

# Copper recovery and cyanide oxidation by electrowinning from a spent copper-cyanide electroplating electrolyte

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Received 25 April 2007; received in revised form 9 July 2007; accepted 11 July 2007

Available online 17 July 2007

## Abstract

Copper-cyanide bleed streams arise from contaminated baths from industrial electroplating processes due to the buildup of impurities during continuous operation. These streams present an elevated concentration of carbonate, cyanide and copper, constituting a heavy hazard, which has to be treated for cyanide destruction and heavy metals removal, according to the local environmental laws. In the Brazilian Mint, bleed streams are treated with sodium hypochlorite, to destroy cyanide and precipitate copper hydroxide, a solid hazardous waste that has to be disposed properly in a landfill or treated for metal recovery. In this paper, a laboratory-scale electrolytic cell was developed to remove the copper from the bleed stream of the electroplating unit of the Brazilian Mint, permitting its reutilization in the plant and decreasing the amount of sludge to waste. Under favorable conditions copper recoveries around 99.9% were achieved, with an energy consumption of about 11 kWh/kg, after a 5-h electrolysis of a bath containing copper and total cyanide concentrations of 26 and 27 g/L, respectively. Additionally, a substantial reduction of the cyanide concentration was also achieved, decreasing the pollution load and final treatment costs.

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**Keywords:** Wasteprocessing; Copper; Cyanide; Electrowinning; Oxidation

## 1. Introduction

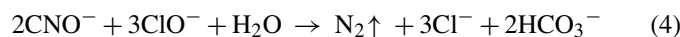
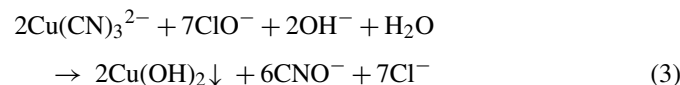
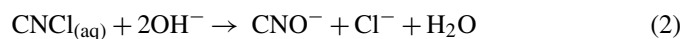
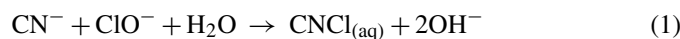
Despite the environmental problems and the toxicity of cyanide, copper electroplating from cyanide solutions presents some advantages over other bath compositions, such as highly adherent, uniform and fine-grained deposits. Consequently, the majority of copper strike-plating baths use cyanide electrolytes [1]. As environmental legislation becomes stricter, waste solutions from these plating baths must be carefully treated to match the local regulatory levels established by the environmental protection agencies. In the case of copper and cyanide, the maximum levels for wastewaters discharge in the environment established by the Brazilian environmental protection agency are 1.0 and 0.2 mg/L, respectively. Copper is not very toxic to animals, but is toxic to algae and plants. Conversely, both hydrogen cyanide and cyanide ions are rapidly acting poisons; a dose of only 60–90 mg is sufficient to kill a human [2].

Electroplating industries generate a large volume of wastewaters, with heavy metals and eventually cyanide, due to metal surface cleaning, rinsing and spent bath bleeding. Rinsing wastewater is the diluted plating bath, while the spent bath bleed is a concentrated solution with an unacceptable level of contaminants. In the case of alkaline electroplating baths, the buildup of potassium carbonate in the electrolyte above concentrations of 120 g/L, due to absorption of carbon dioxide from atmosphere and cyanide oxidation, complicate the control of free cyanide in the bath [3], furthermore, at higher concentrations, it can lead to the formation of rough deposits and increase energy consumption. At the Brazilian Mint, the maximum allowed potassium carbonate concentration is 350 g/L. This limit is kept by continuous bleeding and reposition of the plating bath. These streams are usually treated by conventional hydroxide precipitation [4]; however, metal-cyanide streams require additional chemicals to destroy the cyanide along with metal precipitation. In the Brazilian Mint the production of one and five cents coins involves the electroplating of copper on mild steel disks in a copper-cyanide bath and all the wastewaters containing cyanide from the plating process are mixed and treated by the alkaline chlorination [2,5],

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according to reactions (1)–(4):

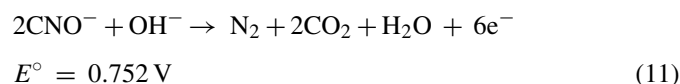
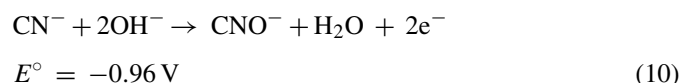


In the alkaline chlorination pH and redox potential must be carefully controlled to avoid undesirable reactions, and the final product is a copper hydroxide precipitate and salt water. The copper hydroxide sludge constitutes a solid hazardous waste (code F006) that has to be disposed properly in a landfill or treated for metal recovery.

Hazardous waste management established that in descending order of desirability the following measures related to hazardous waste should be accomplished [2]: (i) do not produce it; (ii) produce only minimum quantities; (iii) recycle it; (iv) treat it, to make it nonhazardous; (v) if it cannot be rendered nonhazardous, dispose of it in a safe manner; (vi) once it is disposed, monitor it for leaching and other adverse effects.

The concentration of wastes and particularly the concentration of wastewaters is a key factor to recover metal values for reuse or selling. A waste that has been concentrated or at least never diluted is often easier and more economical to process than those dispersed in a large quantity of water. Consequently, the different types of electroplating wastewaters such as bleeding and rinsing streams should not be mixed.

Considering the measures exposed above, electrolytic treatment comes out with an alternative process to treat wastewaters without producing, or producing minimum quantities of sludge [6], permitting the recovery of copper along with the oxidation of most of the cyanide in solution without using a considerable amount of toxic chemicals. The main cathodic and anodic reactions in an electrolytic cell for a copper-cyanide stream can be represented by reactions (5)–(8) and (9) and (10), respectively. The predominance of cathodic reactions (5)–(7) depends on the relative cyanide ion and copper concentrations. For lower  $[\text{CN}^-]/[\text{Cu}^+]$  ratios reactions (5) and (6) predominate, while for a higher ratio (greater than 4), reactions (6) and (7) predominate. Hydrogen evolution (reaction (8)) occurs throughout the electrolysis and is major responsible for the decrease in current efficiency, especially when copper concentration is low. On the anodic side, the main reactions are oxygen evolution and cyanide ion oxidation to cyanate, according to reactions (9) and (10), respectively. Cyanate can be oxidized to carbon dioxide and nitrogen according to reaction (11). Although the hydrolysis of cyanate to ammonium and bicarbonate ions (reaction (12)) is more favorable for pH lower than 7 [5], the local conditions at the vicinity of the anode, due to the consumption of  $\text{OH}^-$  ions through reaction (9), can provide this condition.



The use of electrolytic processes as an alternative for cyanide oxidation with simultaneous copper and precious metals recovery from diluted solutions has been investigated by a number of researches [7–9]. These researches used high surface area electrodes, as reticulated vitreous carbon or carbon felt for the removal of metals from solutions with concentrations lower than 1 g/L of copper or in the range of 5–30 mg/L for silver and gold. In all the cases a current efficiency drop with the metal recovery increase was observed. Lu et al. [7] obtained a copper recovery of 40% with a current efficiency ranging from 50 to 80%. Stavart et al. [8], after a 15-min electrolysis achieved efficiencies from 6 to 12% for a recovery of 90% of the gold present in the effluent, besides a substantial reduction in its free cyanide content.

Nehl et al. [10] investigated the selective electrowinning of gold and silver from copper-bearing cyanide solutions using square wave and pulsed voltages with different electrodes materials. The best separation of silver and gold from copper was achieved with steel wool cathode and square wave electrowinning at 70 °C, by applying 2.5 V during the duty cycle, 0.0 V the rest of the period, a duty cycle of 10–30%, and a period of 0.1–1.0 s, when silver concentration decreased from 34 to 0.1 mg/L, gold concentrations decreased from 54 to 0.2 mg/L and copper concentration remained almost constant at 560 mg/L. The charge used in each experiment was 0.042 A h/90 mL of electrolyte, which was provided by an operating mine. The authors attributed the selectivity to the faster redissolution of copper in the cyanide solution during the low voltage portion of the square wave.

Felix-Navarro et al. [11] studied the simultaneous cyanide destruction and copper recovery in a continuous flow electrochemical reactor with two graphite cathodes and a reticulated vitreous carbon anode. Under the best experimental conditions, the total cyanide concentration was reduced from 590 mg/L to less than 2 mg/L while copper concentration dropped from 300 mg/L to about 4 mg/L. The specific energy consumption for 75% destruction of cyanide depended on electrolyte composition and varied from 12.5 to 3.6 kWh/kg, for a cell potential of 5.0 V. The lower energy consumption was achieved when sodium chloride was added to the electrolyte, which enhanced cyanide

destruction in solution through its oxidation with the hypochlorite generated on the anode. It was also observed that as the flow rate increased the rate of total cyanide destruction increased as well because the mass-transfer rate was higher between the electrode surface and the bulk of the solution as the flow rate was increased.

Lu et al. [12] investigated the anodic behavior of copper-cyanide solutions with a graphite rotating disc electrode and verified that copper had a significant catalytic effect on cyanide oxidation. They proposed that in the low potentials region (0–0.4 V versus SCE), cuprous cyanide was oxidized to cupric cyanide complexes which produced cyanogen, which in turn reacted with hydroxide to form cyanate. In the potential region of 0.4–0.6 V copper cyanide was oxidized to copper oxide and cyanate. For potentials higher than 0.6 V, it was suggested that oxygen evolution was dominant. The potential for the precipitation of copper oxide was dependent on the mole ratio of cyanide to copper and temperature. The higher the mole ratio of cyanide to copper, the higher the potential for the precipitation of copper oxide. They also verified that the electrochemical kinetic behavior was dependent on the CN:Cu mole ratio, pH and total cyanide concentration. Under the conditions tested they observed a decrease on the Tafel slope with decreasing hydroxide concentration.

Szpyrkowicz et al. [13] characterized the catalytic films formed on stainless steel anodes employed for the electrochemical treatment of cuprocyanide wastewaters. They identified the presence of cuprous and cupric oxides, and cupric hydroxide in the anodic film obtained after a constant current density electrolysis at 2.3 A/dm<sup>2</sup> for 15 min of a solution containing 3.5 g/L of KCN plus 2.14 g/L of CuCN. They also verified that the nature of the catalytic film depended on the hydrodynamic conditions in the electrochemical reactor.

Although porous electrodes can be efficient for the treatment of diluted solutions, for the concentrate solutions treatment the rapid pores plugging, due to intensive metal deposition, arise as problem to be overcome. In this case, other electrode type should be employed [14].

In the case of more concentrated solutions, as those of the bleeding streams of electrorefining operations, the cupric ions are usually recovered on plate cathodes in two or three stages, from acidic sulfate solutions containing 45 g/L of copper up to concentrations of 200 mg/L [15,16]. However, when copper concentration drops below 15 g/L the cathodes may require re-smelting or re-refining. Agrawal et al. [17] used the copper bleed solution generated from an Indian copper smelter to produce pure copper powder by electrolysis. Copper recoveries of 95% were achieved at a current density of 700 A/m<sup>2</sup>, with current efficiencies of 88% and energy consumption in the range of 2.3–3.8 kWh/kg.

The objective of this paper is evaluating the possibility of recovery the copper and, at the same time, as a secondary goal, oxidizing the cyanide from an industrial electroplating bleed stream, in order to recycle or selling the electrolytic copper and reduce the amount of sodium hypochlorite and other chemicals used for cyanide destruction and copper precipitation.

Table 1  
Composition of copper electroplating cell bleed stream

Cu(I) (g/L)	KOH (g/L)	KCN (g/L)	K <sub>2</sub> CO <sub>3</sub> (g/L)	Organic additives % (w/v)
26	13	12	350	2.5

## 2. Experimental

### 2.1. Voltammetric tests

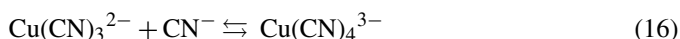
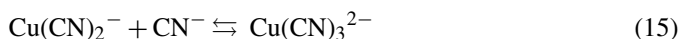
An EG&G PAR model 273A potentiostat/galvanostat connected to a microcomputer with the M270 software was used for the voltammetric tests. The cell was a 600 cm<sup>3</sup> glass beaker with compartments separated by a glass frit for the working and counter electrodes. The working electrode was a stainless steel rotating disc ( $\phi = 1.1$  cm), polished to a mirror finishing; a platinum wire spiral was the counter electrode and a saturated calomel (SCE,  $E^\circ = 0.244$  V versus SHE, Standard Hydrogen Electrode), in a Luggin probe, the reference. The electrolyte was prepared from analytical grade CuCN, KCN, KOH, K<sub>2</sub>CO<sub>3</sub> and a commercial organic brightening additive, simulating the electroplating cells bleed stream whose composition is shown in Table 1. The copper was added as CuCN, with an excess of KCN in order to produce K<sub>2</sub>Cu(CN)<sub>3</sub>. Prior to each test, the electrolyte was deaerated by nitrogen bubbling for at least 2 h, to avoid the influence of dissolved oxygen. The experiments were carried out at 25 and 50 °C.

### 2.2. Electrowinning tests

The electrolytic removal of copper from a synthetic effluent was carried out in a 500 mL acrylic cell with five anodes and four cathodes. The anodes were titanium grid covered with iridium and tantalum oxides with an area of 88 cm<sup>2</sup> each. The cathodes were AISI 304 stainless steel plates with an area of 74 cm<sup>2</sup> or folded stainless steel mesh, rendering a surface area of 477 cm<sup>2</sup> per cathode. One liter of solution was continuously circulated from a reservoir on a hot plate to the cell by a peristaltic pump. Copper concentration was monitored by atomic absorption spectrophotometry, while total cyanide and free cyanide were measured by UV–vis spectrophotometry and potentiometric titration, respectively.

## 3. Copper-cyanide equilibrium calculation

The equilibrium of cuprous ions in alkaline cyanide solutions can be represented by the reactions (13)–(16), which are associated with their respective formation constants  $\beta_i$ .



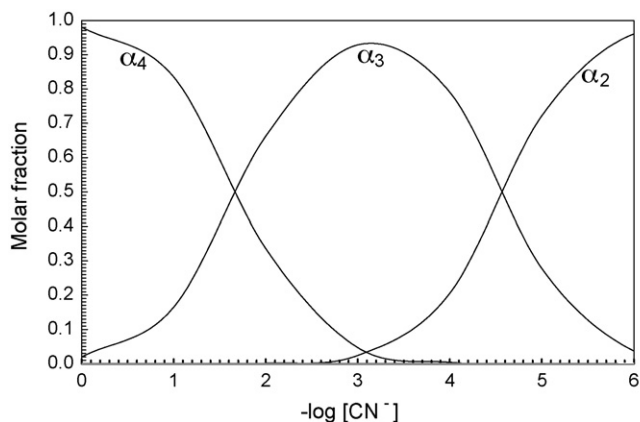


Fig. 1. Distribution diagram of cuprous-cyanide ions as function of free cyanide concentration.

Based on the formation constants [18] and considering that  $\text{CuCN}$  can only exist as a solid phase, due its very low solubility, for a copper-cyanide alkaline solution with an excess of free cyanide ( $[\text{CN}^-]/[\text{Cu(I)}]$  molar ratio higher than 2), a distribution diagram as function of logarithmic molar concentration of cyanide ion can be plotted, as shown in Fig. 1, where  $\alpha_2$ ,  $\alpha_3$  and  $\alpha_4$  correspond to the molar fractions of the complexes  $\text{Cu}(\text{CN})_2^-$ ,  $\text{Cu}(\text{CN})_3^{2-}$  and  $\text{Cu}(\text{CN})_4^{3-}$ , respectively. Although the thermodynamic data ( $\beta_2 = 1.84 \times 10^{15}$ ,  $\beta_3 = 7.16 \times 10^{19}$  and  $\beta_4 = 3.59 \times 10^{21}$ ) were established for diluted solutions (zero ionic strength), the diagram provides a reasonable approach for the concentration of the copper complexes. It can be observed that for cyanide ion concentrations higher than 0.001 M only a very small amount of  $\text{Cu}(\text{CN})_2^-$  is present in solution, consequently,  $\text{Cu}(\text{CN})_3^{2-}$  and  $\text{Cu}(\text{CN})_4^{3-}$  coexist in higher concentrations. These species demand very high negative potentials to be reduced, according to reactions (6) and (7).

## 4. Results and discussion

### 4.1. Voltammetric tests

A cyclic voltammogram of a solution containing 13 g/L of KOH, 12 g/L of KCN, 350 g/L of  $\text{K}_2\text{CO}_3$  and 26 g/L of copper with a stainless rotating disc electrode is shown in Fig. 2. The presence of two crossover potentials is clearly observed,

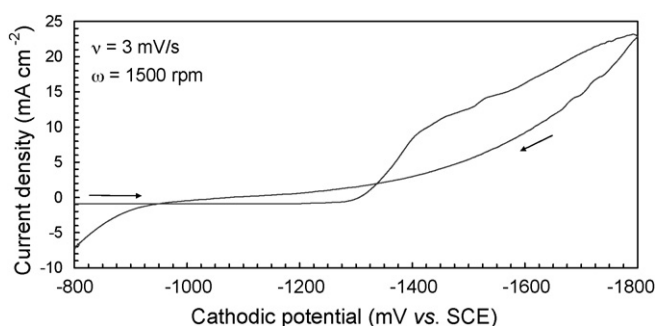


Fig. 2. Cyclic voltammogram of a solution containing 13 g/L of KOH, 12 g/L of KCN, 350 g/L of  $\text{K}_2\text{CO}_3$  and 26 g/L of copper.  $\omega$ : rotation speed;  $v$ : potential scan rate.

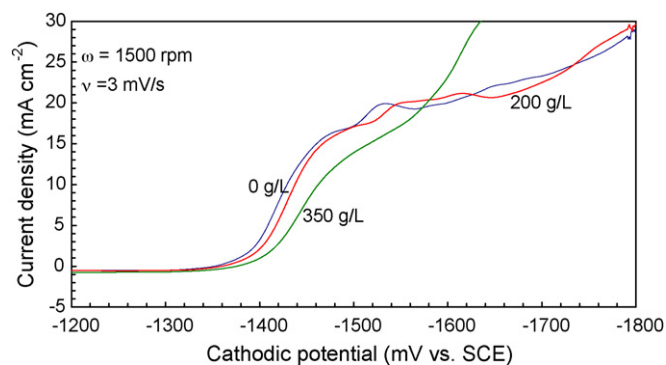


Fig. 3. Influence of potassium carbonate concentration on the linear sweep voltammograms of a solution containing 13 g/L of KOH, 12 g/L of KCN, 350 g/L of  $\text{K}_2\text{CO}_3$  and 26 g/L of copper, at 25 °C.

where the first one, at  $-1330$  mV, can be attributed to presence of both  $\text{Cu}(\text{CN})_3^{2-}$  and  $\text{Cu}(\text{CN})_4^{3-}$ , since their equilibrium potentials under the conditions of the experiment are very close, being, respectively  $-1384$  and  $-1394$  mV versus SCE. This observation indicates that these species are reduced on the cathode almost simultaneously. The second crossover potential, at  $-940$  mV can be attributed to the presence of a small amount of  $\text{Cu}(\text{CN})_2^-$ , around  $4 \times 10^{-6}$  M, according to the distribution diagram shown in Fig. 1, rendering an equilibrium potential according to Nernst equation of about  $-921$  mV versus SCE. To the purpose of copper removal from the waste solution under test, the  $\text{Cu}(\text{CN})_4^{3-}$  and  $\text{Cu}(\text{CN})_3^{2-}$  are more important since they predominate in the system. The consideration of  $\text{Cu}(\text{CN})_2^-$  will be important if the free cyanide ion concentration drops considerably.

The influence of potassium carbonate concentration on the linear sweep voltammograms of a solution containing 13 g/L of KOH, 12 g/L of KCN, 350 g/L of  $\text{K}_2\text{CO}_3$  and 26 g/L of copper, at 25 °C, is presented in Fig. 3. It can be observed that when carbonate concentration increases the curves are displaced in a negative direction, elevating the energy consumption during electrolysis. Furthermore, it is well known [3] that excessive amount of carbonate causes roughening of the deposited copper and reduces the plating speed. Consequently, when the carbonate concentration builds up beyond certain limits, part of the solution must be bled from the cell.

The influence of working electrode rotating speed on the cathodic linear sweep voltammograms for copper deposition on a stainless steel disc is presented in Fig. 4. It can be observed that copper deposition begins around  $-1250$  mV and the effect of increasing electrode rotating speed becomes more evident in a potential range from  $-1400$  to  $-1500$  mV versus SCE, which corresponds to a limiting current density plateau associated to the reduction of both  $\text{Cu}(\text{CN})_3^{2-}$  and  $\text{Cu}(\text{CN})_4^{3-}$ , whose deposition potentials are very close to each other [19]. These curves indicate that an increase in the electrode rotating speed will increase the copper deposition rate due to a thinning of the diffusion layer, which leads to an increase on the rate of mass transport by diffusion. This effect is more evident in the potential range of  $-1400$  to  $-1500$  mV. For potentials more negative than  $-1550$  mV an intensive hydrogen evolution,

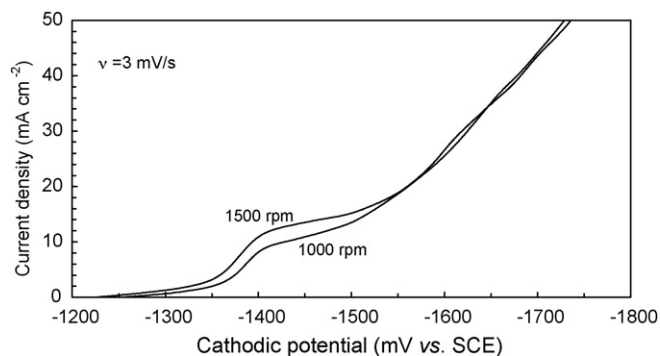


Fig. 4. Influence of electrode rotating speed on the cathodic linear sweep voltammograms of a solution containing 13 g/L of KOH, 12 g/L of KCN, 350 g/L of  $K_2CO_3$  and 26 g/L of copper, at 25 °C.

according to reaction (4), will decrease the current efficiency of copper deposition.

The influence of temperature on the cathodic linear sweep voltammograms for copper deposition is presented in Fig. 5. It can be observed that a temperature increase from 25 to 50 °C depolarizes the cathodic reactions, causing a dramatic increase in the copper deposition rate and in the potential for initial copper deposition, which are around  $-340$  and  $-1200$  mV, at 25 and 50 °C, respectively. An increase in limiting current density of about 30% was observed at  $-500$  mV. The effect of temperature elevation seems to be more evident to copper deposition than increasing electrode rotating speed; however, temperatures higher than 60 °C should be avoided to prevent water losses by evaporation. Then, the copper electrowinning tests were carried out at 50 °C with a moderate solution flow rate.

#### 4.2. Copper recovery and cyanide oxidation

The influence of cathodic current density and cathode type (plate or mesh) on the copper recovery from 1 L of synthetic solution containing 13 g/L of KOH, 12 g/L of KCN, 350 g/L of  $K_2CO_3$ , 26 g/L of copper and 2.5% (w/v) of an organic brightening additive after a 5-h electrolysis at 50 °C with a solution flow rate of 0.27 L/min is presented in Table 2. Additional results for a real industrial electroplating bleed solution with two different flow rates are also presented in Table 2. It can be observed that current intensity plays an important role on copper recovery. For

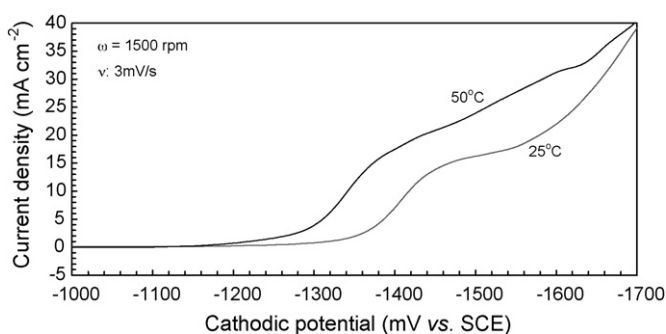


Fig. 5. Influence of temperature on the cathodic linear sweep voltammograms of a solution containing 13 g/L of KOH, 12 g/L of KCN, 350 g/L of  $K_2CO_3$  and 26 g/L of copper, with a rotation speed of 1500 rpm.

Table 2

Influence of cathodic current density and cathode type on the copper recovery after a 5-h electrolysis at 50 °C with a solution flow rate of 0.27 L/min

Test number	Cathode type	Current (A)	Current density ( $mA\ cm^{-2}$ )	Cu recovery (%)
1	Plate	12	40.6	81.7
2	Plate	14	47.4	93.7
3	Plate	16	54.1	98.2
4	Plate	18	60.9	99.4
5	Mesh	3.8	2.0	48.3
6	Mesh	10	5.2	75.2
7	Mesh	12	6.3	87.9
8	Mesh	14	7.3	96.8
9	Mesh	16	8.4	98.7
10	Mesh	18	9.4	99.9
11 <sup>a</sup>	Mesh	18	9.4	99.9
12 <sup>a,b</sup>	Mesh	18	9.4	99.9

<sup>a</sup> Industrial bleed solution.

<sup>b</sup> Flow rate: 0.5 L/min.

higher current intensities more copper can be recovered. The 65-mesh type cathodes have shown a performance slightly superior on copper recovery than the plate cathodes. The reason of this behavior is the higher surface area of the mesh which permitted the current density to be smaller than the limiting current density, rendering also a higher current efficiency and lower energy consumption due to the lower polarization of the mesh cathodes, as shown in Fig. 6, where the cathodic potential for the mesh cathode is from 600 to 350 mV smaller than that observed for the plates. This difference confirms a substantial decrease in the specific energy consumption of the cell and provides a lower current density, rendering a more compact structure of the copper deposit than that obtained on plates, which presents undesirable dendrites. The presence of dendrites can lead to a cell short circuit, interrupting the electrolysis, or to copper losses, if they break. The aspect of the copper deposits on plates and mesh cathodes are presented in Fig. 7(a and b), respectively. The cathodic potential drop observed after the second half of the experiment, in Fig. 6, can be attributed to cyanide ion concentration decrease, due to its oxidation, which depolarizes copper deposition [19].

The influence of solution flow rate on copper recovery on stainless steel mesh cathodes throughout a 5-h electrolysis at

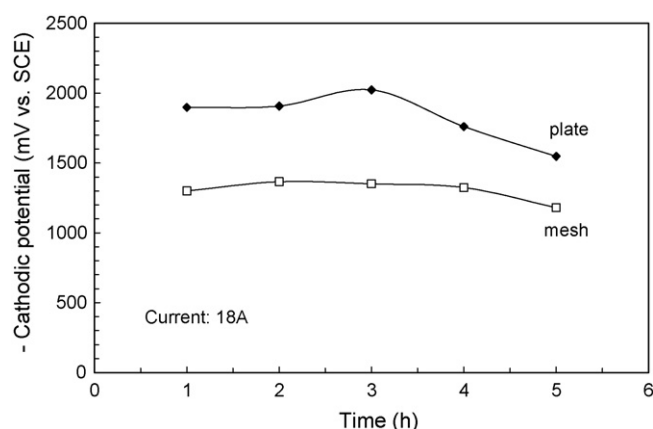


Fig. 6. Evolution of cathodic potential with time for an electrolysis at 18 A, 50 °C and a flow rate of 0.27 L/min.

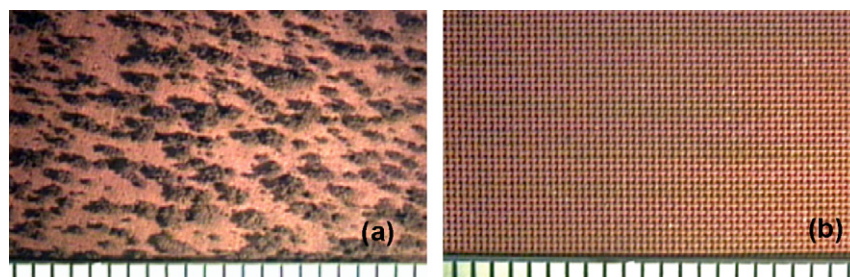


Fig. 7. Copper deposit obtained with a current of 18 A on a plate (a) and on a mesh cathode (b).

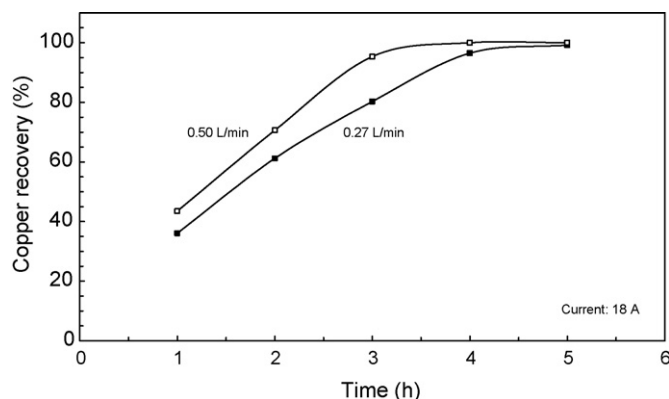


Fig. 8. Influence of solution flow rate on copper recovery with time for an electrolysis at 18 A, with stainless steel mesh cathodes at 50 °C.

50 °C is presented in Fig. 8. It can be observed that the increase of flow rate from 0.27 to 0.50 L/min permits a faster recovery of the copper from the solution, due to better mass transport conditions, which tend to decrease the diffusion layer thickness. Current efficiency should increase for the higher flow rate due to the higher limiting current density for copper deposition.

The influence of current on current efficiency and specific energy consumption for copper recovery on stainless steel mesh cathodes after a 5-h electrolysis with a flow rate of 0.27 L/min, at 50 °C, is presented in Fig. 9. It can be observed that as current increases current efficiency drops and energy consumption

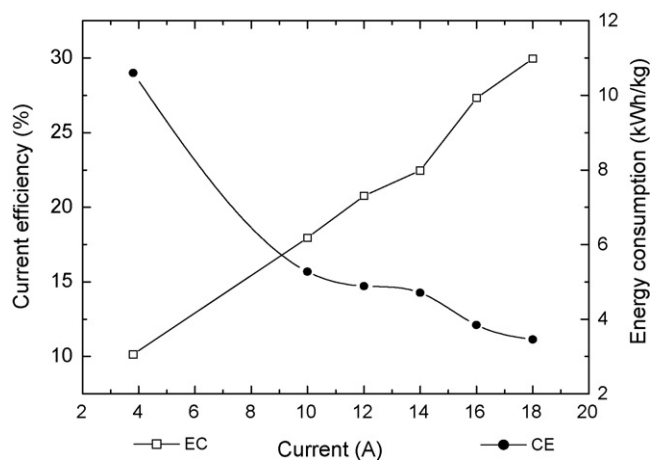


Fig. 9. Influence of cell current on the current efficiency and specific energy consumption for a 5-h electrolysis with mesh cathodes a solution flow rate of 0.27 L/min, at 50 °C. EC: energy consumption; CE: current efficiency.

is increased. This behavior can be attributed to the increase of hydrogen evolution rate for higher currents. Energy consumption can be lower and current efficiency higher if the flow is increased, due to the increase of the limiting current density for copper deposition. Furthermore, expressive improvements on energy consumption and current efficiency can be achieved for shorter electrolysis time; however, in this case copper recovery will be slightly lower, as indicated in Fig. 8, which shows a 95% copper recovery after 3 h, for a solution flow rate of 0.50 L/min.

The influence of cell current after a 5-h electrolysis with stainless steel mesh cathodes and a solution flow rate of 0.27 L/min, at 50 °C, on the cyanide destruction is presented in Table 3. It can be observed that current intensity increase causes a slight positive effect on the total cyanide oxidation. Reactions (10) and (11) are the main cyanide and cyanate oxidation reactions; however, reaction (12) also occurs due to a slight ammonium hydroxide smell detected at the end of the test. In this work, no growth of copper oxides films on the anodes was observed, probably because of the intense oxygen evolution, which inhibits film formation [12]. In fact, almost all of the copper in solution was removed on the cathode, since the weight of the cathodes before and after the electrolysis matched fairly well with the chemical analysis of the solution.

The copper removal from the steel mesh can be easily carried out through a replating in a typical acidic copper sulfate solution, under the conditions normally used by the copper refining industry (40 g Cu/L, 180 g H<sub>2</sub>SO<sub>4</sub>/L and a few ten mg/L of organic additives, like glue, thiourea, etc.) [20]. The copper is anodically dissolved from the stainless steel mesh and cathodically deposited on a plate electrode, from which it can be stripped, while the stainless steel mesh remains unattacked. A typical SEM micrograph of a replated copper deposit with its respective EDS are presented in Fig. 10(a and b), respectively. A typical structure of electrolytically refined copper can

Table 3

Influence of cell current after a 5-h electrolysis with stainless steel mesh cathodes and a solution flow rate of 0.27 L/min, at 50 °C, on the cyanide oxidation

Current (A)	Total cyanide removal (%)
14	98.8
16	98.3
18	99.7
18 <sup>a</sup>	99.5

<sup>a</sup> Industrial bleed solution.

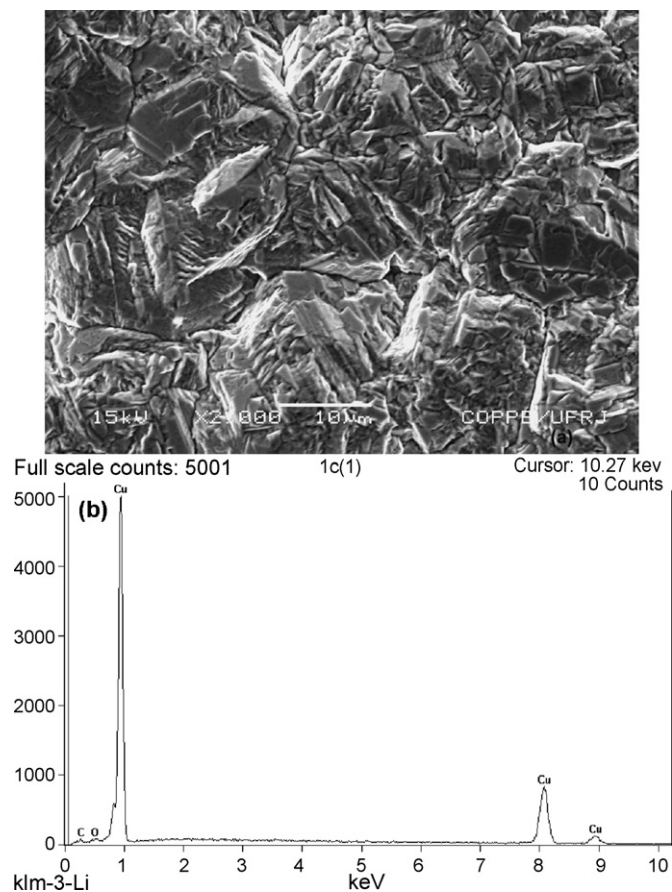


Fig. 10. Typical SEM aspect of replated copper from stainless steel mesh in acidic sulfate solution (a) and respective EDS (b).

be observed. The EDS microanalysis gives an idea of the copper purity obtained by replating of the copper removed from an industrial bleed solution. The tiny carbon and oxygen peaks can be attributed to presence of organic additives in the electrolyte and superficial oxidation of the copper during sample handling, respectively.

Despite the environmental standards for copper and cyanide, the electrolytic treatment process seems to be promising. At the present levels, copper price is around US\$ 7.93/kg (July 4, 2007), while the cost of electric energy, paid by the Brazilian Mint, is about US\$ 0.10/kWh. With the specific energy consumption for copper recovery of 11 kWh/kg, plus an average value of 0.4 kWh/kg, for copper replating on a stainless steel plate, under typical conditions for copper electrorefining [20], it gives, roughly, a cost of US\$ 1.14/kg of electrolytic copper recovered. Considering that most of the electroplating industries do not operate at full capacity, there is no need of considerable capital investments. Furthermore, the amount of chemicals to be added to the process is minimum. Then, besides the copper recovery a significant saving in the purchase of chemicals, used in the traditional alkaline chlorination process should be achieved, since most of the cyanide is electrolytically destroyed, and an additional savings due to the reduction of hazardous sludge handling and disposal costs is also accomplished.

## 5. Conclusions

Copper electrowinning from the electroplating cells bleed stream seems to be an attractive technological option to complement current alkaline chlorination treatment.

After a 5-h electrolysis of 1 L of solution, at 50 °C, with a flow rate of 0.27 L/min and a current density of 9.4 mA/cm<sup>2</sup>, more than 99.9% of the copper was recovered on stainless steel mesh cathodes, along with the destruction of more than 99% of total cyanide, with an energy consumption of about 11 kWh/kg.

Lower energy consumption can be achieved for smaller copper recovering, favoring the economic balance of the process; however, the hazardous load of the effluent will increase.

With the current copper price, substantial savings can be achieved due to the reuse of the recovered copper. Additional savings are achieved in the purchase of chemicals for alkaline chlorination. The reduction of hazardous sludge produced by the chemical treatment with its handling and disposal costs is also an advantage to be considered.

## Acknowledgements

The authors are grateful to CNPq and FAPERJ for the financial support.

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