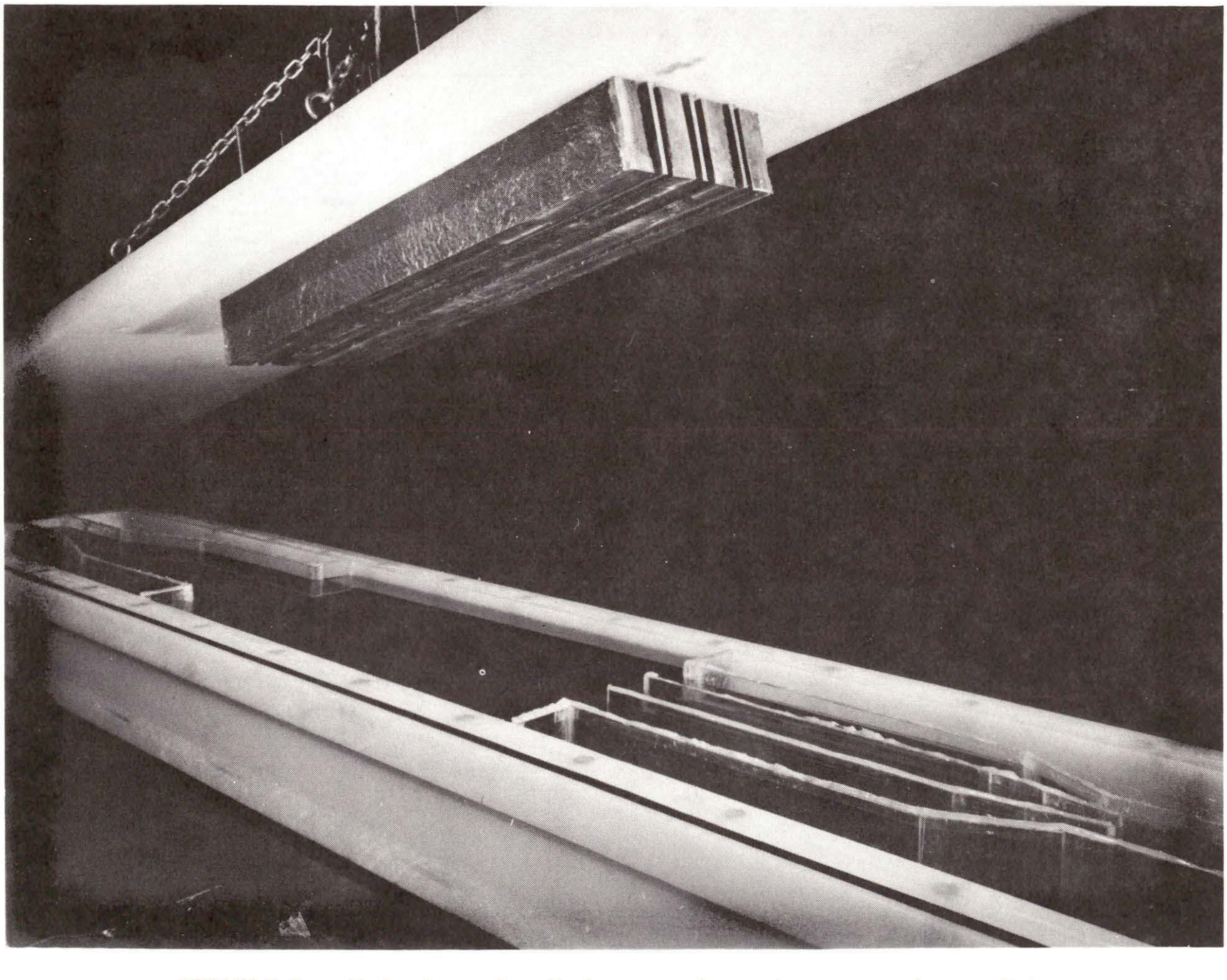

FIGURE 5. - Multichannel cell showing electrodes mounted on cell lid.

lid assembly being lowered into the cell body. A Neoprene gasket and steel clamps were used to seal the lid and body of the cell.

The cathodes and anodes were 34 in long and 4 in high, and were constructed of 0.25-in-thick titanium sheet, and 1.5-in-thick industrial copper anodes. Although initial experiments were conducted with the anodes in their original cast condition, they were milled to a flat surface in later experiments to obtain uniform and identical interelectrode spacing in each channel. Prior to each test the anodes were wire brushed to remove oxide film and residual slag but otherwise remained similar to the original cast industrial material. The cathodes were sanded to a 240-grit finish, then insulated on the edges with electroplating tape to produce separate deposits on each side. The electrodes were given a final washing with water prior to assembly in the cell.

Industrial electrolyte was used exclusively during the operation of the multichannel cell and was of similar composition to that listed in table 1. It was stored in a 220-gal-capacity polyethylene holding tank. A 15-hp, 450-gal/min plastic pump circulated the electrolyte throughout the system. The flow rate of the solution was controlled manually by a 3-in plastic ball valve at the cell entrance and was measured with a magnetic flow meter positioned between the channel cell exit and the holding tank. The circulation loop was constructed of 3-in PVC piping and valves. Before the electrorefining tests, the electrolyte was heated to 50° to 55° C with a quartz-jacketed immersion heater. However, after reaching temperature, a water-cooled stainless steel heat exchanger was needed to dissipate excess heat generated by friction.

Power for the multichannel cell was supplied from a 2,000-A, 15-v silicon rectifier. Electrical contact was made through parallel 0.25-by 0.75-in copper bus bars connected to each electrode through several 0.375-in-diam copper rods. The rods were inserted through leak-tight seals on the top of the lid and threaded directly into the top of the anodes. To make electrical connections to the thinner cathodes, 0.75-in-diam cylinders of copper with inside threads were welded to the top of the titanium sheets and recessed into the lid. The copper-rod feed throughs were then threaded into the cylinders to provide both mechanical support and electrical contact. Figure 6 shows the individual anode and cathode electrodes.

Current to the individual cathodes was measured through shunts connected in series with each cathode. At the termination of a test all deposits were stripped from the titanium surfaces, washed in water, air dried, and weighed. From the individual cathode currents and deposit weights, the current efficiency and distribution were obtained. Purity of the electrorefined copper was determined by emission spectrographic analysis.

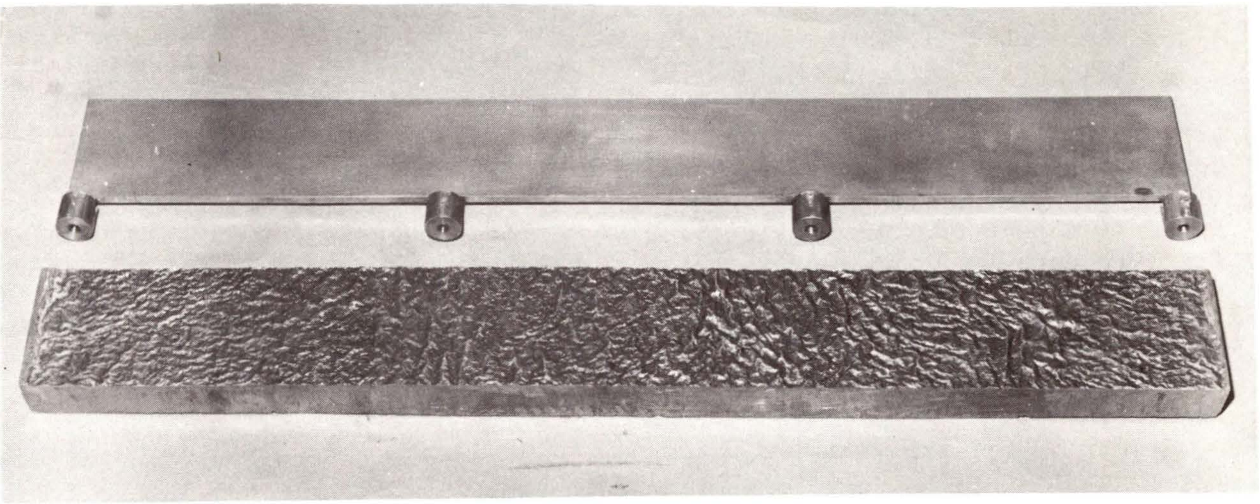

FIGURE 6. - Cathode (top) and anode (bottom) of multichannel cell.

RESULTS

Rotating Electrode Cells

Ring Electrodes

The first series of experiments was conducted using the ring electrodes to determine the effect of current density and rotation rate on the overvoltage for copper deposition and dissolution, and on the morphology of the electrodeposits. Deposition studies were carried out at 110, 288, and 575 rpm, corresponding with tangential velocities at the center of the ring of 20, 53, and 106 ft/min, respectively. For each rotation rate, deposits were made at a number of current densities between 40 and 720 amp/ft^2 from an electrolyte containing 36 g/l of copper ion as $CuSO_4$ and 200 g/l of free sulfuric acid. Figure 7 shows the cathode overvoltage as a function of current density at each rotation rate. As expected, the overvoltage increases with increasing current density at a fixed rotation rate, and decreases with increasing rotation rate for a fixed current density. No sudden increases in overvoltage are observed in these curves showing that, at the high

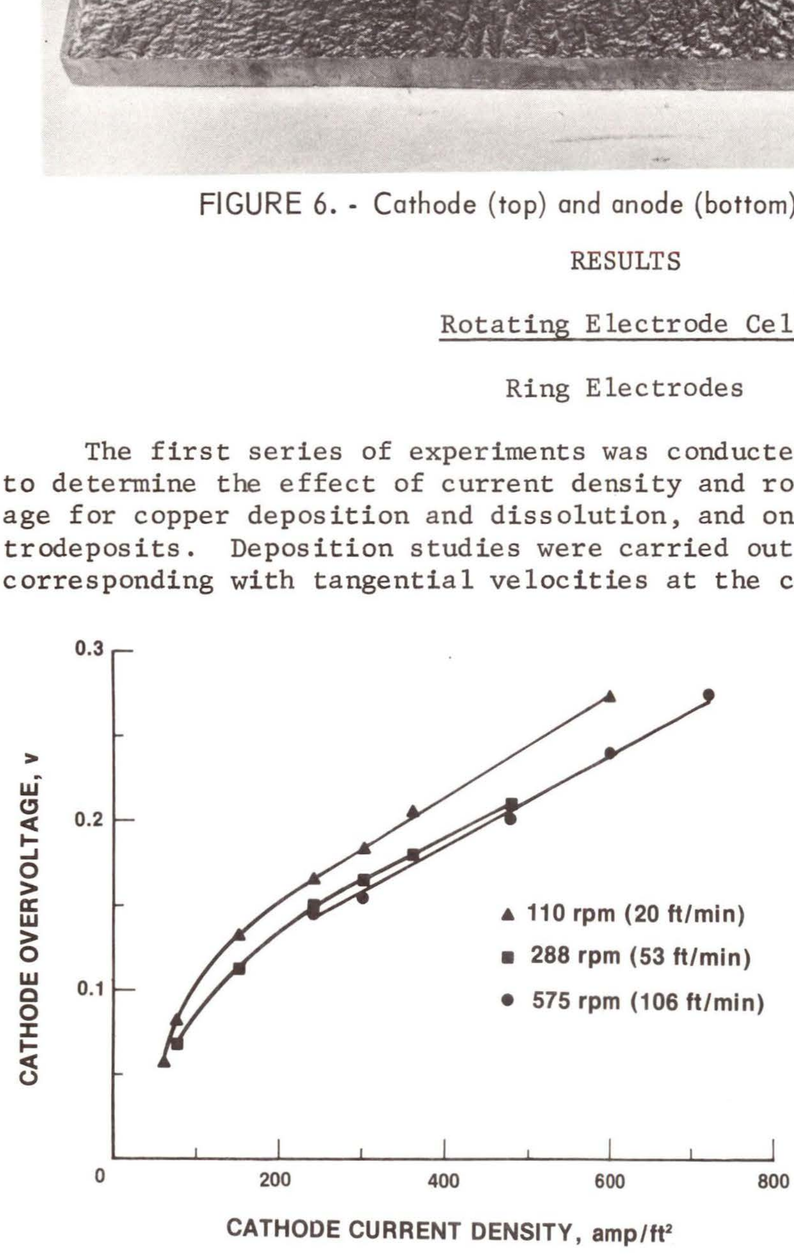

FIGURE 7. - Cathode overvoltage versus current density.

current densities, the limiting mass transport rate for copper ion transport from the bulk electrolyte to the cathode has not been exceeded. For all of these tests the current efficiency for copper deposition was found to be over 99 percent.

Figure 8 shows cross sections of typical deposits produced. It is evident from these photomicrographs that well-consolidated, void-free deposits can be obtained at increasingly higher current densities as the rotation rate is increased. With increasing current density, voids eventually appear in the deposits, although there are no apparent changes in the overvoltage curves or current efficiency that predict void formation. However, a comparison of the overvoltage curves and the photomicrographs indicate that voids begin to appear when the overvoltage exceeds ≃180 mv.

The effect of current density and rotation on the dissolution process was studied using anodes constructed from both commercially refined and crude industrial anode copper. In tests conducted using the pure copper anodes at rotation rates of 110 and 285 rpm and for

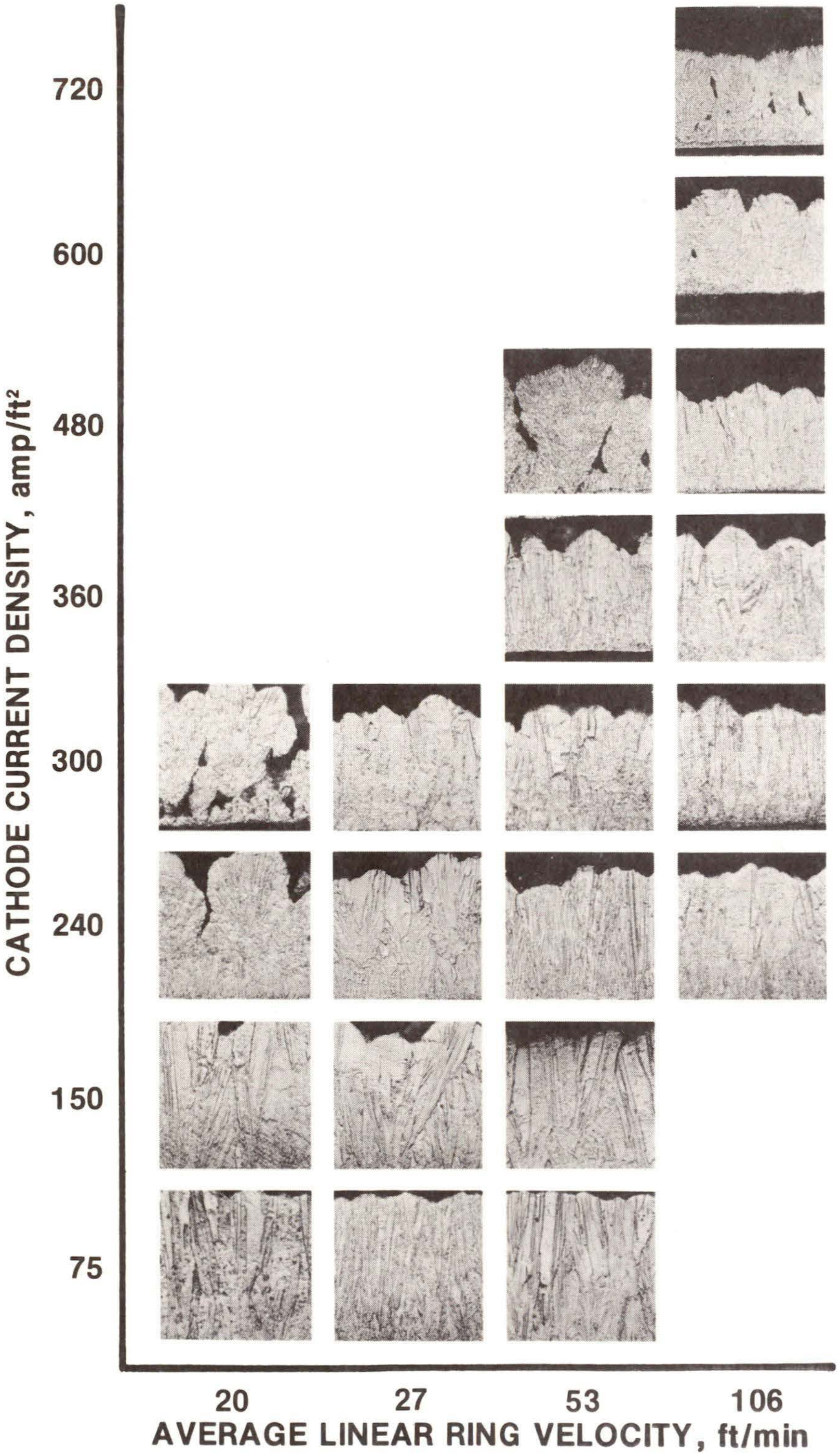

FIGURE 8. - Cross-sectional photomicrographs of copper deposited at various current densities and rotation rates.

current densities in the range 50 to 360 amp/ft^2, the overvoltage was found to be 50 to 60 mv and nearly independent of current density or rotation rate. Visual examination of the anodes after the dissolution tests revealed that the anodes dissolved evenly up to a current density of 240 amp/ft^2. At 300 and 360 amp/ft^2, a spiral dissolution pattern was observed for both rotation rates.

In the case of the crude copper ring anodes, tests were conducted at 288 rpm at current densities of 240, 300, and 360 amp/ft^2. At 240 and 300 amp/ft^2, the dissolution overvoltage was $\approx$120 mv, or about double the value observed for the pure copper. At 360 amp/ft^2, the voltage was irregular, rising, then falling throughout the experiment. After undergoing dissolution, all of the crude copper anodes had a rough surface with pits and voids. The surfaces also were covered with a dark, adherent film which is believed to be associated with insoluble anode impurities.

Cylinder Electrodes

Several series of tests were conducted with the cylindrical cathode to determine the effects of thiourea and copper and sulfate ion concentrations on the structure of the copper deposits. These tests were conducted at a current density of 300 amp/ft^2 using a rotation rate of 478 rpm, which corresponds with a tangential velocity of 125 ft/min at the cylinder surface.

Metallographic examination of deposits produced using a total sulfate ion concentration of 200 g/l while varying the copper ion concentration from 10 to 50 g/l established that well-consolidated, void-free deposits were produced when the copper ion concentration was 30 g/l or greater. Increasing the copper ion concentration above 30 g/l made no noticeable improvement in the deposits, whereas, decreasing the concentration below 30 g/l caused an increase in nodular growths and void formation. Over the copper concentration range of 10 to 50 g/l, the current efficiencies were in excess of 99 percent. The cell voltage increased uniformly from $\approx$0.7 to 0.9 v as the copper ion concentration was increased from 10 to 50 g/l.

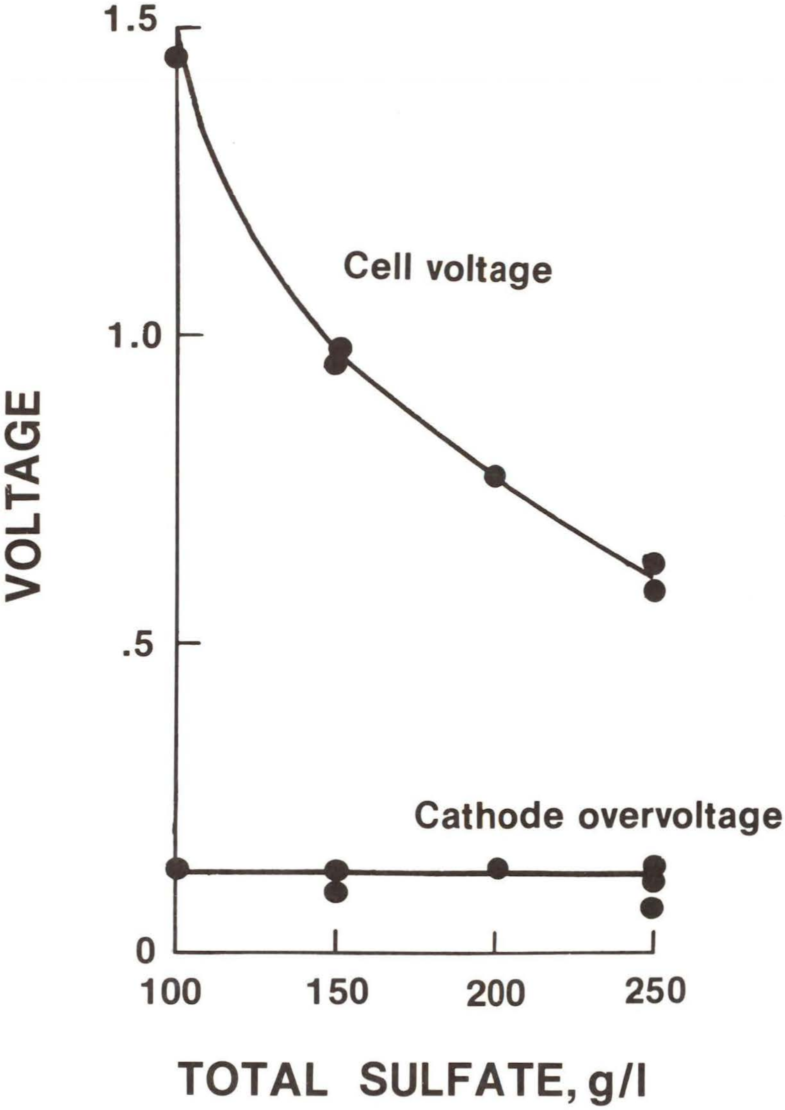

FIGURE 9. - Dependence of the cell voltage and cathode overvoltage on sulfate ion concentration for the cylindrical cathode. Current density 300 amp/ft^2, rotation rate 478 rpm.

Another set of electrodeposits was produced at total sulfate concentrations of 100, 150, 200, and 250 g/l when the copper ion concentration was kept constant at 30 g/l. The total sulfate ion concentration was adjusted with additions of concentrated sulfuric acid. At each of these sulfate ion concentrations, the deposits were well consolidated and void free. Visually, those prepared at the lower sulfate ion concentrations appeared to be slightly more consolidated and dense. However, the cell voltage increased rapidly below a sulfate ion concentration of 150 g/l (fig. 9).

In general, the copper and sulfate ion concentration range of electrolytes that yield acceptable copper deposits at the high current density and flow rate are close to the concentrations used industrially. Typical industrial electrorefining of copper is carried out at copper ion concentrations of 35 to 55 g/l and sulfate ion concentrations of 150 to 250 g/l. With the high flow rate, it may be possible to reduce these concentrations slightly because of the higher mass transport in the electrolyte.

Copper electrodeposition experiments were conducted using the rotating cylinder cathode to determine the concentration of thiourea required to produce acceptable fine-grained copper deposits at high current densities and rotation rates. Cross sections of the 0.032-in-thick deposits were microscopically examined and the grain size was determined by X-ray diffraction. The addition of as little as 0.2 mg/l of thiourea to the electrolyte produced a high degree of grain refinement (fig. 10). Increased amounts of thiourea up to ≈0.5 mg/l continued to improve the grain structure, but amounts beyond 0.5 mg/l had little further effect. When the thiourea concentration reached

NO ADDITIVE **0.2 mg/1 THIOUREA**

FIGURE 10. - Effect of thiourea on the grain structure of electrodeposited copper. Deposition current density 300 amp/ft^2, rotation rate 478 rpm.

8 mg/1, the copper deposits became dark and brittle. The excess thiourea apparently acted as a detrimental impurity. Further illustration of the effect of thiourea on grain refinement is shown in figure 11 which shows the full-width-at-half-maximum (FWHM) of the Bragg X-ray diffraction peak for the (311) face. The FWHM values are inversely proportional to the grain size, and the curve clearly shows the excellent grain refinement achieved at a thiourea concentration of about 0.2 mg/1.

In another series of tests, electrodeposits were repeatedly grown from an electrolyte containing an initial thiourea concentration of 0.2 mg/1. Micrograph and X-ray diffraction examination of successive deposits showed a steady increase in grain size as a function of total electrolysis time. X-ray diffraction studies, figure 12, show that the thiourea is depleted or becomes inactive as a grain refining agent after about 30 hr of electrolysis. The rate of decrease in the effectiveness of thiourea closely approximates the thiourea required per pound of copper deposited in a low-current-density cell as reported by Eichrodt and Schloen (3).

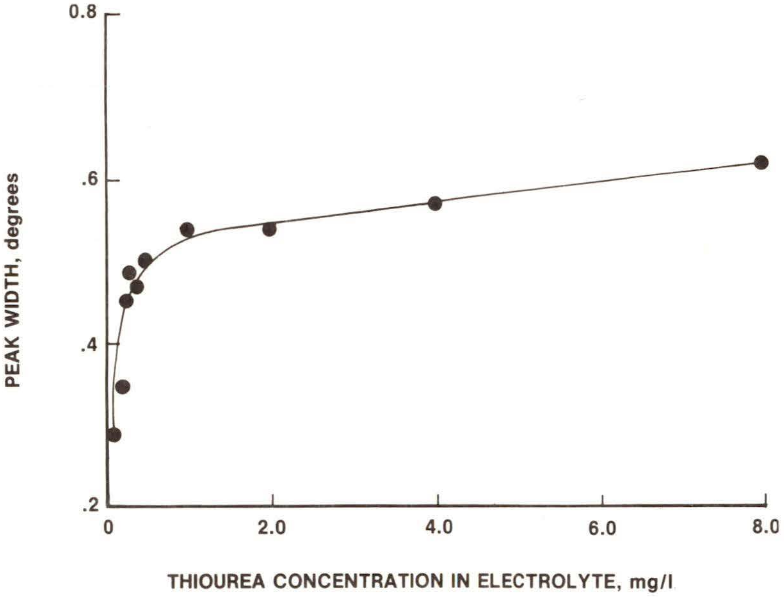

FIGURE 11. - X-ray diffraction peak width for the (311) plane of copper electrodeposited at different thiourea concentrations.

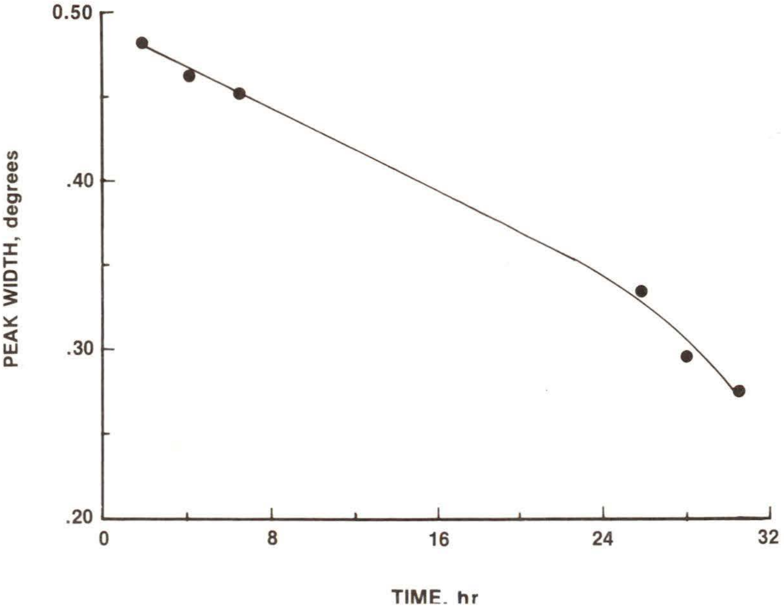

FIGURE 12. - X-ray diffraction peak width for the (311) plane of copper versus time after thiourea addition.

Additional tests in which 0.2 mg/1 of thiourea was added to the electrolyte, which was allowed to stand without electrolysis for various periods of time, showed a similar effect, that is, grain refinement decreased with time. It is apparent from these results that thiourea is not totally consumed by electrolysis, but also undergoes a time-dependent deterioration in the electrolyte. The decomposition, shown in equation 1, may be similar to that which occurs in boiling concentrated H_2SO_4.

$$(NH_2)_2C=S + 2H_2O \rightarrow CO_2 + 2NH_3 + H_2S. \quad (1)$$

The cathode overvoltage also increased noticeably as the thiourea concentration of the electrolyte was increased. As shown in figure 13, the cathode overvoltage increased by ≃100 mv due to the addition of 0.5 mg/1 of thiourea. Although the complete mechanism for the action of thiourea at the deposit surface is not fully understood, it is generally accepted that some physical adsorption is involved that produces finer grains and smoother deposits but at a cost of increased cell voltage.

In industrial electrorefining of copper, thiourea is a widely used agent added to the electrolyte to produce fine-grained, well-consolidated copper deposits. An electrorefining bath that does not contain grain refining additives produces copper electrodeposits that have a coarse, columnar crystalline structure.

These coarse deposits can readily entrap liquid and solid impurities. Furthermore, in the absence of a refining agent, large and irregular dendrites often grow rapidly and electrically short the electrodes, lower the current efficiency, and increase the power consumption. The effects of small concentrations of thiourea on the crystal growth of copper are well known for copper deposited at current densities of 20 to 40 amp/ft^2, but little is known about its effect at higher current densities. Hofer and Hintermann (7) reported that the use of 5 to 10 mg/1 of thiourea produced a small grain size at a current density of 26 amp/ft^2. Fagan (4) reported that the amount of thiourea to cause grain refinement rarely exceeded 3 to 4 mg/1 in the normal deposition range. Shreir and Smith (14) and Lamb and Valentine (11) suggested that the transition from coarse to fine grain occurred at a concentration of 1.5 to 5 mg/1 for current densities between 2 and 40 amp/ft^2. Ibl, Javet, and Stahel (9) were able to improve the quality of the normally very rough or powdery copper produced on a cylinder cathode at the limiting diffusion current by additions of up to 200 mg/1 of thiourea to the electrolyte. Their investigations were conducted in a solution very dilute in copper ions (3 g/1 CU^{2+}, 150 g/1 H_2SO_4) under natural convection conditions. Improvement in deposit quality was attributed to a transport-controlled codeposition of the thiourea and the degree of improvement found to be proportional to the additive concentration in the electrolyte.

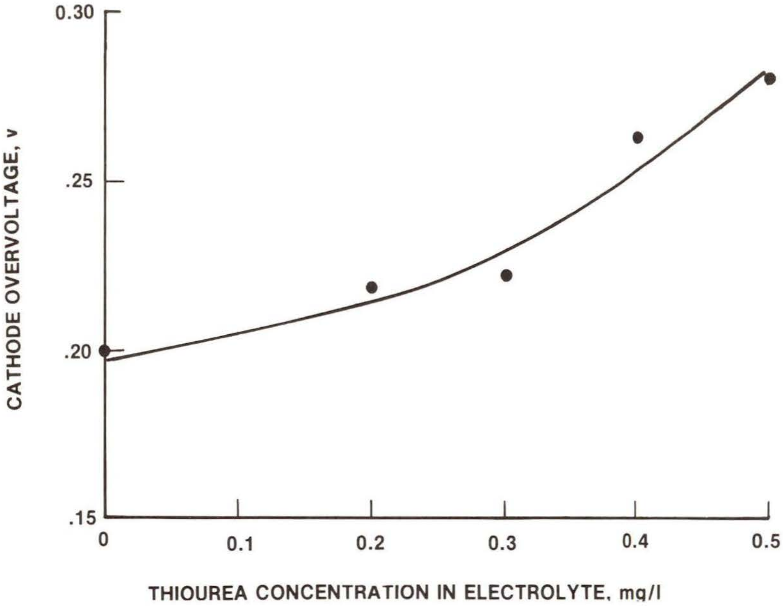

FIGURE 13. - Dependence of cathode overvoltage on thiourea concentration. Current density 300 amp/ft^2, rotation rate 478 rpm.

In the present study, we have found that fine-grained deposits can be obtained at a concentration of 0.2 to 0.5 mg/1 in the rotating electrode cells at a high current density. These concentrations are about 1 order of magnitude less than the concentrations reported by others as being required for grain refinement, supporting studies which show that the rate of transport of thiourea to the cathode may be a significant factor affecting the degree of grain refinement.

Single-Channel Cell

On the basis of the results obtained with the rotating electrodes, which demonstrated that copper can be electrodeposited at current densities much above those used in conventional refineries, the single-channel cell was designed and constructed. Studies in this cell were directed towards (1) confirming that acceptable copper deposits could be produced at high current densities with the more practical geometry; (2) obtaining the range of operating conditions, that is, flow rate, current density, and electrolyte composition that yielded quality copper; (3) producing deposits that were sufficiently thick to be practical; and (4) obtaining engineering data for scale-up to a larger demonstration unit.

Synthetic Electrolyte Tests

Initial tests in the single-channel cell were conducted with the synthetic electrolyte without grain refining agents using both pure and crude copper anodes. A series of deposits was made at a flow rate of 400 ft/min for current densities of 100, 200, and 270 amp/ft^2. Table 2 shows the operational data obtained during these tests. The deposits weighed between 1.3 and 5 lb, corresponding with thicknesses of 0.03 to 0.11 in. A typical deposit is shown in figure 14. Metallographic examination of each deposit showed they were void free with a large-grained crystal structure. As seen in table 2, the current efficiency increases with increasing current density. The polarization voltage obtained by subtracting the calculated electrolyte resistive component from the cell voltage increases with increasing current density, as expected. The polarization voltage for the industrial anode was also about 50 mv higher than for the pure copper anode. This voltage represents both the anode and cathode components and the increase for the crude anode probably arises because of the insoluble constituents in the crude anode.

TABLE 2. - Operational data for single-channel cell

Parameter	Pure copper anode			Industrial copper anode		
Current density................amp/ft^2..	100	200	270	100	200	270
Flow rate.....................ft/min..	400	400	400	400	400	400
Copper concentration[1]..............g/l..	34.8	38.5	32.9	30.8	31.4	31.4
Sulfate concentration[1].............g/l..	253	265.2	230.6	226.8	227.6	225.6
Cell voltage........................v..	0.23	0.43	0.63	0.29	0.50	0.70
Current efficiency...............pct..	94.4	95.6	100	97.6	98.8	99.8
Production rate.............lb/ft^2-hr..	0.246	0.499	0.704	0.255	0.515	0.703
Electrolysis energy.....kwhr/lb copper..	0.093	0.172	0.241	0.134	0.194	0.269
Electrolyte resistivity[2]........ohm-ft..	0.044	0.044	0.047	0.047	0.047	0.047
Resistive voltage drop[2].............v..	0.18	0.37	0.53	0.19	0.39	0.53
Polarization voltage[3]...............v..	0.05	0.06	0.10	0.10	0.11	0.17

[1] Synthetic electrolyte without additives.
[2] Calculated [see reference (10)].
[3] Cell voltage minus resistive voltage.

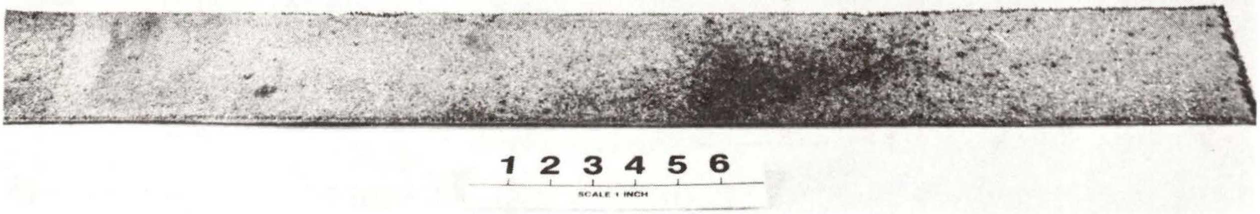

FIGURE 14. - Typical copper cathode refined in the single-channel cell. Current density 200 amp/ft^2, flow rate 400 ft/min.

Tankhouse Electrolyte Tests

Another series of tests in the single-channel cell were conducted using tankhouse electrolyte without additional grain refining agents and crude anodes. Cross-sectional photomicrographs of several of these deposits are shown in figure 15. Void-free deposits are obtained at current densities of 100, 200, and 270 amp/ft^2 for flow rates of ≃125, 300, and 400 ft/min, respectively. Lower flow rates at each of these current densities produced voids in the deposits. The flow rates in the channel cell required for void-free copper are much larger than the equivalent tangential velocities required with rotating electrodes. This is consistent with calculations of the diffusion boundary layer thicknesses (12) for the two geometries. Calculations show that for fully developed flow, the flow velocity in the channel cell must be about 2.2 times larger than the equivalent tangential velocity at the surface of a rotating ring to have the same diffusion layer thickness.

With thiourea, consolidated electrorefined copper could be continuously deposited up to 0.5 in thick using the single-channel cell. Table 3 illustrates the test conditions under which several of these thick copper deposits were prepared. Formation of dendrites, or "trees," caused electrical shorting to occur during a few of these tests. In each case, however, the nucleation of the "tree" was believed to be associated with foreign matter in the electrolyte, imperfections on the electrode surface and/or electrode edge effects rather than any inherent effect of the high current density electrorefining technique. Tapering the anodes at the edges and shielding the top edge of the cathode largely eliminated dendrite shorting, and thick deposits could be obtained consistently at all current densities.

TABLE 3. - Conditions for producing thick deposits of electrorefined copper in a single-channel cell[1]

Cathode current density, amp/ft^2	Electrolyte flow rate, ft/min	Electrolysis time, hr	Deposit thickness, in
80	300	111.0	0.50
100	125	39.5	.22
110	300	54.0	.33
200	300	27.0	.30
200	350	13.0	.15
200	350	32.0	.36
300	400	26.0	.44

[1] Industrial electrolyte; no additional additives; original thiourea presumed decomposed.

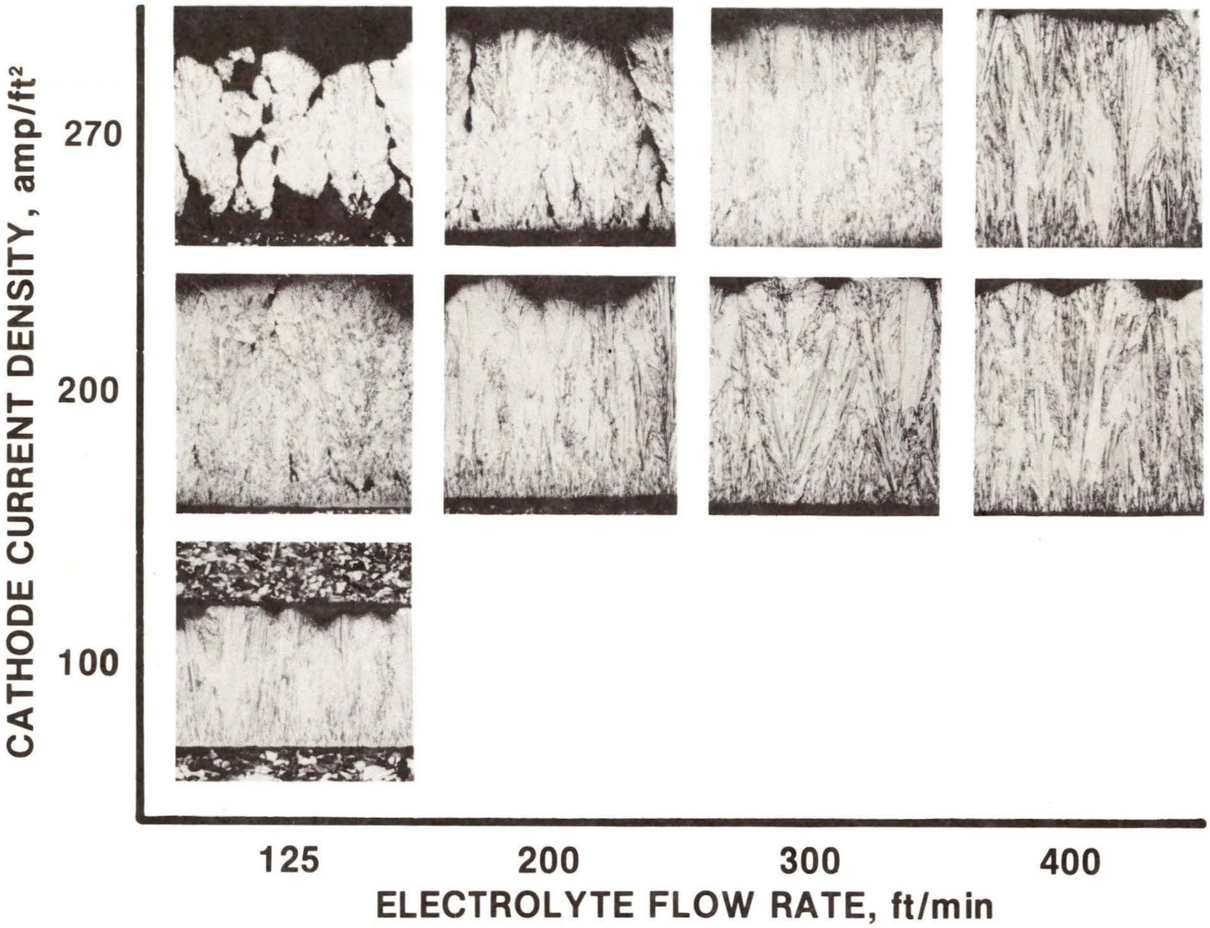

FIGURE 15. - Cross-sectional photomicrographs of copper deposited at various current densities and flow rates in the single-channel cell.

Metallographic examination of the thick deposits made without the addition of thiourea showed large-grained, columnar, consolidated structures. With the addition of thiourea to the electrolyte, substantially smaller grain size could be achieved but only for a limited time before further additions of thiourea were required. Figure 16 shows the initial grain refinement due to the addition of thiourea and the subsequent increase in grain size as the effect of thiourea diminished during 32 hr of continuous electrolysis. Without a periodic analysis for thiourea concentration in the electrolyte, there was no direct evidence of a correlation between a decrease in thiourea concentration and a change in the grain structure of the deposit. However, the fine- and coarse-grained structures obtained at the beginning and end of the test are similar to the structures shown in table 10 for individual deposits formed with and without thiourea.

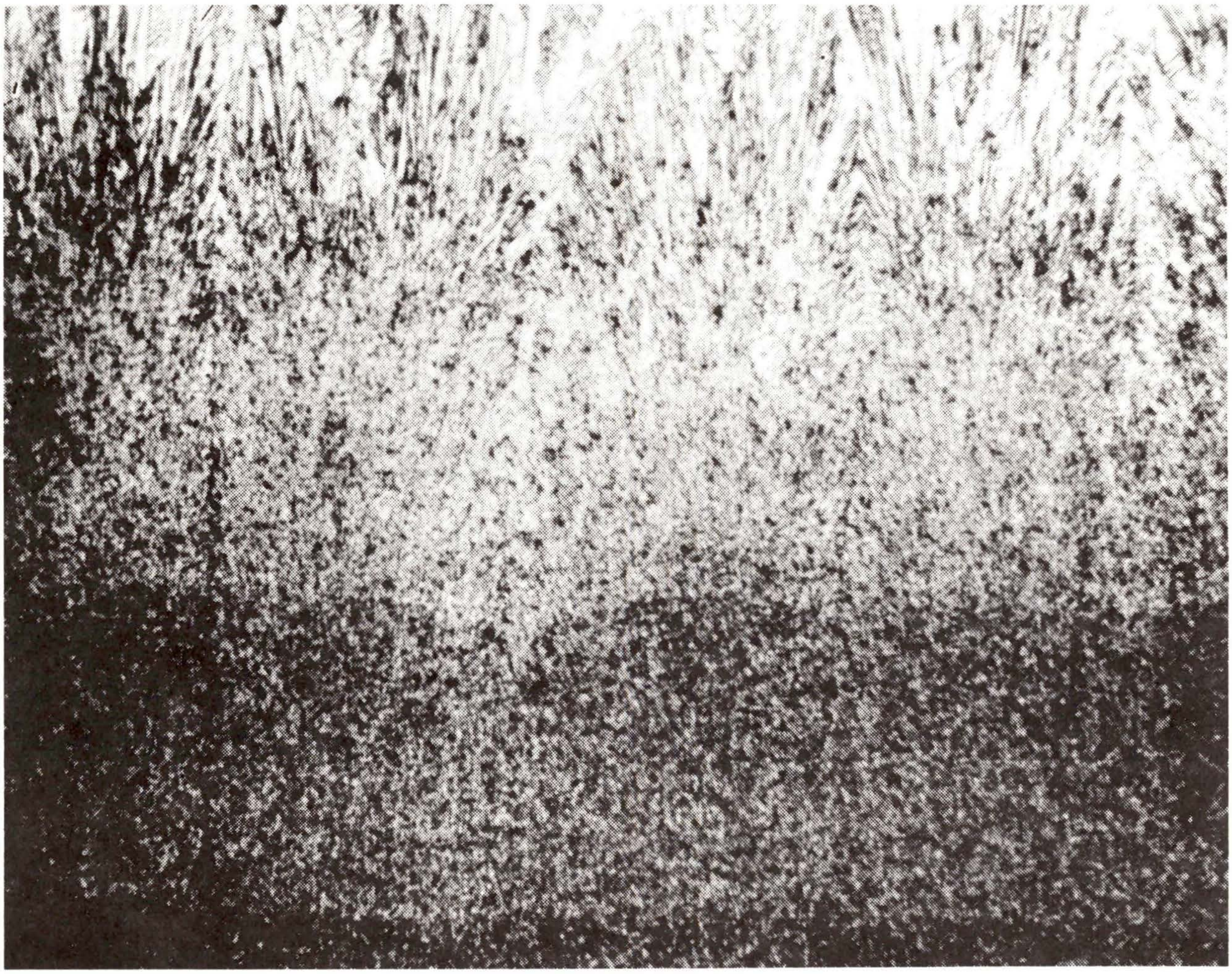

FIGURE 16. - Effect of thiourea depletion on grain size. Initial thiourea concentration 2 mg/l. Bottom of photograph shows fine-grained copper produced in earlier part of electrolysis test. Current density 200 amp/ft^2, flow rate 300 ft/min.

In another series of experiments conducted at 300 amp/ft^2 and 300 ft/min electrolyte flow rate, the effect of thiourea concentrations up to 2 mg/l were investigated. Metallographic examination of these deposits showed significant grain refinement at a thiourea concentration of 0.2 mg/l, and a uniform small-grained structure was achieved at a level of 0.5 mg/l. The FWHM of the X-ray diffraction peak of these deposits revealed that a maximum peak width (minimum grain size) occurred at a thiourea concentration of 0.5 mg/l (fig. 17). When the flow rate was reduced to 200 ft/min, there was a similar grain-refining effect but small voids formed throughout the deposits. At a flow rate of 100 ft/min, the deposits were very poorly consolidated with large voids throughout. Doubling the thiourea concentration at this latter electrolyte flow rate did not consolidate the deposit nor eliminate the voids.

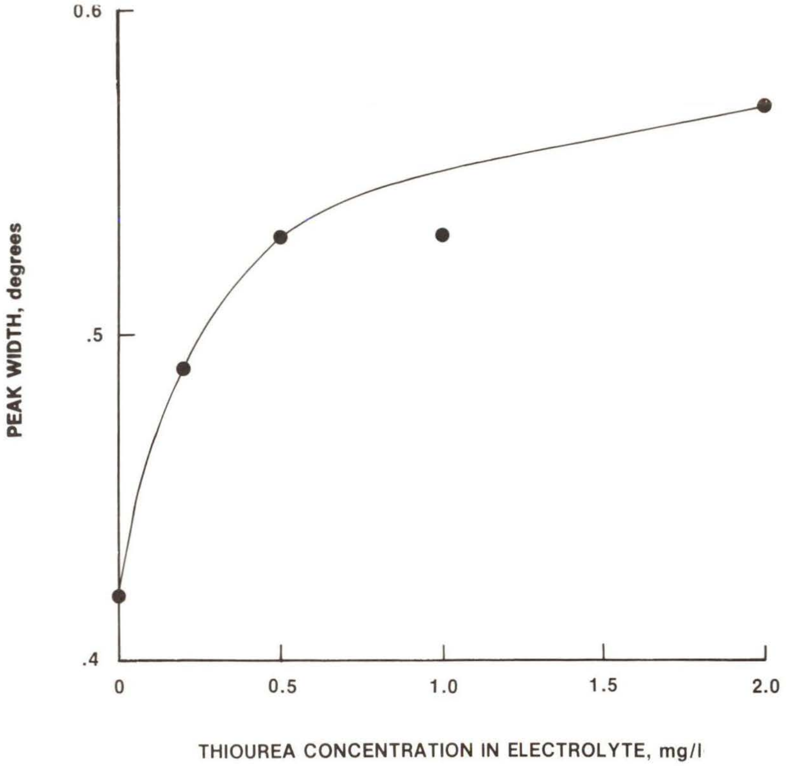

FIGURE 17. - X-ray diffraction peak width for the (311) plane of copper electrodeposited in the single-channel cell at different thiourea concentrations.

Comparison With Industrial Refining Cells

Table 4 shows the operating parameters for two commercial refineries. In general, the electrolysis energy required to electrorefine copper increases with increasing current density. However, at 200 amp/ft^2, the energy required to refine a pound of copper is only 1.5 times the energy required in the industrial cell at 20.3 amp/ft^2. This is a net result of the smaller electrode spacing used in the channel cell to reduce the electrolyte resistivity component and the higher current efficiency obtained at the higher current density. Optical spectroscopic analysis of copper deposits at 100, 200, and 270 amp/ft^2 using the tankhouse electrolyte and industrial anodes are shown in table 5. Iron, nickel, arsenic, gold, lead, and bismuth levels in the deposits are comparable to those obtained in industrial refineries. Consistently high concentrations of silver are observed which increase with increasing current density. The silver may be incorporated into the deposits as physically entrapped insoluble silver selenide and silver telluride from the sludge, or as codeposition of silver dissolved in the electrolyte. During these experiments, no attempts were taken to remove the dissolved silver by the addition of chloride ion as is done in industrial copper refineries. Most of the anode sludge was carried from the cell by the flowing electrolyte and subsequently settled in the holding tank.

TABLE 4. - Typical operational data for industrial refineries

Parameter[1]	Refinery 1	Refinery 2
Current density.............amp/ft^2..	20.0	20.3
Copper concentration............g/l..	47.0	45.0
Sulfate concentration...........g/l..	257.0	249.0
Cell voltage.......................v..	0.22	0.25
Current efficiency..............pct..	85.0	85.0
Production rate..........lb/ft^2-hr..	0.04	0.04
Electrolysis energy........kwhr/lb..	0.11	0.13

[1] The values listed are representative of 2 of the most recently built refineries in the United States.

TABLE 5. - Impurity content of copper deposits from single-channel cell

Current density, amp/ft^2	Electrolyte velocity, ft/min	Impurity level, ppm							
		Fe	Ni	As	Ag	Sb	Au	Pb	Bi
20[1]	0.03	5.0	3.0	2.0	10.0	3.0	0.6	1.0	0.7
100	125	2.0	3.0	2.0	23.0	9.0	1.0	1.0	.5
200	300	2.0	3.0	2.0	31.0	2.0	.5	1.0	.5
270	375	.5	2.0	2.0	40.0	5.0	.5	1.0	.5

[1] Typical impurity levels of industrially refined copper.

Multichannel Cell

Using this scaled-up channel cell design, over 600 hr of electrolysis were conducted at current densities up to 200 amp/ft^2. Operational data were obtained on the production rate, energy consumption, current distribution, and the use of solution additives in producing uniformly thick electrorefined copper deposits. In addition, experiments were conducted also to determine the settling and filtration characteristics of anode sludge in the high mass transport system. These data are compared with industrial cells.

Initial Electrolysis Studies

During the initial high current density tests conducted in the multichannel cell, rapid nodule growth and subsequent electrical shorts frequently limited the deposition periods to relatively short times. Most of the nodule growth occurred at the top of the cell where the electrodes were attached to the cell lid, and the front, back, and bottom edges of the cathodes. The growth at the top was largely eliminated by inserting a 0.25-in polyacrylic spacer between the top of the anode and the lid. This effectively reduced the current density near the top of the cathode and largely eliminated excessive growth at this location. Excessive nodular growths on the other three edges were reduced by tapering the anodes at each edge. Some excessive copper deposition then occurred on the cathodes in the areas where the electrical feed throughs were attached. This was attributed to voltage gradients over the surfaces of the cathodes, such that the deposition voltage was largest near the electrical contact and decreased away from the contact. These gradients also would be expected to be largest during the initial part of the deposition and to decrease with deposit thickness because of the relatively large resistivity of titanium compared with copper. This was overcome by gradually increasing the current density from 70 amp/ft^2 to the final higher value during the first several hours of each initial start-up to build up a more conducting copper deposit before setting the current density at the maximum value. Following these changes, thick electrodeposits could be produced simultaneously on each of the six cathode surfaces for tests lasting up to 56 hrs. However, some difficulty was experienced in producing deposits of the same weight on each of the six individual cathodes. Based on the total weight of the six deposits, there was a 20-percent variation of individual cathode weights in some runs. This variation in weight arises from different current densities in the individual channels and is believed to be caused by slight differences in the interelectrode spacings and in the surface roughness of the cathodes and anodes. These differences produce different mass transport conditions and perhaps different polarization voltages. By carefully maintaining a uniform and equal interelectrode spacing in each channel, the variation in weight and thickness among the cathodes could be improved, but the best run, carried out at 100 amp/ft^2 using a flow of 185 ft/min, still gave a variation of 4 percent (table 6) in the weight of one individual cathode when compared with the weight expected for a perfectly equal current distribution. It is not believed that variations in the weight of the cathodes or the nonuniform current distribution pose a serious problem, except when the specific current distribution and hydrodynamic conditions at one specific location on a cathode favor nodular growth. Most runs were eventually terminated when one electrode pair shorted because of nodular growth bridging. However, before shorting occurred, the deposits were nearly always about 0.3 in thick.

TABLE 6. - Current distribution in multichannel cell

Cathode	Channel number	Deposit thickness, in	Weight of copper, lb	Channel-variation from equal distribution, pct	Cathode-variation from equal distribution, pct
1......	1	0.321	14.11	+3.3	+2.6
	2	.317	13.92	+1.9	
2......	3	.299	13.15	-3.8	-2.3
	4	.309	13.56	-.8	
3......	5	.322	14.14	+3.5	-.3
	6	.299	13.13	-4.0	

Filtration and Settling of Anode Sludge

The recovery of precious metals and other metal values from the anode sludge formed during copper refining is a significant part of the economics of copper refining; up to 6,000 tons of sludge are recovered and processed each year. In conventional cells, the anode sludge settles to the bottom of the cells in the relatively quiescent electrolytes and is collected at the end of each 28-day refining cycle. In the high-flow channel cells, most of the sludge is carried from the cell. A small fraction settles in the cell bottom, 50 to 80 wt-pct settles in the holding tank, and the rest remains suspended in the electrolyte where it is continuously recirculated. The particle size of the sludge ranges from 0.5 to 15 µm with a mean volume distribution of about 3 µm (fig. 18). Several tests were carried out to determine the settling rate and filtration characteristics of the sludge. Settling tests in glass cylinders showed that ≃60 wt-pct of the sludge settles at a rate of 2 ft/min. The remainder has a much slower settling rate, ranging down to 10^{-3} ft/min. These tests were conducted in quiescent solutions with sludge concentrations up to 2.5 percent. In the holding tank, the moderate agitation produced by pumping would decrease the settling rate, and the smaller solid concentrations may increase the settling rate. However, a great deal of settling, 60 to 80 wt-pct, does occur, so that only the finer fraction which has an extremely slow settling rate must be filtered. Initial filtration experiments were conducted using an auxiliary pump that cycled 15.1 l/min of the

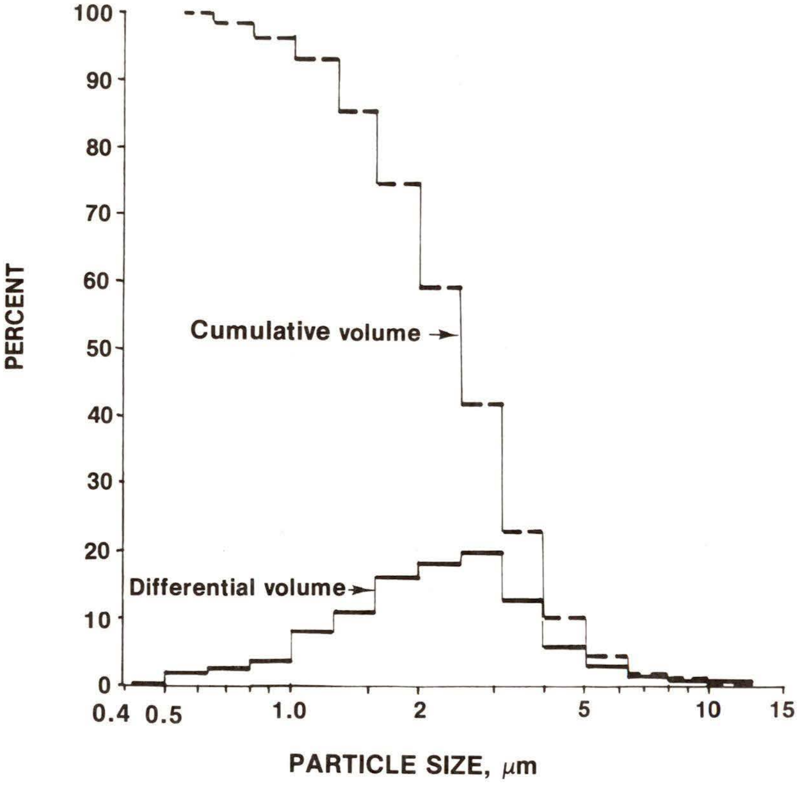

FIGURE 18. - Particle size distribution of the anode sludge in multichannel cell.

holding tank electrolyte through a 10-μm ceramic filter cartridge that effectively removed the fine sludge from the electrolyte. Spectroscopic analysis showed the finer material had the same composition as that which settled in the bottom of the holding tank.

Another filtration test was conducted during electrolysis using the auxiliary pump to circulate the electrolyte through a plate and frame filter with a 1-ft^2 polypropylene cloth. Prior to this 26-hr electrolysis, the electrolyte was filtered for several hours to remove most of the sludge that had been produced in previous experiments. A crude anode that typically yields 7 lb of sludge-forming material per ton of cathode copper then was refined at an average current density of 140 amp/ft^2 (maximum 200 amp/ft^2) at an average flow rate of 310 ft/min (maximum 370 ft/min). The electrolysis period before and during a 4-hr filtration period produced a calculated total of 74.2 grams (54 mg/l) of sludge in the channel cell system. As shown in table 7, approximately 20 grams of sludge that was produced by this electrolysis was recovered during the short period of operation of the filter using an auxiliary flow rate of ≃17 l/min.

TABLE 7. - Recovery of anode sludge

Filtering time, hr	Average electrolyte flow, l/min		Average filter pressure, psi	Total sludge produced, g	Sludge recovered by filtration, g
	Cell	Filter			
4	1,175	17	6	74.2	19.8

Operational Parameters for the Multichannel Cell

Table 8 summarizes the conditions and operating parameters obtained in the multichannel cell at current densities of 70, 100, 135, and 200 amp/ft^2. For the flow rates listed in table 8, the deposits were all essentially void-free with a large-grained crystal structure. The cathode current efficiency was always about 99 percent. It is interesting that the electrolysis energy required to refine copper at 70 amp/ft^2 in the channel cell is about the same as that required in an industrial cell operating at 20 amp/ft^2. As discussed above, for the single-channel cell, this is a net result of the smaller electrode spacing and the increased current efficiency obtainable by operating at higher current densities. The last point may have a great deal of practical significance in refining. Generally, cathode current efficiencies less than 100 percent can be attributed to redissolution of the cathode copper by corrosion reactions or to the coreduction of impurities at the cathode. Both the relative rate of redissolution and coreduction, when referenced to the rate of deposition, should decrease with increasing current density, leading to higher current efficiencies. Considering the increased energy losses due to bus bar and electrolyte resistance against the energy gain obtained through an increase in current efficiency, it appears that there is an optimum current density at which the electrolysis energy required to produce a unit weight of copper is at a minimum. It is also interesting that operation of the multichannel cell at 70 to 135 amp/ft^2 falls very nearly within the operating range of 37 to 121 amp/ft^2 calculated by Ibl (8) to be the optimum current density range for balancing energy utilization against investment cost when electrorefining copper in a flow system.

TABLE 8. - Operational data for multichannel cell

Parameter	Value[1]			
Current density.........................amp/ft^2..	70	100	135	200
Flow rate...............................ft/min..	200	225	250	370
Copper concentration........................g/l..	50.5	50.5	50.8	50.5
Sulfate concentration.......................g/l..	260.0	260.0	280.5	260
Cell voltage..................................v..	0.29	0.45	0.54	0.83
Current efficiency..........................pct..	99	99	99	99
Production rate.....................lb/ft^2-hr..	0.181	0.258	0.348	0.516
Electrolysis energy.....................kwhr/lb..	0.112	0.174	0.209	0.321
Electrolyte resistivity[2]................ohm-ft..	0.054	0.054	0.051	0.054
Resistive voltage drop........................v..	0.16	0.23	0.30	0.45
Polarization voltage[3].......................v..	0.13	0.22	0.24	0.38

[1] Glue and thiourea maintained at approximately 4 and 8 mg/l by periodic additions.

[2] Calculated [see reference (10)].

[3] Cell voltage minus resistive voltage.

Figure 19 shows a set of six cathodes produced at an average current density of 120 amp/ft^2 and a flow rate of 250 ft/min. At the start of this electrorefining test the current density was gradually increased from 70 amp/ft^2 to the final 135 amp/ft^2. The total electrolysis time was 56 hr, and the average deposit thickness was 0.37 in. At the start of this test 4 mg/l of glue, 8 mg/l of thiourea, and 8 mg/l of ammonium lignin sulfonate buffer were added to the electrolyte. Glue was also metered in continuously during the electrolysis period at the rate of 4 mg/l-day. An additional 8 mg/l of thiourea was added after 24 and 48 hr of electrolysis. The cathode deposits are relatively smooth but with striations or grooves running parallel to the electrolyte flow. Many of the striations were continuous along the entire length of the cathodes. Their origin is believed to reflect the

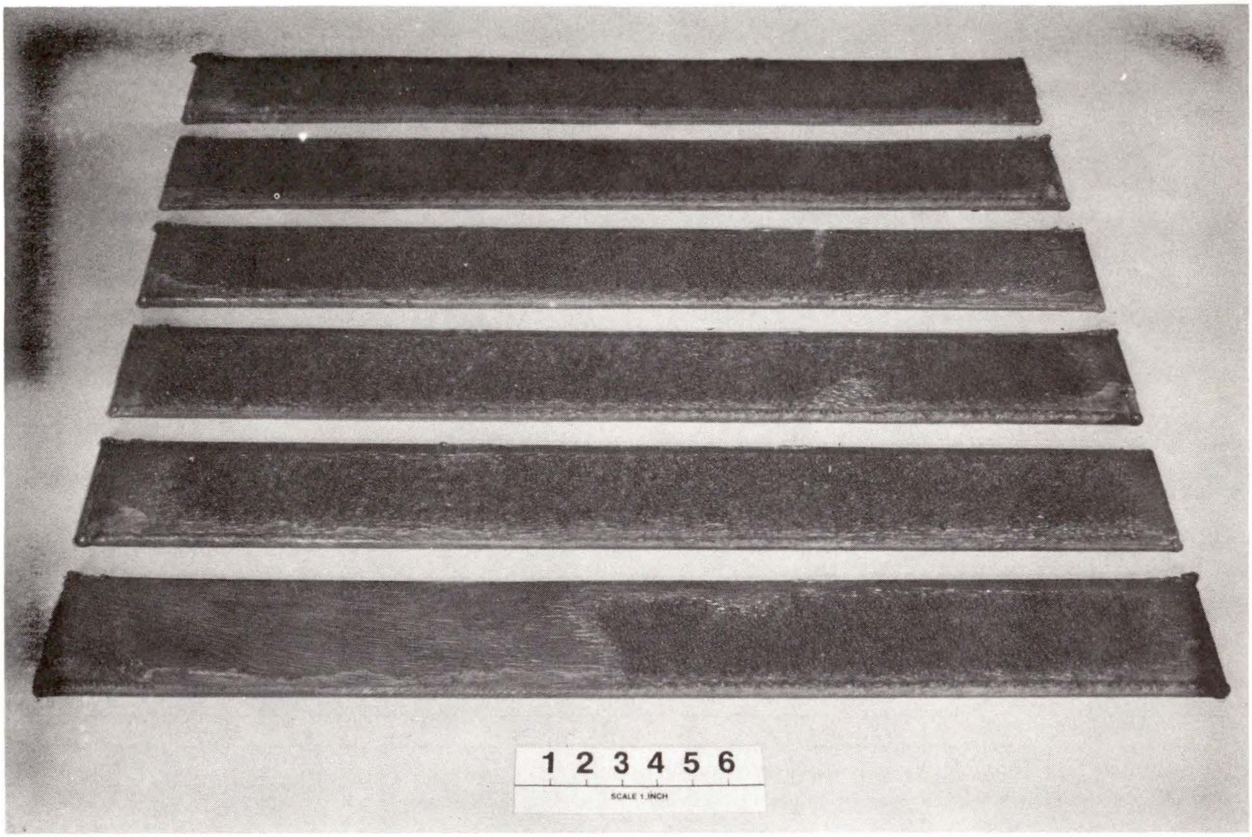

FIGURE 19. - Refined cathodes from multichannel cell. Average current density 120 amp/ft^2, flow rate 250 ft/min.

hydrodynamic flow conditions close to the surface. It appears that either a ridge or groove, once initiated at the front edge of the cathode, propagates along the entire length. Although their origin is not known, similar but spiral grooves were observed at the ring electrodes. At the flow rates used in the multichannel cell, the flow is believed to be turbulent. Considering the geometry, one would expect laminar flow at Reynolds numbers up to 2,000, a laminar-turbulent transition region for Reynolds numbers between 2,000 and 10,000 and turbulent flow above 10,000. At 200 ft/min, the calculated Reynolds number for the channels is 24,000. In addition, the short entrance chamber, pump fluctuations, and uneven electrodes should also increase turbulence. However, for the practical flow rates used here, there still will be laminar flow at and near the surface of the electrode, and this is most likely the reason for the propagating grooves.

Table 9 shows the results of quantitative impurity analysis of the cathodes produced during two separate tests in the multichannel cell. Typical impurities of industrial refined copper are also listed for comparison. Although the high flow rate used in the multichannel cell kept some of the anode sludge in suspension, the concentrations of the trace impurities found in the cathodes were about the same as those found in industrial cathodes except for Ag, Se, and S. On the basis of stoichiometric balance of silver with respect to tellurium and selenium, $\approx$90 percent of the silver may be present as occluded telluride and selenide, and therefore may arise from the anode sludge.

TABLE 9. - Impurity content of copper deposits produced in multichannel cell

Maximum current density, amp/ft^2	Maximum flow rate, ft/min	Impurity level, ppm									
		Fe	Ni	As	Ag	Sb	Pb	Bi	Te	Se	S
20[1]	0.03	5.0	3.0	2.0	10.0	3.0	1.0	0.7	1.0	2.0	20.0
135[2]	250	5.0	2.0	1.0	17.0	1.0	1.0	.3	1.0	7.5	58.0
200[3]	370	2.0	2.0	1.0	14.0	2.0	1.0	.3	.3	3.3	40.0

[1] Typical impurity levels of industrially refined copper.
[2] Deposits shown in figure 19.
[3] Prefiltration of electrolyte and 4-hr filtration during electrolysis.

CONCLUSIONS

Electrorefining tests were carried out on rotating electrodes, in single-channel flow cells, and in a larger multichannel flow cell to assess the technological feasibility of electrorefining copper at current densities much larger than those currently used in copper refineries. It was shown that well-consolidated, void-free copper can be electrorefined at very high current densities using a high flow of electrolyte past the anode-cathode surfaces. The purity of the copper in the flow cells is comparable to commercial electrorefined copper except for the levels of Ag, Se, and S. Tests using thiourea showed that it is an effective grain refining agent at high current densities.

With increasing current density in the channel flow cells, the major contribution to the cell voltage and a major source of energy consumption is the resistive power loss across the electrolyte. This can be reduced by using a closer interelectrode spacing or a higher conductivity electrolyte. Even at the highest current densities, no excessive overvoltages were observed at the anodes or cathodes as long as the flow rate was sufficiently large.

The suspension of a fine fraction of anode sludge in the rapidly flowing electrolyte appeared to affect the cathode quality adversely. Most of the sludge, 60 to 70 wt-pct, had a fast settling rate and settled in the holding tank. Either a larger holding tank with a longer electrolyte retention time or filtration techniques would be required to remove the finer fractions and prevent their inclusion in the cathodes. Although most of this work was carried out with the objective of materially increasing the current density to about 1 order of magnitude over that used commercially, the results suggest that a more moderate optimum current density exists where the energy consumption per unit weight of copper would be at a minimum. Increases in current density above that used in traditional refineries may increase the current efficiency, partly offsetting the increased energy due to resistive losses in the bus bars and the electrolyte.

A preliminary cost-analysis study of the channel cell electrorefining process indicates it is probably not competitive at the present time with traditional refinery cells. However, the advantages associated with more rapid production rates, smaller plant size, and possibly lower capital investments along with the high probability of regulations requiring safer and healthier work environments may make closed channel cell systems competitive in the future.

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