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Advances and future prospects in copper electrowinning

W. CHARLES COOPER

Department of Metallurgical Engineering, Queen's University, Kingston, Ontario, K7L 3N6, Canada

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In recent years research on the electrowinning of copper has led to a number of significant advances. These developments include improved mass transfer and higher current density operation through air sparging, reduced anode overvoltage in the conventional cell as a result of cobalt(II) addition to the electrolyte or the use of alternative types of anodes, and the production of high quality cathodes in the electrowinning of copper from solvent extraction strip liquor. The fluidized-bed cathode offers the possibility of continuous electrowinning as well as the direct electrowinning of copper from dilute solutions. The problem of high power consumption may find its solution in the adoption of an alternate anode reaction or in the electrowinning of copper(I) electrolytes. Noteworthy is the development of unique electrowinning cells in conjunction with the hydrometallurgical treatment of copper concentrates. These cells utilize cuprous or ferrous anodic oxidation with the resulting cupric or ferric ions being active lixiviants of sulphide copper minerals. The numerous advances combined with the increasing tonnage of copper being produced by the electrowinning route ensure an interesting and promising future for this process.

1. Introduction

In recent years there has been a marked increase in the production of copper by electrowinning. At present some 15% of the copper produced is obtained by this route and it is estimated that this figure will rise significantly during the 1980s.

The development of specific reagents, in particular the hydroxyoximes, for the selective extraction of copper from sulphuric acid leach solutions has been a major step in copper extraction technology. Solvent extraction of copper followed by electrowinning has replaced, to a very large degree, the older cementation process. The increased activity in heap and dump leaching has been aided considerably by the upgrading of dilute leach liquors by solvent extraction. The heap and dump leaching is not restricted to low-grade oxide copper ores but is being applied successfully to low-grade sulphide ores aided in many cases by microbiological leaching.

The environmental constraints which have been imposed on copper smelters in many countries have led to greatly improved smelting processes and the increased capture of SO_2 emissions. At the same time considerable research has been devoted to developing hydrometallurgical processes for the treatment of copper concentrates. In the great majority of these hydrometallurgical alternatives the copper is recovered by electrowinning. Thus far it appears that no hydrometallurgical process has yet been developed which can compete successfully with the newer pyrometallurgical processes on the basis of overall cost and energy requirements [1]. A major cost component of the hydrometallurgical processes is the electrowinning operation which requires 8 to 10 times more power than electrorefining (2.0 $\mathrm{kWh\,kg^{-1}}$ versus 0.25 $\mathrm{kWh\,kg^{-1}}$).

The high power consumption associated with the electrowinning of copper is an important consideration in any improvements in the process. Also of importance are means of increasing the operating current density and the possibility of electrowinning copper directly from dilute leach solutions. Advances and the future prospects for copper electrowinning will be discussed in this paper in the light of the above considerations.

2. Methods for increasing the critical current density

The critical current density is the maximum current density at which one can expect to obtain an acceptable cathode deposit. Above this value the deposit becomes rough, less dense, less pure and generally unacceptable from a commercial standpoint.

To be able to operate the cell house successfully at higher current density and to increase productivity, it is necessary to improve the mass transfer via increased agitation. A word of caution should be noted here as regards electrolytes which contain significant amounts of ferric ion since, as will be discussed later, improved agitation can be counter-productive in the case of such solutions.

In recent years improved electrolyte agitation has been investigated via a number of avenues including forced circulation of electrolyte, ultrasonic agitation, the use of tapered anodes, and air sparging.

Balberyszski and Andersen [2] developed a high current density copper electrowinning cell which incorporated the concept of an injected and directed flow of electrolyte to each electrode surface. The electrolyte was injected through a series of 0.64 cm diameter orifices drilled 5 cm apart in a 5 cm diameter pipe located centrally in the cell and near the cell bottom. The electrolyte outlet pipes were located parallel to the inlet pipe and had a diameter of 5 cm, and 1 cm diameter outlet openings 10 cm apart and 5 cm from the centre of each cathode. The critical circulation rate (defined as the circulation rate below which a satisfactory deposit could not be obtained at any current density) was related linearly to the current density. Copper was electrowon from both synthetic and actual solutions at current densities of 38 to 43 mA cm^{-2} at circulation rates of 1.1 to 2.2 US gal $\mathrm{min}^{-1}\,\mathrm{m}^{-2}$. An actual solution was a solution produced in a leach solvent extraction circuit and had the following composition: Cu: 49.4 g dm^{-3}, Fe (total): 1.6 g dm^{-3}, Cl: 0.04 g dm^{-3}, H_2SO_4: 50.0 g dm^{-3}. The solution contained no organic additives or surface demisting agent.

Balberyszski and Andersen's cell which was also known as the CCS (Continental Copper and Steel) directed circulation system does not permit uniform circulation over the face of the entire cathode due to the rapid damping of the electrolyte movement. In addition, the high pumping costs associated with the circulation rates employed in the CCS system and possible problems associated with the orifices are sufficient to lead to only marginal benefits. As will be discussed later, air sparging is a much more attractive approach to improved agitation and higher current density operation.

The electrowinning of copper at higher current densities in ultrasonically agitated cells has been investigated on a laboratory scale by Davy Powergas Limited [3]. Eight stainless steel cylindrical ultrasonic probes excited by magnetostrictive transducers operating at 13 kHz were located along the bottom of the experimental cell. The working range was 146–1000 W or 710–4842 W m^{-2} of electrolyte plan area. The electrolyte flowed at right angles to the electrode face at a rate of 0.65 US gal m^{-2} of immersed cathode. The spent electrolyte (temperature 45° C) had the composition: 25 g dm^{-3} copper, 150 g dm^{-3} sulphuric acid and 2 g dm^{-3} iron (total). The copper drop amounted to 10 g dm^{-3}.

The results showed that dense, compact deposits could be obtained at substantially higher current densities (range investigated 10.8 to 54 mA cm^{-2}). As expected the voltage increased with current density. However, ultrasonic agitation which effectively eliminated the barrier layer, resulted in a decrease in the cell voltage.

A serious disadvantage with ultrasonic agitation was the serious lead contamination of the cathode deposit which was noted when 6% antimonial lead anodes were used (170–350 ppm lead in cathodes at a current density of 43 mA cm^{-2}). Thus the ultrasonic agitation dislodges the oxide layer on the anode resulting in high lead levels in the cathodes and rapid wear of the anodes. Although no tests were conducted on other anode materials, it was considered that lead–calcium anodes and noble metal-type anodes should be stable under ultrasonic agitation.

Although ultrasonic agitation provides the possibility of electrowinning copper at higher current densities with reduced power costs and capital costs, there are a number of factors which must be considered including cost and maintenance of ultrasonic agitation transducers and modifications to conventional cells. Noise might present a problem. Regular antimonial lead anodes could not be used. Also if high current densities such as 80 to 90 mA cm^{-2} were employed, problems related to acid mist and electrode shorts could be serious. Also it should be noted that ultrasonic agitation, like forced electrolyte circulation, does not result in uniform mass transport over large cathode surfaces.

In examining the problem of current distribution over the face of the cathode in copper electrowinning, Ettel and Gendron [4] noted that in the conventional cell the evolution of oxygen at the anode provides superior agitation and hence higher mass transfer rates only in the upper part of the cell. To overcome this problem and to realize a more uniform current density over the surface of the entire cathode, Ettel designed the tapered anode (Fig. 1). This anode which permits a higher current density operation (30 mA cm^{-2}), is being used commercially in INCO's copper electrowinning tankhouse at Copper Cliff, Ontario.

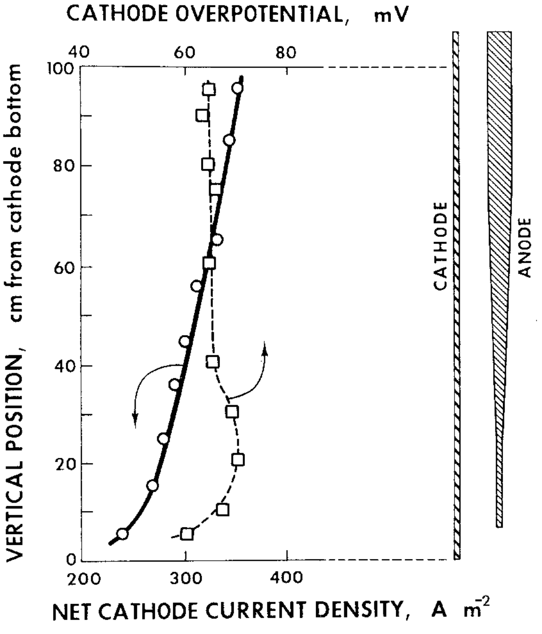

Fig. 1. Current distribution using tapered anode. The net current density was obtained by weighing sections of the deposit. (Average current density 30 mA cm^{-2}, temperature 60° C, 60 g dm^{-3} Cu, 150 g dm^{-3} H_2SO_4) [4].

Ettel and Gendron's data show in the case of the tapered anode a quite uniform cathode overvoltage with distance and a current density which increases linearly from 25 to 35 mA cm^{-2}. This behaviour is a marked improvement over that in the regular electrowinning cell where the mass transfer coefficient increases by a factor of three in the upper region of the cell.

The use of air sparging for improved mass transfer in copper electrowinning is a development of great interest as regards improved tankhouse performance. Although gas agitation in metal electrowinning has been known for some time and has been applied to a limited extent, it was not until the pioneering work of Harvey and co-workers at Kennecott [5–9] that definitive studies on this technique were carried out with a view to its application on an industrial scale. Harvey *et al.* examined in considerable detail the means of bubble generation (i.e. the cell hardware) and its optimization in commercial-sized cells, the inter-electrode spacing, current density, and electrolyte composition. These variables were related to the nature and purity of the cathode deposit, current efficiency, and power consumption. One of the principal objectives of this work was to demonstrate the viability of air-agitation electrowinning in copper electrolytes produced from heap leaching, vat leaching, and solvent extraction. As Harvey and Hsueh [9] point out, air agitation has the three capabilities of improving cathode quality, making possible a higher rate of production and allowing closer spacing of electrodes.

The data in Table 1 give an indication of the results that can be achieved using air sparging in the cases of a vat leach liquor and a simulated solvent extraction strip liquor. It will be noted that the current density in both experiments is well above that employed in conventional copper electrowinning. Even at this elevated current density excellent quality cathodes were obtained with surprisingly low lead and sulphur contents.

In demonstrating the superiority of air sparging over forced electrolyte circulation and conventional electrowinning Ettel *et al.* [10] developed a method for determining the mass transfer coefficient for Ag^+ which in turn can be related to that for Cu^{2+}. (Under the experi-

Table 1. Air-agitation copper electrowinning data [7, 9]

Experiment	EW3A	EW5A
Electrolyte	vat leach solution	*
Average c.d., $mA\,cm^{-2}$	64.0	63.4
Cu, $g\,dm^{-3}$ (initial)	20.4	29.9
H_2SO_4 $g\,dm^{-3}$ (initial)	49	180
Temperature, °C	60	60
Anode–cathode spacing, cm	3.12	2.67
Current efficiency, %	84.6	98.3
Power consumption, $kWh\,kg^{-1}$ Cu	4.0	1.96
Analysis of cathodes		
Pb, ppm	0.26	0.62
S, ppm	<2	<2.5

* Simulated solvent extraction strip liquor-actually stripper section electrolyte containing as major impurities nickel at $0.1\,g\,dm^{-3}$ and iron at $0.15\,g\,dm^{-3}$. The addition agent was removed by treatment with activated charcoal and the electrolyte saturated with 40% LIX 64N in kerosene.

mental conditions employed Ettel *et al.* [10] calculated $k_{Cu^{2+}} = 0.75k_{Ag^+}$.) The cathode mass transfer coefficient was measured in terms of k_{Ag^+} in a copper electrowinning cell under conditions of electrolyte forced flow and air sparging. The results show concrete evidence of a much greater and a uniform mass transfer coefficient in the case of the air sparged cell (Fig. 2).

As expected air sparging greatly reduces the thickness of the boundary layer. This behaviour contrasts sharply with the much thicker and nonuniform boundary layer in the conventional cell without sparging (Fig. 3).

In the electrowinning of copper from an acid leach solution containing Fe^{3+} ions, the following reactions are to be noted:

Cathode reactions:

$$Cu^{2+} + 2e \longrightarrow Cu \tag{1}$$

$$Fe^{3+} + e \longrightarrow Fe^{2+} \tag{2}$$

Anode reactions:

$$H_2O \longrightarrow 2H^+ + 1/2O_2 + 2e \tag{3}$$

$$Fe^{+} \longrightarrow Fe^{3+} + e \tag{4}$$

The reduction of ferric ions at the cathode causes a decrease in the current efficiency so that

$$\text{Current efficiency } (CE) = i_1/i_c = 1 - \frac{i_{2L}}{i_c} \tag{5}$$

where i_1 = current density, Reaction 1, i_c = cathode current density, i_{2L} = limiting diffusion current density, Reaction 2 and

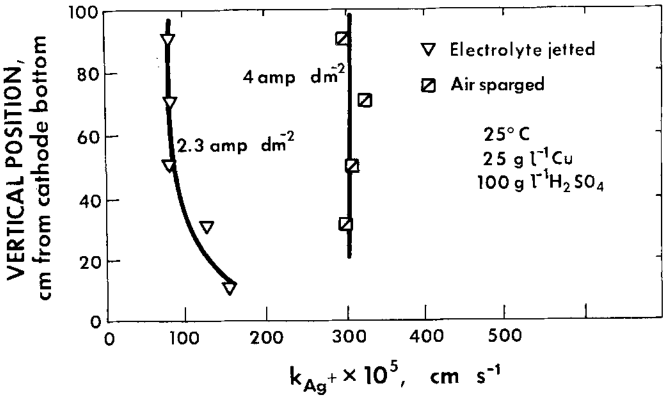

Fig. 2. Vertical distribution of k_{Ag^+} in electrolyte jetted and air sparged copper electrowinning cell [10].

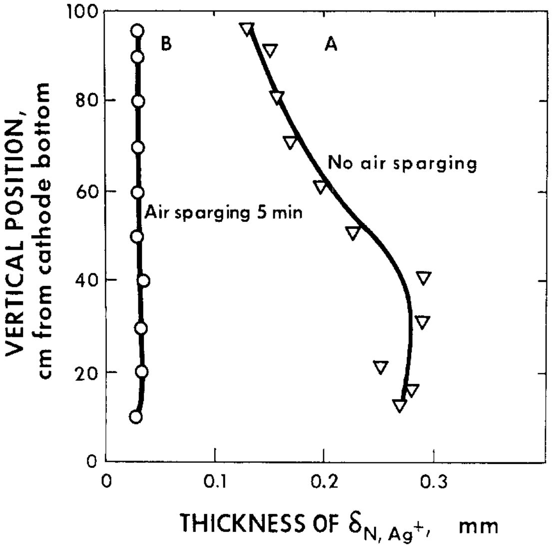

Fig. 3. Diffusion layer profiles showing beneficial effect of air sparging [11].

$$CE = 1 - \frac{FD_{Fe^{3+}}C_{Fe^{3+}}}{\delta i_c} \qquad (6)$$

where $D_{Fe^{3+}}$ = diffusion coefficient of Fe^{3+} ion; F = Faraday constant.

From the above equation we can see that the current efficiency is affected adversely by increased agitation and higher ferric ion concentration. The effect of the ferric ion concentration on the current efficiency in copper electrowinning at different current densities is shown in Fig. 4. It will be noted that the effect becomes less pronounced at higher current density. Thus according to Andersen *et al.* [12] it is possible to increase the current efficiency in the recovery of copper from an acid leach solution by decreasing the temperature, increasing the inert salt concentration, decreasing the ferric ion concentration, increasing the applied current density and decreasing the agitation.

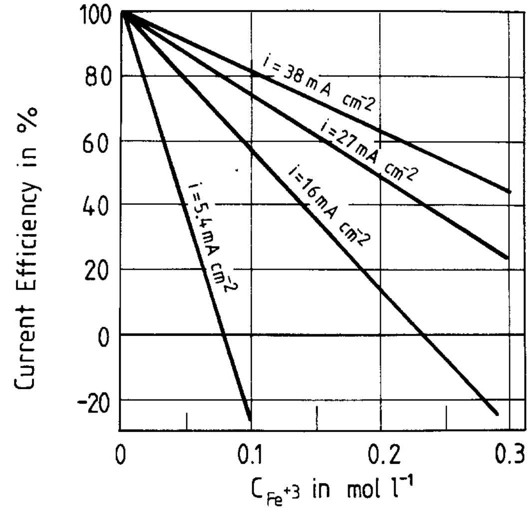

Fig. 4. Cathodic current efficiency as a function of concentration of Fe^{3+} ions and current density [12].

In the use of periodic current reversal (PCR) to achieve higher current densities in copper electrowinning one is confronted with the problem of a substantial back e.m.f. to the rectifier upon switching the direction of the current. It has been suggested that this problem can be overcome by short circuiting the cells after the current has been interrupted [13]. This has the effect of producing an intense current in the reverse direction. A more serious problem is the effect of current reversal on anode wear and contamination of the cathode deposit. No published data are available on the behaviour of the noble metal-type anodes in PCR but indications are that PCR could be detrimental to these anodes as well.

3. Reduction in the cell voltage

The power requirement in electrowinning can be decreased by effecting a reduction in the cell voltage. The cell voltage can be reduced by decreasing the oxygen overvoltage in the conventional cell or by means of a change in the anode reaction.

In the conventional cell recent studies have shown that the addition of cobalt(II) to the electrolyte can lower the oxygen overvoltage on the Pb–Sb anodes with an even greater reduction in the overvoltage (500–600 mV) being realized by the substitution of dimensionally stable anodes (DSA) for the lead alloy anodes (Fig. 5). The particular anodes referred to in Fig. 5 are titanium anodes with an oxygen low potential (OLP) coating of selected non-stoichiometric compounds of certain platinum metals, notably iridium and platinum [15].

In recent years considerable work has been carried out on the development of new and improved anodes for metal electrowinning [16]. The problems associated with the stability of the coating on titanium anodes has led to the study

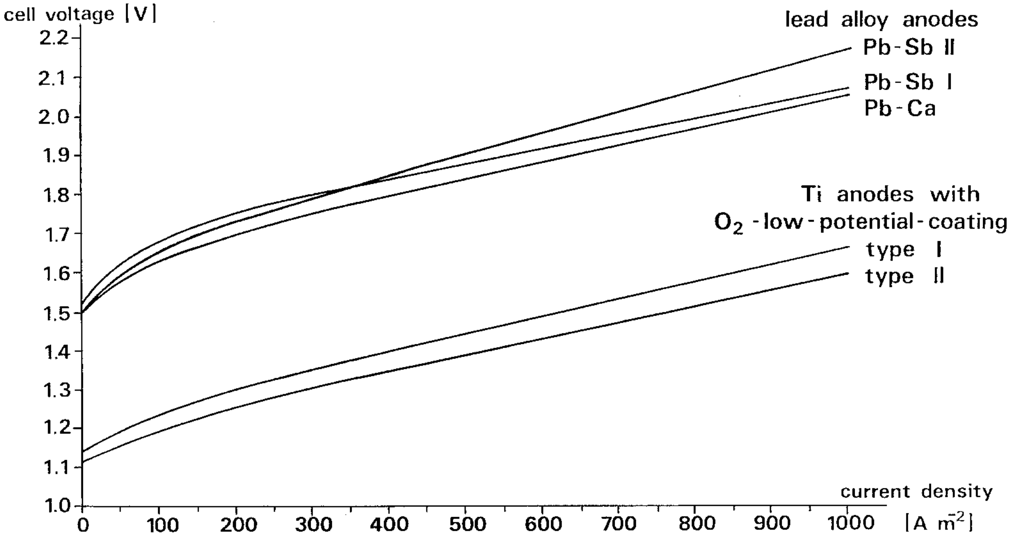

Fig. 5. Current density–voltage curves for copper electrowinning using different types of anodes [14]. Electrolyte: 50 g dm^{-3} Cu, 50 g dm^{-3} H_2SO_4, temperature 40° C; Cathode: copper clad graphite.

and adoption of oxides other than RuO_2 such as the OLP coatings mentioned above and to anodes having an oxide subcoating [17]. Of interest is the activated lead electrode (ALE) in which RuO_2-coated titanium sponge is embedded into the lead substrate by pressing or rolling [18]. In commercial copper electrowinning tests this electrode has provided a voltage reduction of 300 mV. In the case of lead alloys, a promising advance appears to be the wrought lead–calcium–tin alloy [19] which is in use in solvent extraction–copper electrowinning operations. The strong dross and crack-free rolled product has a fine uniform grain structure, superior to that of the cast alloy.

Gendron *et al.* [20] found that the addition of Co^{2+} ions to the electrolyte to give a cobalt concentration > 10 mg dm^{-3} lowered the voltage at the Pb–Sb anode and reduced the corrosion rate of the anode significantly.

In the presence of cobalt the anode reaction becomes

$$Co^{2+} \longrightarrow Co^{3+} + e \qquad (7)$$

followed by the oxidation of H_2O by Co^{3+}

$$4Co^{3+} + 2H_2O \longrightarrow 4Co^{2+} + 4H^+ + O_2 \qquad (8)$$

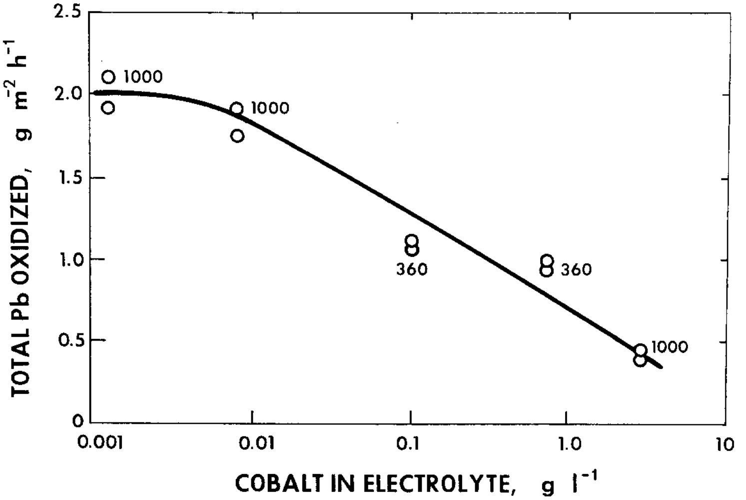

Fig. 6. Corrosion rate of Pb–Sb anode as a function of cobalt level in electrolyte. Figures in parenthesis denote duration of test in hours [20].

Thus in the presence of small amounts of Co^{2+} the polarization of the Pb–Sb anode in H_2SO_4 solution is reduced, the cobalt facilitating the evolution of oxygen. The favourable effect of the cobalt addition to the electrolyte on the corrosion rate of lead is shown in Fig. 6. The addition of as little as 50 to 100 ppm of cobalt to the electrolyte appears to be sufficient to give copper cathodes containing less than 10 ppm lead when using 6% antimonial lead anodes [21].

Koch [22] noted that in the presence of 200 mg dm^{-3} Co^{2+} as cobaltous sulphate in 1 M H_2SO_4 very much less PbO_2 was formed on the surface of lead anodes and that in some cases the metallic appearance of the surface was unchanged when O_2 was evolved. Koch demonstrated that cobalt has no effect on the initial sulphation of lead and only becomes effective when the potential reaches a value where the oxidation of Co^{2+} to Co^{3+} can occur.

A significant reduction in the cell voltage in copper electrowinning can be realized if the conventional anode reaction is replaced by a reaction such as

$$Fe^{2+} \longrightarrow Fe^{3+} + e \qquad (9)$$

or

$$2H_2O + SO_2 \longrightarrow SO_4^{2-} + 4H^+ + 2e \qquad (10)$$

A comparison of the SO_2 oxidation and the conventional oxygen evolution reaction reveals the following thermodynamic data:

Net cell reaction – SO_2 process:

$$CuSO_4 + H_2SO_3 + H_2O \longrightarrow Cu + H_2SO_4$$

$$\Delta H^0 = -77.28\,\text{kJ mol}^{-1}\,\text{Cu} \qquad (11)$$

$$\Delta G^0 = -31.76\,\text{kJ mol}^{-1}\,\text{Cu}$$

Net cell reaction – conventional process:

$$CuSO_4 + H_2O = Cu + 1/2\,O_2 + H_2SO_4$$

$$\Delta H^0 = 221.46\,\text{kJ mol}^{-1}\,\text{Cu} \qquad (12)$$

$$\Delta G^0 = 172.21\,\text{kJ mol}^{-1}\,\text{Cu}$$

The enthalpy difference between the two reactions amounts to 298.74 kJ mol^{-1} of Cu in favour of the SO_2 reaction. This value works out to be 1.30 Wh kg^{-1} Cu less for the SO_2 reaction. From the free energies of reaction, it can be shown that the SO_2 reaction takes place at a theoretical potential which is 1.05 V less than that for the conventional electrowinning process.

Pace and Stauter [23] succeeded in electrowinning copper directly from synthetic pregnant leach liquors utilizing the SO_2 sparging of the electrolyte in the presence of a graphite anode. They were able to demonstrate that copper cathodes can be produced at higher current efficiencies than those encountered in conventional electrowinning practice for electrolytes in which the copper is plated down from 10 to 2 g dm^{-3} in the presence of 10 g dm^{-3} iron.

The rather slow kinetics of the sulphur dioxide oxidation especially at higher current densities results in an unfavourable anode overvoltage and makes for an anode potential which is less advantageous than that indicated by thermodynamic considerations alone.

The opportunity afforded by the anodic reaction:

$$Fe^{2+} \longrightarrow Fe^{3+} + e, \qquad (13)$$

$E^0 = 0.77$ V versus SHE, as an alternative to the conventional reaction:

$$H_2O \longrightarrow 1/2O_2 + 2H^+ + 2e, \qquad (14)$$

$E^0 = 1.23$ V versus SHE, in realizing a reduced cell voltage was investigated by Cooke *et al.* [24]. Anode polarization curves were obtained to assess the effect of anode sparging with air and nitrogen as well as mechanical oscillation of the anode to improve the transfer of ferrous ions.

The regeneration of the ferrous ions is very important since the reduction of Fe^{3+} at the cathode, as has been shown by Andersen *et al.* [12], greatly reduces the current efficiency in the electrowinning process. Cooke *et al.* [24] explored the problem of ferric ion reduction using as reducing agents sulphur dioxide, cuprous sulphide, sugar, and coal. However, they failed to come up with a satisfactory regeneration procedure.

In recent work Mishra and Cooper [25] have demonstrated that the ferrous ion is a more effective anode depolarizer in copper electrowinning than is sulphur dioxide. The data presented in Fig. 7 show that reductions in anode potential while sparging 10, 20, and 100% SO_2 at a current density of 20 mA cm^{-2} are in the order of 100,

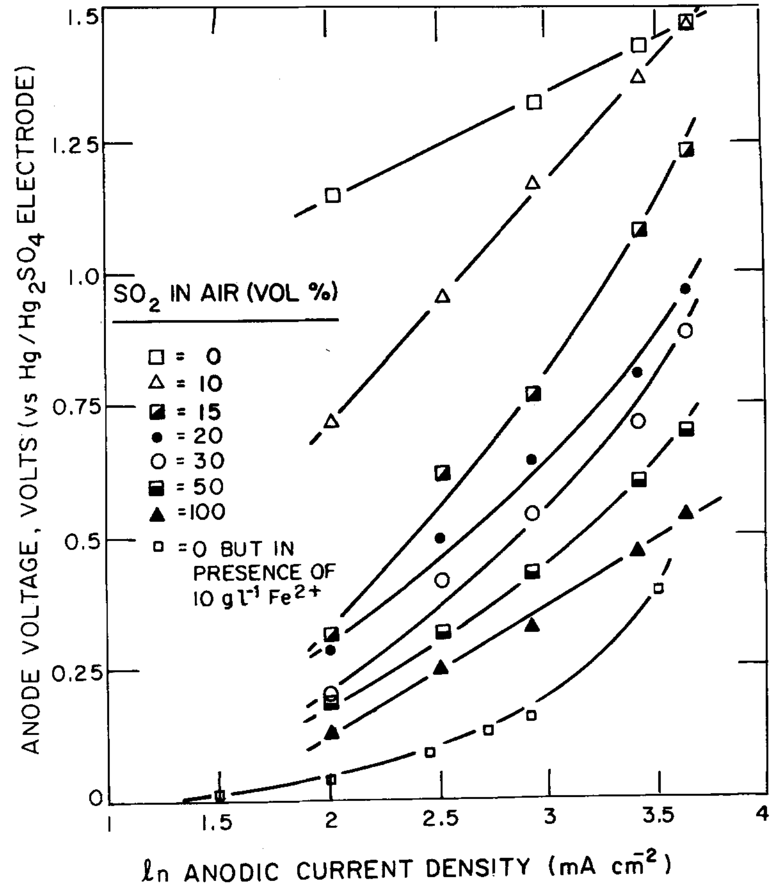

Fig. 7. Anode polarization curves using sulphur dioxide and air for sparging [25]. Experimental conditions: Cu 10 g dm^{-3}, H_2SO_4 50 g dm^{-3}, temperature 50° C, sparging rate 60 cm^3 min^{-1}, graphite anode (Speer Carbon of Canada Ltd, 890-S).

700, and 1000 mV respectively whereas in the presence of 10 g dm^{-3} of ferrous ion and sparging air at the same rate the reduction amounts to 1200 mV.

In the ferrous oxidation process it is essential to regenerate the ferrous ions from the ferric ions produced at the anode. This reduction can be accomplished by SO_2 sparging which also serves to improve mass transfer in the electrolytic cell.

Dissolved sulphur dioxide can act as a strong reducing agent for ferric ions as well as an oxidant for ferrous ions in the presence of oxygen as shown by the following equations:

$$2Fe^{3+} + SO_2 + 2H_2O = 2Fe^{2+} + H_2SO_4 + 2H^+ \quad (15)$$

$$2Fe^{2+} + SO_2 + O_2 = 2Fe^{3+} + SO_4^{2-} \quad (16)$$

Fig. 8 shows the effect of SO_2 concentration in the sparging gas on the ratio of ferric iron to total iron after 3 h of gas sparging. The results indicate that SO_2 first acts as an oxidant when its concentration is between 0 and 5% of SO_2 in air and above 5% as a reducing agent for ferric ions. The rate of reduction of ferric ions increases with the increase in the SO_2 concentration in the air. These findings agree with the conclusions of Tiwari *et al.* [26] that the oxidation of ferrous ions or the reduction of ferric ions depends upon the ratio of SO_2 to oxygen in the gas phase.

As discussed later in this paper Mishra and Cooper used a mixture of 15% SO_2 in air as the sparging gas to electrowin copper directly from actual sulphuric acid leach solutions.

4. The electrowinning of copper following leaching and solvent extraction

The production of copper by the leaching of lower grade copper ores (both oxide and sulphide), solvent extraction and electrowinning is

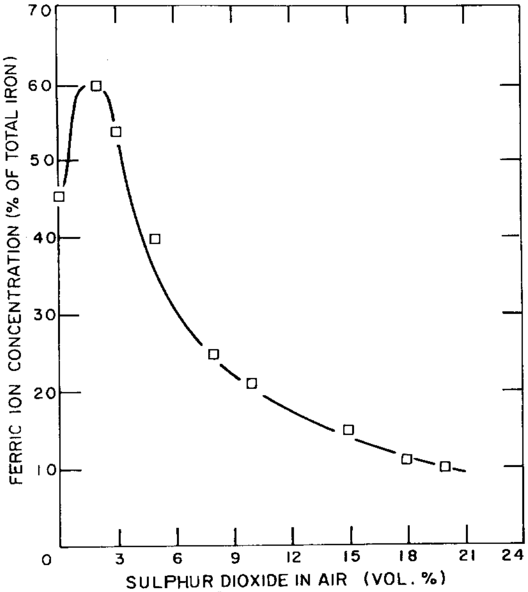

Fig. 8. Effect of sulphur dioxide concentration on the ferric ion concentration [25]. Experimental conditions: Cu 10 g dm^{-3}, H_2SO_4 50 g dm^{-3}, total Fe 7 g dm^{-3}, temperature 50° C, gas mixture sparging rate 500 $cm^3 min^{-1}$, electrolyte volume 250 cm^3, sparging duration 3 h.

a process which is accounting for an increasing percentage of total copper production. Consequently it is important to consider the extent to which the solvent extraction operation affects the electrowinning procedure.

The advantages of solvent extraction prior to electrowinning reside principally in the upgrading of leach solutions of low copper concentration which result from heap and dump leaching and in the purification of the leach solutions particularly as regards iron.

The problems that arise in the electrowinning of copper from the solvent extraction loaded strip liquor appear to be related principally to the carry-over with the strip liquor of any of the organic phase. The presence of entrained organic is indicated by the dark brown colouration of the copper deposit known as organic burn.

In studies on the electrowinning of copper from loaded strip liquor Hopkins *et al.* [27] observed that kerosene itself had no effect on the electrodeposit but organic burn appeared under their experimental conditions when the concentration of the organic phase (20 to 40% LIX 64N in kerosene) in the electrolyte exceeded 200 ppm. It is noteworthy that Harvey *et al.* [7] reported good quality copper deposits in electrowinning at 65 mA cm^{-2} using air sparging in an electrolyte saturated with 40% LIX 64N in kerosene.

The most definitive studies on the effect of entrained organic on the nature of the copper deposit have been conducted by MacKinnon *et al.* [28–30]. These investigators studied the effect of LIX 65N (the active component of the organic extractant LIX 64N) in combination with the chloride ion and the additives glue and thiourea on the morphology of electrowon copper. In an investigation of the effect of LIX 65N and chloride ion concentration on copper electrodeposition at a current density of 43 mA cm^{-2} [28], it was found that a low LIX 65N concentration (8 ppm) appears to improve the copper deposit. However, entrained LIX 65N at levels of 50 and 100 ppm has a deleterious effect on the copper deposits, causing them to be extremely pulverulent and nodular. This harmful effect can be offset to some extent by the addition of 100 ppm of chloride ion.

The combined effects of glue and LIX 65N at LIX 65N concentrations greater than 8 ppm were found to result in pulverulent non-crystalline deposits [30]. In agreement with previous work [29] it was noted that the adverse effect of LIX 65N could be compensated by the presence of sufficient chloride ion. In the case of the glue and LIX 65N study, the chloride ion concentration required was $\geqslant$40 ppm.

In the presence of glue 30 ppm, chloride ion (0 to 40 ppm) and LIX 65N (8 ppm), variation in the current density from 21.5 to 43 mA cm^{-2} produced no significant effect on the preferred orientations or surface morphologies of the copper electrodeposits [30]. The electrolyte contained 20 g dm^{-3} Cu and 150 g dm^{-3} H_2SO_4 and was maintained at 35° C.

No distinctly different results were obtained in the studies involving thiourea, LIX 65N and chloride ion although no experiments were conducted in which both glue and thiourea were present in the same electrolyte.

5. The direct electrowinning of copper from dilute leach solutions

The direct electrowinning of copper from more concentrated leach solutions such as are obtained following vat leaching has been practiced for many years. However, even here if the leaching produces solutions containing deleterious impurities such as ferric iron and dispersed colloidal silica, it may be advantageous to subject the leach liquor to solvent extraction prior to electrowinning. Such a procedure is employed by the Kennecott Copper Corporation in the treatment of the chrysocolla ores at Ray Mines, Arizona.

The direct electrowinning of copper from dilute leach solutions would, if successful, eliminate the solvent extraction step in the overall process.

Several approaches to the direct electrowinning of copper from dilute leach solutions have been investigated but so far no process has been developed and used on a commercial scale.

An interesting process which was piloted successfully by Kennecott [31] involves the deposition of copper onto a packed coke bed cathode from a solution containing less than 2 g dm^{-3} copper. The deposited copper forms a strongly bonded copper–coke material which following removal from the cells would be melted, fire refined, and cast as a final copper product.

The process chemistry embraces the following cathodic and anodic reactions.

Cathode reactions

$$Cu^{2+} + 2e \longrightarrow Cu \tag{17}$$

$$Fe^{3+} + e \longrightarrow Fe^{2+} \tag{18}$$

$$2H^{+} + 2e \longrightarrow H_2 \tag{19}$$

Anode reactions

$$Fe^{2+} \longrightarrow Fe^{3+} + e \tag{20}$$

$$H_2O \longrightarrow 1/2\ O_2 + 2H^{+} + 2e \tag{21}$$

From these reactions it can be seen that the current efficiency in terms of copper production is reduced substantially.

The operating conditions for a prototype electrowinning system based on this process as applied to waste dump leach solutions are given in Table 2.

Although this process permits the direct electrochemical recovery of copper from extremely dilute solutions, its power consumption is excessive to the point where the process economics become unattractive.

Table 2. Operating conditions for a prototype direct electrowinning unit for use with waste dump leach liquors [31]

Leach liquor composition	
Copper	0.6 g dm^{-3}
Iron(III)	0.6 g dm^{-3}
pH	approx. 2
Cell Conditions	
Feed rate	20 US gal min^{-1}
Potential	4.7 V
Current density	21.5 mA cm^{-2}
Cell performance	
Copper recovery	> 85%
Energy consumption	7.0 kWh kg^{-1} Cu
Copper loading	16.6 kg Cu m^{-2} cathode
Cathode turnaround time	3–4 days

Skarbo and Harvey [5] have demonstrated that air-agitation electrowinning can be used to recover copper directly from dilute leach solutions containing less than 5 g dm^{-3} copper. The use of sparged sulphur dioxide for anode depolarization at a graphite electrode offers the potential of electrowinning copper directly from dilute leach liquors at a significantly reduced power consumption. In fact Pace and Stauter [23] obtained good quality cathodes with a current efficiency of 95% in electrowinning copper from 10 g dm^{-3} down to 2 g dm^{-3} in SO_2 sparged synthetic leach liquors. The operating cell voltage at a current density of 21.5 mA cm^{-2} was 2.5 V for an initial solution containing copper, iron(II), and H_2SO_4 each at 10 g dm^{-3}. This value is well above the open-circuit voltage of 0.3–0.4 V and indicates substantial overvoltages.

The direct electrowinning of copper from leach solutions from oxide copper ores has been carried out by Mishra and Cooper [25] using ferrous ion oxidation together with SO_2 sparging. Following dissolution of the ore, the filtered leach solutions were sparged with a mixture of air and SO_2 (15%) until most of the iron was reduced to the ferrous state. The current density was selected so as to produce bright, dense copper deposits. Electrowinning data on one of the copper ores are presented in Table 3.

Table 3. Electrowinning copper from sulphuric acid copper leach solution from oxide copper ore, Noranda Inc., Mines Gaspé Division, Murdochville, Quebec [25]

Copper drop ($g\,dm^{-3}$)	*CD ($mA\,cm^{-2}$)*	*CE (%)*	*Sulphuric acid (final concn.) ($g\,dm^{-3}$)*	*Ferrous ion (final concn.) ($g\,dm^{-3}$)*	*Ferric ion (final concn.) ($g\,dm^{-3}$)*
6.4–5.8	20	87	20	5.20	0.80
5.8–2.7	16.7	86	43	4.98	1.02
2.7–2.1	10	85	53	5.00	1.00
2.1–1.6	8	75	61	5.12	0.88
1.6–0.87	7.5	65	65	5.12	0.88
0.87–0.45	5	45	70	5.23	0.77

Power requirement 0.94 $kWh\,kg^{-1}$ copper at 20 $mA\,cm^{-2}$.
Sparging 15% SO_2 in air at 200 $cm^3\,min^{-1}$ between the electrodes.
Sulphuric acid initial concentration 11 $g\,dm^{-3}$.

While this study was aimed primarily at the direct electrowinning of copper from leach solutions, it should be possible to apply the ferrous oxidation–SO_2 sparging technique to the solvent extraction–electrowinning process to reduce the energy requirements of copper production.

The use of a fluidized-bed cathode appears to offer a viable means of electrowinning copper directly from very dilute leach solutions, e.g. $< 2\,g\,dm^{-3}$ Cu [32, 33].

In the fluidized-bed electowinning cell particles of copper are fluidized by the upward flow of electrolyte through the bed. The bed is rendered cathodic by the presence of a feeder electrode which can be a copper or titanium rod. In the plane parallel cell configuration (Fig. 9) the anode is placed in the electrolyte in the upper part of the cell. Alternatively the anode and cathode can be placed in adjoining compartments and separated by a diaphragm or porous partition as in the side-by-side configuration (Fig. 10). This latter configuration seems to be the option to be considered in any scale-up for commercial purposes.

The large surface area presented by the cathodic copper particles means that in electrowinning the actual current density per unit surface area of the particles may be in the order 0.2 $mA\,cm^{-2}$ which is one hundredth of the current density used in conventional electrowinning. The nominal current density calculated on the basis of the cross-sectional area of the fluidized-bed cell is, of course, very much larger. Operation at a current density of 300 $mA\,cm^{-2}$ of cell cross-sectional area has been proposed [33].

The excellent agitation in the cathode bed greatly reduces the thickness of the Nernst boundary layer and increases the limiting dif-

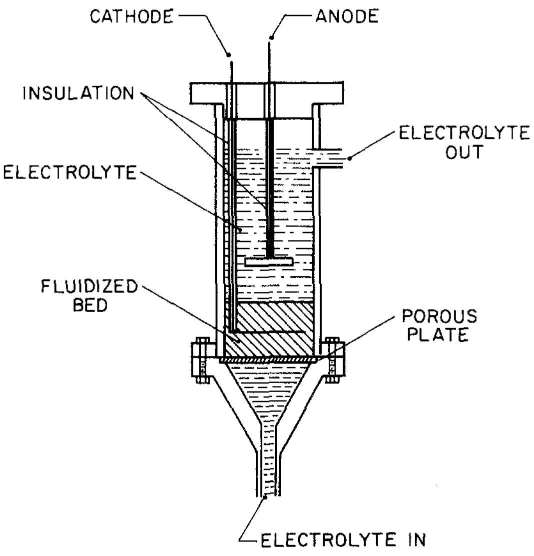

Fig. 9. Fluidized-bed electrowinning cell having a plane parallel configuration [34].

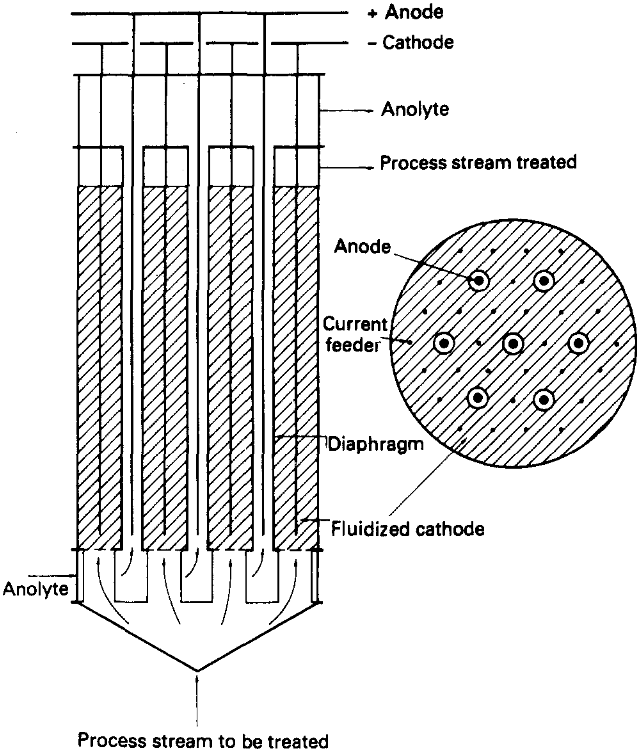

Fig. 10. Fluidized-bed electrowinning cell having a side-by-side configuration [35].

fusion current density. The net result is that in fluidized-bed electrowinning copper can be plated down to a concentration of 0.01 $g\,dm^{-3}$ before the onset of polarization as shown by a sharp rise in the cell voltage [33].

Monhemius and Costa [34] in a statistical modelling study of the interaction of the important variables in the fluidized-bed electrowinning of copper from dilute solutions, have drawn attention to two serious problems. The first is the problem of ferric iron which, as has been discussed earlier, can have a strong negative effect on the current efficiency and hence on the power consumption. This problem would be ameliorated to some extent in the side-by-side cell configuration in which the anode and cathode are separated by a suitable membrane.

The second problem concerns the low conductivity of the dilute leach solutions in which the H_2SO_4 concentration may be at a level of 10 $g\,dm^{-3}$ as opposed to 100 to 150 $g\,dm^{-3}$ in conventional copper electrowinning. This low conductivity has the effect of increasing the *IR* drop in the cell and raising the cell voltage and in turn the power consumption.

The power consumption data which have been reported for electrolytes of low copper and H_2SO_4 concentrations are not favourable. Thus Wilkinson and Haines [32] reported power consumption values which are 1.5 to as much as 5 times higher than the figure for conventional copper electrowinning (2 $kWh\,kg^{-1}$ Cu) in the fluidized-bed electrowinning of copper from sulphuric acid solutions having a pH of 2 to 3. Had the electrolytes contained ferric iron the power consumption would have been even higher.

The recent data of Dubrovsky *et al.* [36] are of particular interest even though these investigators did not study the fluidized-bed electrowinning of copper from dilute solutions. They did examine the effect of the anode and the anode reaction on the cell voltage and were able to attain improved power consumption values (Tables 4 and 5). The use of noble metal-type anodes or DSA anodes was effective in reducing

Table 4. Fluidized-bed copper electrowinning [36]; summary of experimental results

	Cylindrical cell	*Side-by-side rectangular fluidized-bed cell*				
	Small anode	*Graphite packed bed anode*				
	Oxygen evolution	*Oxygen evolution*	*Cuprous oxidation*	*Cuprous-anode plus cathode*	*$FeSO_4$ oxidation*	*SO_2 oxidation with $FESO_4$*
Temperature (°C)	50	50	50	50	50	35
Electrolyte resistivity (Ω cm)	3.0	2.53	4.25	4.25	5.1	6.1
Cell voltage (V) (at 0.45 A cm^{-2})	6.2	6.5	4.20	4.60	3.95	4.6
Energy consumption at 100% efficiency (kW h kg^{-1} Cu)	5.24	5.48	3.54	1.94	3.33	3.88
Current efficiency (%)	89	–	–	–	–	–
Energy consumption (kW h kg^{-1} Cu)	5.94	–	–	–	–	–

the power consumption to a level which was less than 50% above the conventional figure. Experiments were also conducted using SO_2, cuprous, and ferrous oxidation in place of oxygen evolution.

The high power consumption associated with the fluidized-bed electrowinning of copper from dilute leach solutions containing ferric iron is an impediment which must be resolved if serious consideration is to be given to this approach to direct electrolytic reduction without the intermediate solvent extraction step.

Table 5. Fluidized-bed copper electrowinning [36]; summary of experimental results

	Side-by-side rectangular fluidized-bed cell				
	DSA double mesh anode			*Diaphragm against DSA mesh. Oxygen evolution 50 g dm^{-3} H_2SO_4*	*Screen-covered lead anode. Oxygen evolution*
	SO_2 oxidation	*Oxygen evolution 50 g dm^{-3} H_2SO_4*	*Oxygen evolution 150 g dm^{-3} H_2SO_4*		
Temperature (°C)	50	50	50	20	30
Electrolyte resistivity (Ω cm)	4.5	4.6	2.5	4.7	3.0
Cell voltage (V)	3.25	3.6	2.90	2.85	3.41 at 1 A cm^{-2}
Energy consumption at 100% efficiency (kW h kg^{-1} Cu)	2.75	3.08	2.44	2.38	2.88
Current efficiency (%)	–	–	98	–	70
Energy consumption (kW h kg^{-1} Cu)	–	–	2.51	–	4.09

6. Electrowinning from copper(I) electrolytes

A significant reduction in power consumption in copper electrowinning can be realized if the copper in the electrolyte is present in the cuprous form. In recent years a number of noteworthy advances have been made in electrowinning from both cuprous chloride and sulphate solutions.

In the electrowinning of cuprous chloride solutions at around 30° C (CuCl 0.7 M, NaCl 4 M, HCl 0.5 M), Winand and co-workers [37, 38] were able to obtain power consumptions of between 0.45 and 0.60 $\mathrm{kWh\,kg^{-1}}$ Cu at current densities ranging from 20 to 30 $\mathrm{mA\,cm^{-2}}$. If oxidation of the catholyte was avoided through the use of a diaphragm in the cell, the current efficiency was quite high at 93%. The copper deposits were dendritic in nature with crystals protruding from the surface. These somewhat rough though coherent deposits present problems as regards occlusion of the electrolyte. The crystals can be broken and recovered continuously on a conveyor belt as is done in the Duval CLEAR process [39]. The CLEAR process is an interesting commercial application of cuprous chloride electrowinning.

Through the use of inert gas sparging Winter *et al.* [40] were able to obtain smooth deposits in electrowinning copper from a 4 M NaCl–1 M HCl cuprous chloride solution at a current density of 30 $\mathrm{mA\,cm^{-2}}$.

The electrowinning of copper from cuprous sulphate electrolytes has been shown by Muir and co-workers [41, 42] to be especially attractive if it is carried out in solutions containing organic nitriles such as acetonitrile. The process appears to be applicable to the upgrading of copper-bearing materials such as scrap copper and cement copper which are not amenable to being cast directly as anodes. These materials provide the cuprous ions for electrowinning via reaction with the Cu^{2+} ions which are generated anodically in the electrowinning cell.

$$Cu^{2+} + Cu \longrightarrow 2\,Cu^{+} \qquad (22)$$

Electrowinning in the diaphragm cell containing $CH_3CN–H_2O–H_2SO_4$ proceeds according to the reactions:

Anode reaction

$$Cu^{+} \longrightarrow Cu^{2+} + e \qquad (23)$$

Cathode reaction

$$Cu^{+} + e \longrightarrow Cu \qquad (24)$$

According to Muir and Parker [42], typical electrolyte composition, conditions and energy requirements for electrowinning copper from a Cu_2SO_4 acidified solution containing acetonitrile are as follows:

CH_3CN	80–240 $\mathrm{g\,dm^{-3}}$
H_2SO_4	100–200 $\mathrm{g\,dm^{-3}}$
Cu^{+}	30–60 $\mathrm{g\,dm^{-3}}$ (RCN : $Cu^{+} \ngtr 4:1$)
Current density	10–20 $\mathrm{mA\,cm^{-2}}$
Temperature	25–50° C
Cell voltage	0.3–0.8 V
Anode	dense graphite

High quality, dense electrodeposits can be obtained at current efficiencies in the order of 95% or better provided Cu^{2+} ions are prevented from entering the cathode compartment. The typical energy requirement is quite favourable at 0.14 to 0.36 $\mathrm{kWh\,kg^{-1}}$ Cu and is the same order of magnitude as the energy requirement in copper electrorefining.

This process has not as yet been developed beyond the laboratory stage. As Muir and Parker [42] have indicated many fundamental data are required for this mixed solvent system. Also processes related to the recovery of copper from ores, concentrates, and other copper-bearing materials using organic nitriles to stabilize Cu_2SO_4 solutions have yet to be subjected to a complete techno-economic analysis.

In the electrowinning of copper from cuprous chloride electrolytes some excellent data have been presented regarding the physicochemical and electrochemical properties of such electrolytes [40, 43, 44]. However, it remains for these results to be applied in the development of an industrial process yielding marketable cathodes. In his review of the status of the electrolytic recovery of metals from aqueous chloride media, MacKinnon [45] draws attention to shortcomings in the present technology.

7. Future prospects in copper electrowinning

There is little doubt that electrowinning will continue to be employed as the final reduction step in the production of substantial tonnages of copper. Support for this statement can be found in the increasing treatment of lower grade copper ores and waste rock by heap and dump leaching followed by solvent extraction and electrowinning. In addition, the continuing research on hydrometallurgical alternatives to the pyrometallurgical processing of copper concentrates is bound to produce processes which will provide unique advantages. The electrowinning of copper in two such processes namely, the Duval CLEAR process and the Electroslurry process should be noted.

The high power consumption in conventional copper electrowinning is a problem which may find its eventual solution in the electrowinning of copper from cuprous electrolytes. In the case of cuprous electrowinning there can be the double advantage of a one-electron reduction and a modified anode reaction which involves the oxidation of cuprous ions in place of oxygen evolution.

In the conventional electrowinning process it would appear that the reduction of the oxygen overvoltage via the use of DSA anodes is at present too expensive and that the addition of cobalt(II) to the electrolyte may be the simplest expedient. Cobalt has the additional advantage of reducing the corrosion rate of the antimonial lead anodes and permitting the production of copper cathodes of low lead content. A number of alternative anodes are available which allow the production of quality cathodes without lead contamination [16]. Continuing advances in anode materials and further increases in energy costs will undoubtedly lead to the wider acceptance in copper electrowinning of anodes having a low oxygen overpotential.

The reduction in the cell voltage and the power requirement in copper electrowinning through the use of ferrous ion as anode depolarizer in place of oxygen evolution requires additional study to define the optimum procedure by which the regeneration of ferrous ions might be achieved. In the application of ferrous ion oxidation in which an SO_2/air mixture is employed for sparging, the problem of SO_2 entering the tankhouse environment from the sparging gas must be resolved. An important development in the use of ferrous iron oxidation at the anode is found in the Electroslurry process [1]. Here not only is the anode voltage reduced significantly, but also the ferric ions which are generated are used for the *in situ* leaching of covellite and chalcocite.

The direct electrowinning of copper from dilute solutions with the elimination of the solvent extraction step is possible down to levels of around 2 g dm^{-3} copper using ferrous oxidation and SO_2 sparging. The difficulty arises when one desires to plate down to ppm concentrations. The answer may well be found by taking advantage of the cell systems which have been designed for the electrolytic recovery of metals from waste solutions [46]. Interesting examples are the Eco-Cell [47] in which metal powders are produced at a rotating cylinder cathode and the impact rod reactor (Fig. 11) in which the metal deposited onto stainless steel rods is removed by the oscillation of the rods [35]. Also noteworthy is the Chemelec cell in which mass transport is facilitated by a fluidized-bed of inert glass beads in which expanded mesh electrodes are immersed [48].

The fluidized-bed electrowinning cell, besides providing the possibility of treating very dilute solutions, affords the opportunity of continuous electrowinning. This application may be especially advantageous when applied to more concentrated solutions. Compared to conventional copper electrowinning fluidized-bed electrowin-

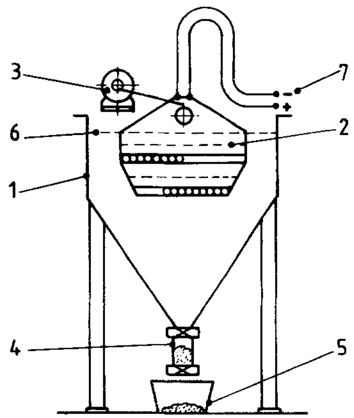

Fig. 11. Impact rod electrolytic cell GOECOMET [35]. 1. Electrolytic cell, 2. electrodes, 3. driving system, 4. reservoir, 5. metal collector, 6. liquid level, and 7. current connecting plugs.

ning, according to a preliminary economic analysis, has substantially lower capital costs. However, this advantage is negated by the higher operating costs when the power consumption in fluidized-bed electrowinning exceeds that in the conventional operation by more than 50% [36]. Consequently, to take full advantage of the fluidized-bed process it is necessary not only to design a cell that will permit continuous electrowinning on a commercial scale, but also a system that has a power demand that is not much higher than that of the present electrowinning process. Dubrovsky *et al.* [36] have shown that the latter requirement is presently close to being met.

In the case of cell design and continuous metal electrowinning, Kammel and co-workers [35, 49] have drawn attention to a number of interesting options which are worth further investigation. It must be emphasized that simplicity of design and operation are two very important criteria for a commercial cell. Many of the electrochemical reactors which have been developed especially in the field of metal recovery from very dilute solution streams are far too sophisticated for trouble-free performance in an industrial environment.

Air sparging has been shown to improve mass transfer and to provide for more uniform electrowinning conditions across the entire cathode surface. This procedure is definitely superior to forced electrolyte circulation as a means of higher current density operation. The technique has a future in upgrading conventional copper electrowinning, but due account must be taken of the effect of increased agitation on current efficiency in the presence of ferric ions, on the enhanced corrosion of the cathode at the air-solution interface, and on the stability of the anode in longer term electrowinning.

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References

[1] C. H. Pitt and M. E. Wadsworth, US Department of Energy, DOE Contract No. DE-AS07-78CS40132, Final Report, December 1980. (Available from National Technical Information Service, US Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161).

[2] T. Balberyszski and A. K. Andersen, *Proc. Aust. Inst. Min. Met.* **244** (Dec. 1972) 11.

[3] G. Eggett, W. R. Hopkins, T. W. Garlick and M. J. Ashley, paper presented at Annual AIME Meeting, New York, February, 1975.

[4] V. A. Ettel and A. S. Gendron, *Chem. Ind.* (1975) 376.

[5] R. R. Skarbo and W. W. Harvey, *Trans. Inst. Min. Metal. Sect. C* **83** (1974) C213.

[6] W. W. Harvey, A. H. Miguel, P. Larson and I. S. Servi, *ibid.* **84** (1975) C11.

[7] W. W. Harvey, M. R. Randlett and K. I. Bangerskis, *ibid.* **84** (1975) C210.

[8] *Idem, Chem. Ind.* (1975) 379.

[9] W. W. Harvey and L. Hsueh, *CIM Bulletin* **69**(768) (1976) 109.

[10] V. A. Ettel, B. V. Tilak and A. S. Gendron, *J. Electrochem. Soc.* **121** (1974) 867.

[11] V. A. Ettel, A. S. Gendron and B. V. Tilak, *Metall. Trans. B* **6B** (1975) 31.

[12] T. N. Andersen, C. N. Wright and K. J. Richards, "International Symposium on Hydrometallurgy", edited by D. J. I. Evans and R. S. Shoemaker (AIME, New York, 1973) pp. 171–202.

[13] H. A. Liekens and P. D. Charles, *World Mining* **40** (April, 1973) 38.

[14] K. R. Koziol and E. F. Wenk, *AIME, TMS* (1980) Paper No. A80-41.

[15] K. R. Koziol, "Technical Information", (CONRADTY GmbH and Co., Metallelektroden KG, (1982).

[16] Proceedings of Sessions, Anodes for Electrowinning, AIME Annual Meeting, Los Angeles, CA, February 1984, edited by D. J. Robinson and S. E. James (AIME, New York, 1984).

[17] I. H. Warren, in Proceedings of Sessions, Anodes for Electrowinning, AIME Annual Meeting, Los Angeles, CA, February 1984, edited by D. J. Robinson and S. E. James, (AIME, New York, 1984) pp. 69–78.

[18] J. K. Walker and J. I. Bishara, *ibid.* pp. 79–86.

[19] R. D. Prengaman, *ibid.* pp. 59–67.

[20] A. S. Gendron, V. A. Ettel and S. Abe, *Cdn. Met. Quart.* **14** (1975) 59.

[21] G. Eggett and D. Naden, *Hydrometall.* **1** (1975) 123.

[22] D. F. A. Koch, *Electrochimica Acta* **1** (1959) 32.

[23] G. F. Pace and J. C. Stauter, *CIM Bulletin* **67**(741) (1974) 85.

[24] A. V. Cooke, J. P. Chilton and D. J. Fray, "Extraction Metallurgy 1981" (The Institution of Mining and Metallurgy, London, 1981) pp. 430–441.

[25] K. K. Mishra and W. C. Cooper, Proceedings of Sessions, Anodes for Electrowinning, AIME Annual Meeting, Los Angeles, CA, February 1984, edited by D. J. Robinson and S. E. James, (AIME, New York, 1984) pp. 13–36.

[26] B. L. Tiwari, J. Kolbe and H. W. Hayden, *Metall. Trans. B* **10B** (1979) 607.

[27] W. R. Hopkins, G. Eggett and J. B. Scuffham, "International Symposium on Hydrometallurgy", edited by D. J. I. Evans and R. S. Shoemaker, (AIME, New York, 1973) pp. 127–154.

[28] D. J. MacKinnon, V. I. Lakshmanan and J. M. Brannen, *Trans. Inst. Min. Metall. Sect. C* **85** (1976) C183.

[29] V. I. Lakshmanan, D. J. MacKinnon and J. M. Brannen, *J. Appl. Electrochem.* **7** (1977) 127.

[30] D. J. MacKinnon, V. I. Lakshmanan and J. M. Brannen, *ibid.* **8** (1978) 223.

[31] P. R. Ammann, G. M. Cook, C. Portal and W. E. Sonstelie, "Extractive Metallurgy of Copper", edited by J. C. Yannopoulos and J. C. Agarwal, (AIME, New York, 1976) Vol. II, pp. 994–1008.

[32] J. A. E. Wilkinson and K. P. Haines, *Trans. Inst. Min. Metall. Sect. C* **81** (1972) C157.

[33] D. S. Flett, *Chem. Ind.* (1972) 983.

[34] A. J. Monhemius and P. L. N. Costa, *Hydrometall.* **1** (1975) 183.

[35] R. Kammel, H. G. Eran and H. W. Lieber, in Hydrometallurgy-Research, Development and Plant Practice, Proceedings of 3rd International Symposium on Hydrometallurgy, AIME Annual Meeting, Atlanta, Georgia, March 1983, edited by K. Osseo-Asare and J. D. Miller (AIME, New York, 1983) pp. 647–657.

[36] M. Dubrovsky, D. Ziegler, I. F. Masterson and J. W. Evans, "Extraction Metallurgy 1981", (The Institution of Mining and Metallurgy, London, England, 1981) pp. 91–103.

[37] P. A. Adrianne, J. P. Dubois and R. F. P. Winand, *Metall. Trans. B* **8B** (1977) 315.

[38] L. Albert and R. F. P. Winand, in Chloride Hydrometallurgy Proceedings, Benelux Metallurgie, Brussels, September 1977, p. 319.

[39] F. W. Schweitzer and R. W. Livingston, in Chloride Electrometallurgy, Proceedings of Symposium, AIME Annual Meeting, Dallas, Texas, February 1982, edited by P. D. Parker (AIME, New York, 1982) pp. 221–227.

[40] D. G. Winter, J. W. Covington and D. M. Muir, *ibid.* pp. 167–188.

[41] D. M. Muir, A. J. Parker, J. H. Sharp and W. E. Waghorne, *Hydrometall.* **1** (1975) 155.

[42] D. M. Muir and A. J. Parker, in Energy Considerations in Electrolytic Processes, Papers Symposium, Society of Chemical Industry, London, 1980, pp. 29–42.

[43] L. Albert and R. Winand, in Chloride Electrometallurgy, Proceedings of Symposium, AIME Annual Meeting, Dallas, Texas, February 1982, edited by P. D. Parker (AIME, New York, 1982) pp. 189–202.

[44] V. D. Karabinis and P. Duby, in Chloride Electrometallurgy, Proceedings of Symposium, AIME Annual Meeting, Dallas, Texas, February 1982, edited by P. D. Parker (AIME, New York, 1982) pp. 203–220.

[45] D. J. MacKinnon, in Hydrometallurgy-Research, Development and Plant Practice, Proceedings of 3rd International Symposium on Hydrometallurgy, AIME Annual Meeting, Atlanta, Georgia, March 1983, edited by K. Osseo-Asare and J. D. Miller, (AIME, New York, 1983) pp. 659–677.

[46] J. L. Weininger, *AIChE Symp. Ser.* **79**(229) (1983) 179.

[47] F. S. Holland, *Chem. Ind.* (1979) 453.

[48] D. Tomlinson, paper presented at the AIME Annual Meeting, Los Angeles, CA, February 1984, AIME TMS Paper No. A84-55.

[49] R. Kammel, Proceedings Hydrometallurgy 81, Manchester, England (Society of Chemical Industry, 1981) pp. G1/1–20.